Characteristics and performance of c-ramic coating systems under thermal cycling

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CHARACTERISTICS AND PERFORMANCE OF C-RAMIC COATING SYSTEMS UNDER THERMAL CYCLING

A thesis submitted in fulfilment of the requirements for the award of the degree of

Doctor of Philosophy

from

THE UNIVERSITY OF WOLLONGONG

by

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ABSTRACT

A thermochemical method has been developed in recent years to coat ceramics on metal substrates. With this method, ceramic coatings can be applied to metal substrates at temperatures lower than 540°C, and the coatings obtained are referred to by the proprietary name of C-ramic coatings. Although the C-ramic coatings are believed to have great prospects of application in various service environments, relatively little work has been conducted on the fundamental study and systematic evaluation of the coatings and the real potential of the coatings is still in doubt.

The present work was carried out to investigate the characteristics of some C-ramic coating systems and their behaviour under thermal cycling, with particular emphasis on their thermal shock behaviour during cooling.

Eight types of C-ramic coating systems, involving four types of coatings and three types of substrates, were investigated in the present research. The four types of coatings are two CZ coatings (C1Z1 and C2Z2) with a mixture of chromic acid and phosphoric acid as the binder/densifier (Z type), one AX coating with chromic acid as the binder/densifier (X type), and one C1X coating with both Z and X type binder/densifiers. The three types of substrates were stainless steel (AISI316), carbon steel (0.9%C) and copper.

Material characterization was carried out using scanning electron microscopy and X-ray diffractometry in order to have a better understanding of the fundamental features of the coating microstructure. Investigation of the influences of thermal shock and coating types with different composition on coating microstructure was also conducted. In addition, thermomechanical and thermogravimetric analyses were used to study the thermal stability of the coating materials.
Thermal cycle tests with heating in a furnace and cooling in both water and air were conducted to observe the performance of the coating systems under various thermal cycle conditions. From this investigation, the general behaviour of C-ramic coating systems under thermal shock, the effects of coating types and substrate types on thermal shock resistance of C-ramic coating systems, and the possible causes of coating failure under thermal shock were revealed and analysed. Performances of the coating systems were evaluated mainly in terms of the critical peak temperature reached on heating and the type of failure. It was found that all coating systems fail by spalling during cooling when the peak temperature of the thermal cycles reached a critical level. Coating spalling occurred in four modes, viz. decohesion at the coating/substrate interface, decohesion along substrate peaks, decohesion within the coating, and decohesion within the substrate. Both critical peak temperatures and spalling mode depended on the type of coating system. Mechanisms for different spalling modes were also analysed and presented in the thesis.

Coating spalling occurs mainly due to temperature induced stresses which in turn, in magnitude, depend on the transient temperature gradient in the system and the mismatch in thermal expansion coefficient between the coating and substrate. To gain a better understanding of the spalling mechanism for general coating systems, a theoretical analysis was also conducted to study the effect of temperature gradient on coating spalling tendency during rapid cooling in terms of unconstrained strain mismatch (USM). Based on this analysis, together with the experimental investigation, it is suggested that coating spalling is probably mainly related to inelastic deformation occurring at high temperature attributed to viscous flow of amorphous phases. As a result of inelastic deformation, the stress free point of a system may shift from the fabrication temperature to a higher value and thus a more severe mismatch in coating and substrate deformation tendency occurs during the cooling process and consequently causes coating spalling.
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Developments in modern science and technology have resulted in many severe service environments and material scientists and engineers have been forced to develop materials to cope with these environments, such as high temperature and corrosive atmospheres in heat engines, extremely high heat flux in nuclear fusion research devices, and severe abrasion in the machining of hard materials in manufacturing industries. Ceramic coatings are one of many choices of material scientists and engineers to cope with these situations.

Ceramics include all the inorganic nonmetallic solid materials [1]. Coating is a form of protective surface, or decorative finish [2]. A ceramic coating is a protective or decorative surface or finish made from inorganic nonmetallic solid materials, including porcelain enamels, oxides, carbides, silicides, borides, nitrides, and so on.

Ceramic coatings have been studied extensively and intensively during the last two decades as protection for metal parts in severe service environments. Although metallic alloys possess high strength and good fabricability, they often suffer from oxidation, corrosion, wear and thermal degradation. On the other hand, ceramics possess better resistance to the above conditions; however, they are usually very brittle and difficult to handle for fabrication of components with complex configurations. The application of ceramic coatings on metal components is one of
the best ways to make use of the advantages of both metals and ceramics and provide solutions to these problems.

Ceramic coatings are playing a more and more important part in industry. According to a report made by a market research organization in the USA in 1988 [3], out of $1.5 billion total sales of structural ceramics, coatings consume $1.2 billion and this trend is expected to continue through 1995, with sales of coatings increasing to $3.3 billion (total $4.1), an annual growth rate of 12%. It is concluded that a significant market already exists for ceramic coatings and their use will redefine the capability of many traditional materials.

The present work is concerned with one kind of the recently developed ceramic coatings, which is believed to have a great prospect in various severe service environments, but has still to be systematically evaluated.

1.1 THE PROBLEMS

Various techniques have been developed to apply ceramic coatings to metal components, e.g. enamelling, physical vapour deposition, chemical vapour deposition, thermal spraying and sol-gel methods [4-8]. A so-called thermochemical method has been developed in recent years with original patents issued in the USA and Canada in 1970's, and introduced into Australia in 1987. By using this method, ceramic coatings can be applied on metals at temperatures lower than 540°C. Practically, the technique possesses some advantages over traditional ceramic coating techniques. For example, the coating process is low cost since no complex equipment is required; there is almost no limitation on the shape and size of components to be coated; and the curing temperature of the coating process is below 540°C, thus many metals can be coated by this method without being thermally distorted or being subjected to deleterious phase transformation.
The coatings obtained by this thermochemical method are referred to as C-ramic coatings in the present work. Although the C-ramic coatings are believed by industry to have a great prospect of application in various service environments, such as wear, corrosion and thermal shock environment, the coatings have received little academic attention and thus not much work has been conducted on the fundamental study and systematic evaluation of the coatings. In particular, very little effort has been devoted to temperature-related investigations such as the coating response to high temperatures and changing temperatures, therefore the performance and the failure mechanisms of the coatings under thermal cycling is unclear. Lack of knowledge about the coatings means the real potential of the coating applications in industries is still in doubt. As an initial step towards a further understanding of the coatings and a primary assessment of their potential in thermal shock environments, the present project was undertaken.

The main objectives of the research included the following aspects.

(1) to investigate the characteristics of some selected C-ramic coating systems;

(2) to study the performance of the coating systems under thermal shock, to provide information about the application potential of the coating systems;

(3) to analyse the correlation between the performance and the material characteristics.

1.2 APPROACHES OF THE RESEARCH

The major part of the present work consists of an experimental investigation, which includes material characterization and thermal cycle tests.
Material characterization was conducted mainly using scanning electron microscopy and X-ray diffractometry. The combination of the results from the examination and thermal cycle tests reveals the characteristics-performance-relationship. Understanding of the relationship allows optimization of the ceramic coatings in their resistance to thermal shock. In addition, thermomechanical and thermogravimetric analyses were carried out to study the thermal stability of the coating materials.

Thermal cycle tests were conducted to observe the performance of different types of ceramic coating systems under various thermal cycle conditions. From these tests, the following information was obtained:

1. the general behaviour of the coating systems under thermal shock;
2. the ranking of the coating systems under thermal shock; and
3. possible causes of failure under thermal shock.

A critical peak temperature was used as an indicator of resistance to thermal shock spalling.

In addition to the experimental work, in order to understand the behaviour of ceramic coating systems under thermal shock, a theoretical analysis was carried out for a primary investigation of the effects of temperature gradient on coating spalling tendency. For this purpose, a finite element scheme was developed to calculate the transient temperature profiles in coating systems. Based on the temperature profiles, the coating spalling tendency was evaluated in terms of 'unconstrained strain mismatch'. The theoretical analysis is an independent part of the research aimed at gaining a better understanding of the effects of rapid temperature change on the coating spalling tendency for ceramic coating systems in general.
CHAPTER TWO

LITERATURE REVIEW

2.1 GENERAL

This chapter is devoted to a review of existing knowledge related to the present research. Techniques and properties of C-ramic coatings are described in §2.2; thermal shock theories and test techniques are presented in §2.3; theories about the mechanical behaviour of coating systems are reviewed in §2.4.

2.2 C-RAMIC COATINGS

C-ramic coatings are also termed thermochemically formed ceramic coatings [9, 10], chemically bonded ceramic coatings [11-15], post-densified Cr₂O₃ coatings [16], chemical densified coatings [17], and K-ramic coatings [11]. It should be stressed here that the C-ramic coatings are still considered state of the art, and most of the available publications reviewed in this section are from industrial sources. Due to the commercially sensitive nature of the information from industry, some of the information needs to be verified by further research work.

Basically, the coating process consists of two steps: application of a base coating and further densification of the base coating. In the first step, a coating slurry is deposited on a substrate and then fired. The coating slurry comprises oxide particles as fillers and chromic acid or mixture of chromic acid and phosphoric acid as a binder. In the second step, the base coating is densified by being impregnated with
chromic acid or mixture of chromic acid and phosphoric acid, and then cured at an appropriate temperature. Details of the coating process are described in §2.2.2.

2.2.1 Thermochemical Principles of the Technique

Basically there are two families of C-ramic coatings in terms of binder/densifier type. One family has chromium oxide as the binder/densifier and is termed as AX type in the present work, while the other has a mixture of chromic acid and phosphoric acid as the binder/densifier and is termed as CZ type.

2.2.1.1 Coatings with chromium oxide as the binder/densifer (AX type)

The technique for this type of coatings was developed by Kaman Science Cooperation [18, 19]. The technique is based on a chromium oxide bonding process which has the functions of bonding, densification, hardening and strengthening for the materials composed of oxide constituents, or the materials will form a well adhering oxide on their surfaces.

In the chromium oxide bonding process, chromium compounds are used as binder/densifiers. The binder/densifiers are normally produced by dissolving chromium anhydride (CrO₃) into water to form chromic acid (H₂CrO₄), or further more adding Cr₂O₃ or Cr₂O₃·xH₂O or chromium hydroxide in the chromic acid to form complex chromium compounds (xCrO₃·yCr₂O₃·zH₂O). In addition to chromium oxides, chromium chloride, chromium nitrate, chromium sulphate and a wide variety of dichromates and chromates can also be used as solutes. Different solutes give binder/densifiers with different properties. Complex chromium compounds can be prepared to contain large concentrations of chromium ions in
solution. Chromates have been found useful for achieving high hardness values in a few densification cycles.

Upon curing at a temperature in excess of 315°C or higher, the soluble chromium compounds are converted to chromium oxides. For example, with increasing temperature, chromic acid first loses its water and the chromium anhydride that remains then begins to lose oxygen at 315°C approximately and higher. The chromium anhydride converts ultimately to chromium oxide of the refractory form (Cr₂O₃ or Cr₂O₃·xH₂O), which can be simply expressed as:

$$4\text{CrO}_3 \rightarrow 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$$

Chromium compounds such as the chlorides, sulphates and chromates will also convert to Cr₂O₃ by heating to a suitable temperature. During the curing procedure, a chromium oxide bond is believed to be established between a binder/densifier and a material composed of oxides. In addition to oxides, nitrides, carbides, silicides, borides, intermetallics, and metals can also be treated by this process. In air or oxidizing atmosphere, a very thin layer of oxide can be formed on the surfaces of the non-oxide materials. During the chromium bonding process, it is believed that the chromium oxide bond is established to the thin oxide film on the metallic substrate.

Samandi [14] studied the thermochemistry of CrO₃ by using differential thermal analysis (DTA). Six different peaks were discerned from the DTA curve. The first endothermic peak at just above 100°C is due to the loss of water absorbed on the surface of the powder. Two other endothermic peaks at 200°C and 490°C and three exothermic peaks at 260°C, 345°C and 400°C are accompanied by liquidisation, oxygen loss, and solidification of the powder. It was concluded that a complex series of reactions involving the occurrence of disproportionation reactions and
apparently non-stoichiometric intermediates can occur when chromium oxides are heated. The reactions are summarised as follows:

\[
\begin{align*}
CrO_3 & \rightarrow CrO_{2.96} \rightarrow CrO_{2.906} \rightarrow CrO_{2.625} \rightarrow CrO_{2.40} \rightarrow CrO_{1.56} \rightarrow CrO_{1.50}(Cr_2O_3)
\end{align*}
\]

In addition, by studying coatings cured at temperatures of 540°C and 450°C respectively using X-ray photo-electron spectroscopy [14], the oxidation states of chromium, i.e. Cr³⁺ and Cr⁶⁺ were identified. The results showed that for coatings cured at 540°C, all Cr⁶⁺ present in the original coating formation and densifier was converted to Cr³⁺, while for the coatings cured at 450°C, the coating surface consisted of Cr³⁺ and Cr⁶⁺ in a molar ratio of 3:1. It is thus concluded that the formation of G-2O₃ requires a temperature of at least 500°C.

### 2.2.1.2 Coatings with mixture of chromic acid and phosphoric acid as the binder/densifer (CZ type)

In an attempt to increase corrosion resistance of the AX type coatings, C-ramic Australia Pty Ltd developed CZ type coatings using a mixture of chromic acid and phosphoric acid as the binder/densifier [13]. Adding phosphoric acid allows the formation of an amorphous matrix in CZ type coatings and thus the coatings have fewer open and interconnected pores, and in turn, better resistance to penetration of corrosives. Although the coatings have been commercially produced, the thermochemical principles of the coatings are not yet identified. In practice, the CZ type can be fabricated at 400°C, which is 140°C lower than the AX type.

### 2.2.2 Process Description

The coating process consists of preparation of a slurry, pre-treatment of substrates, application of the slurry on substrates, curing at required temperatures to form a base coating, and further densification of the base coating (Fig.2.1).
Substrate and slurry preparation

Slurry Deposition

Curing at 540°C or 400°C to form base coating

Impregnation with densifiers

Curing at 540°C or 400°C

repeat for several cycles

Fig. 2.1 Processing steps for typical C-ramic coatings
The slurry used in the coating process is water based. Chemicals for the formation of binder/densifiers (CrO3, or CrO3 and H3PO4) are mixed with filler materials, such as oxides, carbides, silicides, nitride and others in forms of particles or fibres, in water and thoroughly ball milled. The density and viscosity of the slurry is adjusted according to the requirement for specific coating deposition methods. It has been found that evacuating a slurry prior to application assures that all of the particles are wetted with binder/densifiers and eliminates lumps and air bubbles [18, 19].

Ceramic coatings can be applied to most metals that can withstand the curing temperatures and are able to form a well adhering surface oxide layer. Suitable substrates for AX type coatings include ferrous alloys, nickel, cobalt, refractory alloys, titanium and Nimonics [9, 11]. Metals having loosely adherent oxides, such as copper or high copper content alloys, can be coated under the conditions of a lower curing temperature, such as CZ type coatings used in the present research, or alternatively by pre-treatment to produce a bond layer such as nickel flash plating. In this case, the thermochemical bonding between the coating and the substrate is formed to the nickel oxide layer rather than to the substrate [18, 19]. It is essential that the substrate surfaces should be in a suitable condition, thus pretreatment of the substrate surface is required. The pretreatment steps usually involve degreasing and grit-blasting [18, 19]. The freshly abraded metal surfaces produced by grit-blasting tend to be chemically active and thin air formed oxide films are readily formed on them [20]. In addition, the surfaces are roughened and hence coating adhesion can be improved by mechanical interlocking.

Techniques of the slurry application are similar to those of painting, including pressure-spraying, dipping, brushing and draining [11, 12]. A technique adopted for a specific component depends on the size and shape of the components. For example, pressure-spraying is used for external surfaces, dipping for shapes with complex geometry and draining for internal surfaces.
After the application of a slurry, the workpieces are dried in air and then cured in a furnace at an appropriate temperature depending on the coating type. As a result, a thermochemical bond is established not only among coating ingredients to form a integrated base coating, but also between the base coating and the substrate. The base coatings are then in a green stage, and are highly porous and fragile. This allows excess coating to be removed from any unwanted areas before further curing.

The base coating is then further densified by impregnation with binder/densifier solutions containing mainly chromic acid ($\text{H}_2\text{CrO}_4$) for AX type coatings, or chromic acid and phosphoric acid for CZ type coatings, and subsequently drying and firing at a suitable temperature. The impregnation-heat treatment cycle is repeated several times to reduce porosity and to increase the adhesive and cohesive strength of the coatings. After the multi-cycle densification, a very hard and dense ceramic coating is formed.

### 2.2.3 Mechanisms of Adhesion and Cohesion Bonding

Studies [15, 17, 21] of the interface between AX coatings and carbon steel substrates show that an intermediate layer, which contains mainly Fe and Cr and a small amount of Si, is formed. A ferric chromate conversion coating layer is believed to be produced by chemical interaction between chromic acid and metal oxide on the substrate [15]. Formation of the conversion coating layer is considered to be one of the main adhesion mechanisms in addition to the mechanical interlocking between the coating and the grit-blasted substrate. The small amount of Si in the intermediate layer is believed to be sub-micron sized silica particles accumulated at the interface [15].

Although the mechanisms of cohesion bonding or interparticle bonding of the coatings are not well understood, it appears that silica particles in the coating
ingredients play an important role in the cohesion bonding. It was stated that for
coatings containing silica particles and alumina particles, the alumina might be
entirely replaced with different materials such as mullite or zirconia, but if silica is
totally replaced, the coating fails to bond and usually fails to remain intact.
Experimental details supporting this statement were not given [15].

It was also found that the morphology and chemical structure of silica particles had
important effects on cohesive bonding strength: a larger surface area and higher
hydroxyl content of silica particles can promote an interaction with the chromic acid
and thus a stronger bond forms [15]. Surface hydroxylation improves the wetting
and activity of the silica particles. When water reacts with the silica, it opens an
oxygen bridge and converts it into silanol (a silicon with an OH attached) groups.
Silanol groups are more reactive than the bridged oxygen.

2.2.4 Coating Characteristics

The C-ramic coatings have a multi-particle and multi-phase microstructure. The basic
microstructure feature is that discrete filler particles are randomly distributed in a
matrix formed from binder/densifiers [15, 17, 21]. The coatings also contain pores
which, in their amount, depend on the number of densification cycles [11, 12]. The
porosity of coatings prior to densification is greater than 30% and decreases
significantly as the number of densification cycles is increased, especially for the first
ten cycles. Porosity of less than 5% can be achieved when the number of
densification cycles reaches 14 (Fig.2.2).

2.2.5 Coating Properties

The properties reviewed here concern mainly AX type coatings unless otherwise
specified.
Fig. 2.2 Relationship between porosity and numbers of densification cycles [11, 12].
Bond Strength

The bond strength of a coating consisting of SiO₂/Cr₂O₃/Al₂O₃, which is referred to as SCA, was investigated by Suzuki et al. [22] using an epoxy pull test. The coating was about 100μm in thickness and had experienced 10 densification cycles. Fig.2.3 and Table 2.1 show the bonding strength test and the test results. The results indicate that all test pieces were broken at the point of epoxy bonding layer, and although the real bond strength could not be measured by this test, it was concluded that the bond strength of the coating was higher than 70N/mm². The strong bond strength was considered as one of the advantages of C-ramic coatings over ceramic coatings produced with other techniques (Fig.2.4) [13].

<table>
<thead>
<tr>
<th>No.</th>
<th>Load (kg)</th>
<th>Break position</th>
<th>Bond strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2960</td>
<td>Epoxy</td>
<td>&gt;59.1</td>
</tr>
<tr>
<td>2</td>
<td>3310</td>
<td>&quot;</td>
<td>66.2</td>
</tr>
<tr>
<td>3</td>
<td>3160</td>
<td>&quot;</td>
<td>63.1</td>
</tr>
<tr>
<td>4</td>
<td>2730</td>
<td>&quot;</td>
<td>54.6</td>
</tr>
<tr>
<td>5</td>
<td>3320</td>
<td>&quot;</td>
<td>66.3</td>
</tr>
</tbody>
</table>

Hardness

According to Schneider [11, 12], coating hardness is a function of the number of densification cycles (Fig.2.5). When the number of cycles exceeds 12, the increase of hardness with the number of the cycles become insignificant.

Samandi [15] reported that an AX type coating, with silica (1200HV) and alumina (1800HV) embedded in a microcrystalline Cr₂O₃ matrix (1400HV) is about 800HV. Leigh and Wiktorek [13] reported that a CZ type coating had an overall hardness
Fig. 2.3  A schematic diagram showing the bond strength test [22].

Fig. 2.4  Comparison of the bond strength between the C-ramic coating and that of other coatings [13].
Fig. 2.5 Relationship between hardness and numbers of densification cycles [11, 12].
about 600HV. According to Nomura et al. [17], C-ramic coatings can reach a Vickers hardness of 1500 to 2000Hv, which is harder than conventional chromium-oxide based ceramic coatings.

**Wear Resistance**

Wear resistance of AX type coatings obtained by Schneider [12] and Suzuki et al. [22] are shown in Fig 2.6a and Fig.2.6b respectively. In Schneider's test, water was used as a lubricant at a contact pressure of 5.9MN/m. In Suzuki et al.'s test, oil was used as a lubricant, and details of the other conditions are given in Table 2.2. C-ramic coatings performed much better in comparison with the reference materials, such as carbon-graphite, hi-fired alumina and hard chrome, tested under the same condition. The good wear resistance is attributed to the high strength of adhesive and cohesive bonding [13] and the very fine particle structure of the coatings [12]. High bond strength reduces the wear damage caused by particle pull-out, which is a main wear mechanism associated with thermal spray ceramic coatings and chrome-plating. A fine particle structure make cavities smaller when the particles are removed by wear.

**Table 2.2 Conditions for wear test with oil lubrication [22]**

<table>
<thead>
<tr>
<th>Test piece 1</th>
<th>Test piece 2</th>
<th>Rotor</th>
<th>Rub distance</th>
<th>Rub Speed</th>
<th>Max. load</th>
<th>Lubricating oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCA (80µm)</td>
<td>Hard chrome (100µm)</td>
<td>Special cast iron</td>
<td>570m</td>
<td>0.121m/sec.</td>
<td>18.9kg</td>
<td>SAE C-C grad #3, 2.5ml/min. drop</td>
</tr>
</tbody>
</table>
Fig. 2.6 Wear resistance of C-ramic coatings.
(a) in a water lubricated test [12], (b) in an oil lubricated test [22].
**Corrosion resistance**

The corrosion resistance of AX type coatings has been evaluated under various conditions. Table 2.3 shows the test results reported by Schneider [11, 12]. The results indicate that the coatings were inert to most acids except hydrochloric or hydrofluoric acid. C-ramic coatings are also insoluble in sea water, alkali, and most other acid and solvents [17].

**Table 2.3 Results of chemical durability test** [11, 12]

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume Concentration %</th>
<th>Duration (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCL</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>HCL</td>
<td>17</td>
<td>72 +</td>
</tr>
<tr>
<td>HF</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>HF</td>
<td>10</td>
<td>72 +</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>17</td>
<td>72 +</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>17</td>
<td>72 +</td>
</tr>
</tbody>
</table>

Although the coatings themselves are inert to most chemicals, corrosive attack of specimens with a C-ramic coating (SCA) was observed by Suzuki et al. [22] in a salt spraying test under the conditions reported in Table 2.4. It was concluded that the coating could not protect the metal substrate from humidity and salt corrosion. The attack was caused by penetration of water and salt through the coating, which causes severe rust on the substrate and thus coating spalling. Results of salt droplet tests reported by Leigh and Wiktorek [13] showed that an AX type coating started to fail at less than 500 hours, but a CZ type coating survived after 1000 hours. The difference in corrosion resistance of the two types is believed to be attributed to the coating microstructure. Adding phosphoric acid to chromic acid allows the formation of an
amorphous matrix in CZ type coatings, and thus the coating has fewer open and interconnected pores. It is obvious that such a structure has better resistance to penetration of corrosives.

Table 2.4 Conditions of salt spraying test [22]

<table>
<thead>
<tr>
<th>Salt Solution Concentration</th>
<th>5±1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air pressure</td>
<td>0.7-0.8 bar</td>
</tr>
<tr>
<td>Ambient temp.</td>
<td>35±2°C</td>
</tr>
<tr>
<td>Spray temp.</td>
<td>33-35°C</td>
</tr>
<tr>
<td>Spray feed</td>
<td>0.5-3.0 ml/80cm/Hr</td>
</tr>
<tr>
<td>Test hours</td>
<td>50 Hours</td>
</tr>
</tbody>
</table>

Thermal shock resistance

Results of water quenching tests of the coatings have been reported by Nomura et al. [17] and Suzuki et al. [22]. According to Nomura et al., no problems developed with the coatings after repetition of quenching from 600°C into cold water, and the coatings are normally safe up to a maximum of 700°C. Details of test conditions were not reported. In Suzuki’s report, a C-ramic coating consisted of SiO$_2$/Cr$_2$O$_3$/Al$_2$O$_3$ (approximately 50μm in thickness) was applied in the bores of two kinds of substrates: thick rings made from stainless steel and thin steel pipe. The specimens were suddenly immersed into water (20°C) from various temperatures. The bores were checked to see if cracks were produced in the coating. Table 2.5 shows the test results. The coating applied in the rings could withstand the quenching from 800°C, whereas the coating applied in the pipes only from 600°C. The lower thermal shock resistance in pipe specimen was attributed to the pipe deformation. The information given by the above work is over-simplified
concerning understanding of the coatings' behaviour. For example, details of specimens are not reported in Nomura's work; details of failure forms and failure mechanism analysis are not presented in either work. Consequently, further study is needed to obtained a better understanding of the coatings' thermal shock behaviour.

Table 2.5 Results of thermal shock test [22]

<table>
<thead>
<tr>
<th>Thermal shock</th>
<th>Test piece</th>
<th>Ring</th>
<th>Steel pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C → water</td>
<td>Ring</td>
<td>no crack</td>
<td>no crack</td>
</tr>
<tr>
<td>700°C → water</td>
<td>Ring</td>
<td>no crack</td>
<td>cracked</td>
</tr>
<tr>
<td>800°C → water</td>
<td>Ring</td>
<td>no crack</td>
<td></td>
</tr>
<tr>
<td>900°C → water</td>
<td>Steel pipe</td>
<td>cracked</td>
<td></td>
</tr>
</tbody>
</table>

note (1) material: stainless steel, OD:78mm, ID:63, length:35mm, coating thickness: 50μm.
(2) OD:107mm, ID:105, length:204, coating thickness: 50μm.

Surface roughness and friction

According to Wiktorek and Ashbolt [10], and Nomura et al. [17], the surface roughness of C-ramic coatings can be controlled to a very low level by grinding and polishing of the coatings using conventional machining methods before full densification. Low roughness combined with high hardness gives low friction coefficient of coating surfaces [9,17].

2.2.6 Applications of the C-ramic Coatings

The C-ramic coatings have been considered for protection of metal components from corrosion, wear and thermal degradation. Examples are given as follows [9, 11, 12, 17].
**Pumps and Compressors**

Due to the combination of chemical attack and abrasive action, the life time of the conventional pumps and compressors which work with slurries of seawater and petrochemicals is limited to only about 100 hours. A test of pumps coated with a C-ramic coating showed that slight wear occurred after 1200 hours, but no abrasion, spalling, or corrosion. In another test, when a C-ramic coating was applied to the plunger of a pump for agricultural chemicals, its life was greatly extended while there was no roughness detected caused by rubbing against the packing as with other chromium oxide coatings in sprays [17].

It is also reported that considerable success has been achieved on high pressure water jet pumps in operation up to 30,000 psi. Traditionally, solid ceramic plungers are used, but they are very expensive and are susceptible to fracture from thermal shock. C-ramic coatings can provide the necessary wear resistance and are unaffected by the thermal shock [9].

**Textile industry**

In the textile industry, due to the abrasion caused by fibre and yarn passing over guides and drum rolls at high speed, the quality of the products is affected. Although some solid ceramics offer satisfactory wear resistance, they are fragile by nature and easily damaged. Ceramic coated components can offer the surface properties of ceramics and bulk strength of the steel substrate. It was concluded that C-ramic coatings can offer good resistance to abrasion due to their low friction coefficients [9, 17].
**High temperature environments**

C-ramic coatings have been recommended for use in high temperature environments to protect metal components from wear, erosion, and thermal degradation. For example, C-ramic coatings can be used for high-temperature abrasion-resistance parts in the iron and steel industry, such as for entry pipes for wire and rod mills, seal packing sleeves, nozzles and screws [17]. Heat engines is another area that can be benefit from C-ramic coatings. The application of C-ramic coatings to combustion chamber components, i.e. the piston crown, cylinder liner, valves, cylinder head and exhaust ports can increase resistance to wear and erosion, and also reduce the heat transfer to the components [9, 12].

### 2.2.7 Relationship between C-ramic Coatings and Traditional Chromium Chromate and Chromium Phosphate Conversion Coatings

In terms of reactants such as chromic acid and phosphoric acid, C-ramic coatings are similar to the traditional chromium chromate conversion coatings and chromium phosphate conversion coatings. The conversion coatings are fabricated by immersing metal substrates into acid solutions containing chromate or phosphate anions. The basic process involved in the formation of the coatings is the precipitation of cations of dissolved metals and anions of phosphate or chromate [23-27].

Although the conversion coatings have been used in industries for nearly half a century, only a small number of conversion coatings have been characterized. The chemical formulae in Table 2.6 are most commonly ascribed to the compounds in the conversion coatings.
Table 2.6 Chemical formulae of conversion coatings [23, 24]

<table>
<thead>
<tr>
<th>Chromium chromate coatings [24]</th>
<th>Chromium phosphate coatings on aluminium substrate [23]</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate oxides and hydroxides: $M_xO_y$, $M_x(OH)_y$</td>
<td>$Al_2O_3 \cdot 2CrPO_4 \cdot 8H_2O$ hydrated chromium phosphate</td>
</tr>
<tr>
<td>substrate chromates: $M_xCrO_4$, $M_xCrO_7$</td>
<td></td>
</tr>
<tr>
<td>chromium oxides and hydroxides: $Cr_2O_3$, $CrOOH$, $Cr(OH)_3$ $Cr_2O_2H_2O$</td>
<td></td>
</tr>
<tr>
<td>chromium chromates: $Cr(OH)CrO_4$, $Cr_x(CrO_4)_y$</td>
<td></td>
</tr>
<tr>
<td>metallic chromium</td>
<td></td>
</tr>
</tbody>
</table>

Although having similar reactants as those of the conversion coatings, the C-ramic coatings do not necessarily have the same adhesion bonding mechanisms as the conversion coatings. The bonding mechanism of the conversion coatings is due to the solid compounds produced by the reaction between cations from the dissolved metal substrate and anions in the process solutions. This type of reaction may happen more or less when the C-ramic coating slurries are applied on metal substrates. However, the adhesion bonding of C-ramic coatings may not be due to the reactions at all. The conversion coatings are normally formed at the temperature not higher than 100°C. In addition, formation of conversion coatings needs not only metal cations and chromate or phosphate anions as reactants, but also other activators such as chloride or fluoride to keep the substrate metal active. However, the C-ramic coatings are cured at about 500°C, and no activators are involved in the coatings. Therefore, the adhesion mechanism of C-ramic coatings may be different from that of the traditional conversion coatings.
2.2.8 Properties of the Materials Used in the Present Research

In the present research, the main ingredients of C-ramic coatings, in addition to chromic acid and phosphoric acid used as binder/densifiers, are silica and alumina particles used as fillers.

There are various forms of silica having different structures, including an amorphous phase, quartz, cristobalite, and tridymite. The silica powder used in the present research contains amorphous and crystalline $\alpha$-quartz. Quartz has two forms depending on temperature [28]. At temperature below 573°C, quartz is in the $\alpha$ form which has a trigonal structure. At 573°C, $\alpha$-quartz is changed rapidly into $\beta$-quartz which has a hexagonal structure. Values of the density of the $\alpha$-quartz and $\beta$-quartz are 2.65g/cm³ and 2.52g/cm³ respectively. Hence the $\alpha \leftrightarrow \beta$ inversion is accompanied with a volumetric change (about 5%). The $\beta$-quartz is stable until the temperature reaches 870°C. At 870°C, $\beta$-quartz tends to convert into tridymite; however, the inversion is sluggish.

Alumina chemically consists of Al₂O₃, and it is one of the most versatile of refractory ceramic oxides. Naturally, a number of transitional Al₂O₃ structures can be formed, including $\alpha$-Al₂O₃, $\beta$-Al₂O₃, and $\gamma$-Al₂O₃. However, with increasing temperatures, all structures will be transformed irreversibly to the $\alpha$-Al₂O₃, which is a corundum crystalline phase of hexagonal structure. The $\alpha$-Al₂O₃ is stable until its melting point which is higher than 2000°C [29]. $\alpha$-Al₂O₃ is used in the C-ramic coatings in the present research.

2.3 THERMAL SHOCK AND THERMAL SHOCK TESTS

One of the purposes of using ceramic coatings is to protect metal components from oxidation or other thermal degradation in high temperature environments, such as
heat engines and nuclear reactors. Under these service environments, the components are required to withstand not only high temperature, but also rapidly changing temperature. For example, in a gas turbine engine, the environment temperature can exceed 1370°C [30]. During take-off, the leading and trailing edges of a first stage turbine blade can rise from 520 to 1090°C in 8 seconds, while during shut-down decrease from 1090 to 520°C in 5-17 seconds [31]. Therefore, the performance of ceramic coatings under rapidly changing temperature is usually one of the most important indicators for the evaluation of ceramic coating systems. In this section, essential concepts and testing techniques related to material performance under rapid changing temperature are reviewed.

2.3.1 Thermal Shock Theories

Thermal shock refers to a sudden transient temperature change which normally produces transient thermal stresses in the body subjected to the temperature change. The origin of the thermal stresses is usually attributed to the difference in thermal expansion of various parts of the body under temperature gradient [32-36]. Thermal shock theories mainly concern evaluation of thermal stresses based on thermoelastic theory.

2.3.1.1 Conventional thermal shock theories

The performance of materials, especially ceramics, under thermal shock has long been the subject of many investigations. The conventional methods of assessing the thermal shock resistance of a brittle body are based on the assumption that the thermal shock fracture is the result of crack initiation and crack propagation. Accordingly, two approaches have been proposed.
One approach is to assess thermal shock resistance in terms of resistance to crack initiation, which is based on the assumption that cracking will occur whenever the tensile thermal stress at any point exceeds the tensile strength of the material. Evaluation of the stresses is based on thermoelastic theory, since it is considered that a non-elastic body is not susceptible to thermal shock failure due to stress relaxation through inelastic deformation. According to thermoelastic theory, as long as the temperature distribution is known, the thermal stresses can be calculated [35]. For example, the surface stress for bodies with simple geometrical configurations, such as infinite slabs, infinite cylinders and spheres can be expressed as [32]:

\[ \sigma = \frac{E\alpha(T_a - T_s)}{(1-\mu)} \]  

(2.1)

where \( E \) is Young's modulus, \( \alpha \) is thermal expansion coefficient, and \( \mu \) is Poisson's ratio. \( T_a \) and \( T_s \) are the average temperature and surface temperature on the body respectively. Due the complexity of transient heat transfer problems, analytical solutions for the real stress are usually available only for objects with simple geometrical configurations, such as infinite slabs, infinite cylinders and spheres, under certain boundary conditions, such as surface heat transfer with infinite or constant heat transfer coefficients [31]. Based on the analytical solutions for the above conditions, by choosing the maximum temperature difference under which the resultant stress is equal to the material's strength as the measure of thermal shock resistance, two basic 'thermal shock resistance parameters' are proposed [32, 33]:

\[ R = \frac{S_t(1-\mu)}{\alpha E} \], \[ R' = \frac{S_t(1-\mu)k}{\alpha E} \]

where \( k \) is thermal conductivity, and \( S_t \) is material tensile strength. \( R \) is derived for an infinite surface heat transfer boundary condition and applies to thermal shock with high rates of heat transfer, whereas \( R' \) is for a constant surface heat transfer boundary condition and applies to thermal shock with low rates of heat transfer.
The other approach is to assess the thermal shock resistance in terms of resistance to crack propagation, which is based on the assumption that the driving force for crack propagation is derived from the elastic energy stored in the body at the instant of fracture and no catastrophic fracture should happen if the total elastic energy is less than the total fracture energy required to propagate a crack over an area equivalent to the cross-section of a specimen. The driving stress for crack propagation is usually evaluated according to the theory of Griffith [33].

Based on the above two approaches, twelve thermal shock resistance parameters have been proposed, as described in detail by Hasselman [36]. The parameters serve only qualitatively as a general indices to material thermal shock resistance. The real stress developed on a body under thermal shock needs to be evaluated based on transient temperature distribution calculated by numerical methods.

2.3.1.2 Thermal shock theories for ceramic coating systems

The application of the conventional thermal shock theories is restricted to homogeneous isotropic bodies. These theories about stress generation under thermal shock are not applicable to coating systems, for which stresses arise not only due to temperature gradient, but also due to the mismatch between the coating and the substrate in terms of their thermal expansion coefficients. The real stress developed in a coating system is a complex interaction of the temperature gradient and thermal expansion coefficient mismatch. Ideally, as with homogeneous and isotropic bodies, the real stress can be evaluated according to thermoelastic theory as long as the temperature distribution in a coating system is known. However, transient heat transfer for composite materials is more complex. As a result, the explanation of thermal shock behaviour of coating systems is sometimes discussed in a qualitative way as "It is felt that ......the thermal expansion mismatch between the substrate and the ceramic coating as well as the temperature gradient within the coating give rise to
additional stresses through the heating and cooling of the samples during thermal cycling. The combination of these stresses with the residual stress can then lead to increased initiation and propagation of cracks, and thus cause spalling" [37].

The basic approach which has been used for more than thirty years to the thermal shock problem of ceramic coatings is to consider the stress in the coating from the mismatch of thermal expansion coefficients and temperature gradient separately [38-43], then either ignore one of them according to specific boundary conditions [38,40,41], or sum them algebraically [38].

The stress originating from thermal expansion mismatch can be derived from elementary stress theory [44]. For a coating system with flat plate geometry and coating on one side, the stress can be expressed as:

\[
\sigma_c = \frac{(\alpha_s - \alpha_c)E_sE_c(T-T_o)}{E_s(1-\mu_c) + \frac{H_c}{H_s}E_c(1-\mu_s)}
\]

where \(H\) is thickness, \(T_o\) is coating fabrication temperature, and \(T\) is temperature. Subscripts "c" and "s" represent the coating and the substrate respectively. Similar expressions have been used in the literature [38-40, 45-47], with only small variations due to some specific considerations. For example, by considering coating on both sides of a flat plate, the temperature dependence of material physical properties, and the identity of the coating and the substrate in their Poisson's ratio, the expression in eq.(2.3) was used by Lauchner and Bennett [38]:

\[
\sigma = \frac{\int_{T_o}^{T} (\alpha_s-\alpha_c) \, dT}{\frac{1}{2H_c} + \frac{1}{2H_s} + \frac{1}{E_c}}
\]
The stress originating from temperature gradients is usually expressed in a form similar to eq.2.1 [39-42] derived from conventional thermal shock theories.

The above expressions for thermal stress have been used either to describe thermal stress in coatings in a general qualitative sense, or to evaluate the possible thermal stress approximately. However, this approach does not completely reflect the real process happening in coating systems. Under rapid temperature change, a coating system is subjected to a transient non-uniform temperature, as depicted in Fig.2.7 for a flat plate coating system. Under this condition, the effect of temperature gradient and thermal expansion coefficient mismatch cannot be separated. Considering the mismatch between the coating and the substrate in their stress-free dimensions, the mismatch is determined not only by the mismatch between the coating and the substrate in their thermal expansion coefficients, but also on the temperature distribution which depends on the combined effects of the coating and substrate thermal physical properties. In addition, stress in the coating may not be a critical measure to thermal shock performance, since ceramic coating systems often fail by coating spalling due to cracking initiation and propagation in or parallel to the coating/substrate interface, which cannot be described properly by using the stress in the coating only. Obviously, approaches reflecting the real process happening in coating systems during thermal shock are needed not only for evaluating stress levels, but also for a better understanding of thermal shock failure mechanisms. In recent years, numerical methods have been used to study transient thermal stress in coating systems, such as in the case of Keribar and Morel [48]. Transient thermal stress analysis using numerical methods may lead to a better understanding of thermal shock failure mechanisms.

2.3.2 Thermal Shock Testing Techniques

Many thermal shock testing techniques have been developed and employed. Basically, the techniques can be classified into two categories. One type of test is
Fig. 2.7 A schematic diagram showing the non-uniform temperature distribution across thickness in a coating system under thermal shock by being immersed into water.
designed to give results which correlate well with specific service conditions. Because of the complexity of thermal stresses originated from thermal shock, it has been recognized that the test results under one condition may be meaningless under another condition [32, 49]. Therefore, to investigate material performance in a specific service condition, the material should be tested under conditions similar to the service conditions and with the real geometry to be used in the service. Examples of this type of test include ASTM standard thermal shock tests simulating the service conditions of ceramic products, such as bricks, glasswear, and porcelain-enameded utensils [50-53], burner rig tests simulating the environment in heat engines [40, 54-57], and high energy tests, such as laser beams, electron beams, photon beams, plasma bombardment, simulating severe 'heat up thermal shock' environments in nuclear devices [58-63].

In addition to tests simulating service conditions, another category of tests is designed for providing a general index of material performance. Quenching tests are the most widely used technique for this purpose. The advantage of the technique is that the required equipment is simple. The apparatus of quenching tests normally comprises a furnace for heating and a bath or sprayer for cooling. In a quenching test, a sample is heated to a pre-determined temperature and then rapidly cooled by immersion into a bath containing a quenching medium [64, 65] or by spraying with quenching medium [66, 67].

Water is the most widely used quenching medium and can produce very severe thermal shock due to high heat transfer coefficients. Heat transfer between a hot body and water depends on the body temperature. At low temperatures, the body does not cause the water to boil and heat transfer occurs solely by convection and is slow. At high temperatures, nucleate boiling occurs at preferred sites on the body surface and the resulting steam bubbles produce vigorous agitation of water to give a very high rate of heat transfer. At still higher temperatures, the body may become
enveloped in a layer of water vapour and the heat transfer rate will fall. Besides, heat transfer in water is also affected by surface condition, geometry and orientation of the quenched body. Fig.2.8 shows the heat transfer coefficient as a function of temperature obtained from a stainless steel plate immersed vertically in still water at room temperature [68].

Practically, quenching tests are used either in a single cycle form or in a multi-cycle form. In the single cycle form, the peak temperature is increased in a series of tests to increase the severity of the test conditions. The temperature required to produce failure is defined as the critical peak temperature. The critical peak temperature or the difference between the critical peak temperature and the quenching medium temperature is usually used as a measurement of the material's capability to withstand thermal shock [64, 65]. In a multi-cycle form, the peak temperature is fixed and the specimen is cyclically heated and quenched until failure occurs. The number of the cycles without failure is used as the specimen resistance to thermal shock fatigue [69].

### 2.3.3 Specimen Forms for Thermal Shock Tests

In most cases, coating specimens used in thermal shock tests have the substrates in the form of flat plates [55,70], discs [71-74] or cylinders [40, 41], which can be prepared easily for a general study. Occasionally, specimens in the real geometry of engineering components are used [75]. For the purpose of understanding the behaviour of a coating system, it is necessary for the coating to be on the substrate, since the behaviour of a coating system depends not only on the coating, but also on the substrate. In a few cases, ceramic coatings have been tested under substrate-free conditions in single-cycle [70] and multi-cycle tests [76]. The substrate-free coatings were obtained by spraying onto salt-coated substrates and then removed
Fig. 2.8 Surface heat transfer coefficient in water as a function of temperature obtained from a stainless steel plate immersed vertically in still water at room temperature [68].
from the substrates by dissolution in water. Test results obtained using the substrate-free coating reveal properties of the coating materials only.

2.3.4 Evaluation of Material Response to Thermal Shock Tests

The essential response of materials to thermal shock is cracking which can lead to spalling and fracture. Material spalling can be observed directly, or quantitatively measured by specimen weight decrease. For a material in which cracks form without shattering, cracks can be observed visually or by using optical and electron microscopy, or indirectly by observing the changes in mechanical or physical properties. Bending and tensile tests are normally used to evaluate material strength changes which demonstrate the severity of cracking [77]. Alternatively, hardness tests are also used for the same purpose [70]. Infrared thermal wave [78], resonance frequency and conductivity [64], and acoustic emission [73] have also been used to monitor crack formation in situ or when non-destructive examination is required.

2.3.5 Behaviour of Ceramic Coating Systems under Thermal Shock

Coating spalling and mud cracking are two main failure forms of coating systems under thermal shock.

Coating spalling is observed in most thermal shock testing and is the most common form of coating failure [40, 41, 55, 70, 72-75, 79, 80]. Spalling is the consequence of cracking propagation at, or parallel to, the interface between the coating and the substrate. For example, partially stabilized zirconia yttria coatings on cylindrical superalloy substrates with a NiCrAl alloy bond coating were tested using a burner rig, with peak temperature higher than 1000°C [40]. The coating performance was evaluated in terms of the number of thermal cycles that induced coating spalling. It was found that coating delamination occurred during the cooling stage, and this
delamination led to coating spalling in the heating stage of the subsequent cycle. It was suggested that stresses arising from metal-ceramic thermal expansion mismatch, rather than temperature gradients, contributed to the failure, and that the stresses were influenced by flow and oxidation at the bond coating-ceramic interface. Coating spalling by similar mechanisms was also observed in thermal cycling of a plasma sprayed spinel consisting of $\text{Al}_2\text{O}_3$ and MgO on a steel substrate with NiCr alloy bond coating [75]. Spalling was observed to begin either at the edge of the specimens, gradually leading to increasing loss of the ceramic, or occurred over the entire specimen area for flat coating systems with yttria partially stabilized zirconia coatings (YPZ) under thermal cycling in a burner rig [54]. Spalling occurred from the specimen edge was also observed in [70] and [73]. Coating spalling during cooling was determined as the primary failure mode of thermal barrier coatings used in gas turbines [73].

Mud cracking, or through-thickness cracking, of coating is another form of coating failure under thermal shock [38, 70, 78]. For example, some enamelled ceramic coatings failed by mud cracking of the coatings during water quenching. The failure was attributed to the sum effects of temperature gradient stresses and thermal expansion coefficient mismatch stresses [38]. Through-thickness cracking was also observed in a coating system subjected to multiple thermal cycles in a flame rig. The cracking was attributed to the volumetric change of oxides forming at the bonded coating/substrate interface and the thermal expansion mismatch between the coating and the substrate [70].

2.3.6 Influence of Material Characteristics on the Performance of Coating Systems Under Thermal Shock

Under thermal shock, the mechanical behaviour of ceramic coating systems is determined by the stresses developed on the coating systems and the related
strengths, which depend on material features such as microstructure, thermal physical properties and material thermal stability.

2.3.6.1 Effect of Microstructure

The most important microstructural features affecting coating system thermal shock behaviour include porosity, microcracks, grain orientation and the presence of amorphous phases.

The porosity of a material may affect the material's ability to withstand thermal stresses in several ways. Pores can increase material toughness by arresting cracks. On the other hand, pores may reduce material strength by decreasing effective cross-sectional area. Additionally, open pores allow gaseous impurities in service environment to penetrate through the coating and to react with the substrate. The effects of porosity on ceramic coating performance under thermal shock have been investigated mainly by using plasma sprayed thermal barrier coatings. A study of ceria-yttria stabilized zirconia (CYZ) coatings showed that porous CYZ coatings perform better than dense CYZ coatings under thermal shock [81]. In another study, a value of approximately 15% mean porosity was suggested as one factor to explain the good thermal shock resistance of $\text{Y}_2\text{O}_3$ and $\text{MgO}$ stabilized $\text{ZrO}_2$ coatings [79]. In a general sense, it has been suggested that a ceramic coating should contain 5-10% fine homogeneously distributed pores in order to obtain a good thermal shock resistance [82].

In addition to pores, random microcracking is able to prevent cracking propagation thus to increase a material's capability of withstanding thermal stresses. Columnar structures with crystals normal to the substrate surface are also beneficial due to their tolerance to thermal stress in the plane of the coating by accommodating small incremental lateral strain displacements at each of the columnar boundaries [82, 83].
Amorphous phases may affect the behaviour of coating systems by inducing inelastic deformation. As temperature increases, amorphous phases soften due to dramatic decrease of viscosity [49, 84] and, in turn, inelastic deformation may occur due to the stress caused by the mismatch between the coating and the substrate in their thermal expansion coefficients. Inelastic deformations of the coating at high temperature will release the stresses at high temperature. However, the stress relief will increase the thermal contraction mismatch when temperature decreases, and then lead to an increase in stress during cooling [40].

2.3.6.2 Effect of Physical Properties

Under thermal cycling, in addition to the temperature range, the severity of thermal stress depends on material physical properties, particularly thermal expansion coefficient, thermal conductivity, thermal diffusivity, and Young's modulus.

It is recognized that the basic cause of ceramic coating failure under thermal cycles is the large thermal expansion mismatch between the coating and the substrate. Thermal expansion coefficients for most common ceramics are in the range of $0.5 \times 10^{-6}/^\circ C \sim 10 \times 10^{-6}/^\circ C$ [49]; while for metals they are much higher. For example, thermal expansion coefficients are in a range of $15 \times 10^{-6}/^\circ C$ for carbon steels [85], and $18 \times 10^{-6}/^\circ C$ for stainless steels [86]. To reduce thermal stresses caused by the mismatch of thermal expansion coefficients, coatings with larger thermal expansion coefficients are preferred [81]. However, in addition to the thermal expansion mismatch stresses, thermal expansion coefficients also affect the stresses caused by temperature gradients. As shown in eq.2.1, normally the larger the thermal expansion coefficient, the larger the stresses. Therefore, to reduce stresses caused by temperature gradient, smaller thermal expansion coefficients of coatings are preferred. Therefore, the effects of thermal expansion coefficient on thermal shock behaviour of ceramic coating systems are in conflict in terms of thermal expansion
mismatch stress and temperature gradient stress. However, since coatings are normally very thin, the effect of temperature gradient is usually not significant and the stresses caused by thermal expansion mismatch are usually believed dominant, therefore larger thermal expansion coefficients of coatings are normally preferred.

Thermal conductivity \( k \) is defined as the heat flow per unit area developed under unit temperature gradient [87]:

\[
k = -\frac{1}{A} \frac{dQ}{dt} \frac{dl}{dT}
\]

where \( \frac{dQ}{dt} \) is the rate of heat flow across area \( A \), and \( \frac{dT}{dl} \) is the temperature gradient. Thermal diffusivity is a measure of how fast a heat flux is transmitted through a solid. It is defined as [87]:

\[
d = \frac{k}{\rho C}
\]

where \( \rho \) is the density and \( C \) is the specific heat. Thermal conductivity and thermal diffusivity play an important role in the establishment of thermal stress by affecting transient temperature distribution under thermal shock, as shown by the heat conduction equations [87]. Normally the lower the thermal conductivity and thermal diffusivity, the steeper the temperature gradient and thus the more severe the thermal stress.

Young's modulus \( E \) reflects a material's elastic deformation behaviour. It is defined as [44]:

\[
E = \frac{\sigma}{\varepsilon}
\]

where \( \sigma \) is the stress on the material and \( \varepsilon \) is the related strain. For the same deformation level, the larger the Young's modulus, the larger the stress.
2.3.6.3 Effect of Material Stability

Material thermal stability, including oxidation, diffusion and phase transformation, may have significant effects on thermal cycle performance of ceramic coating systems.

Oxidation of metals will produce a layer of scale on the metal surfaces. For many metal-scale systems, stresses will result due to the mismatch of volume and thermal expansion coefficients for the metal and the scales [88,89]. Material oxidation has been considered to be responsible for coating spalling under thermal shock, especially under thermal shock fatigue tests with a large number of thermal cycles. The oxides which formed at the substrate or bond coating near the coating-substrate or coating-bond coating interface weaken the coating adhesion due to the oxidation induced stresses or poor adhesion or cohesion of the oxides and eventually cause coating spalling [40, 70, 90-93].

In a coating system, due to the chemical potential between the coating material and the substrate material, element diffusion may occur at high temperature. If the reaction products have poor mechanical strength, or unusual thermal expansion coefficients, the diffusion will be detrimental to the coating performance under thermal shock. Thus the chemical compatibility between the coating and the substrate is considered very important [94].

A phase transformation normally involves structural change which may be accompanied by a volumetric change and the volumetric change may promote coating spalling. For example, the crystallographic destabilization of magnesia-stabilized zirconia coatings at temperature above 954°C decreases coating life significantly [30].
2.4 MECHANICAL BEHAVIOUR OF COATING SYSTEMS

The mechanical behaviour of bimaterials, constructed with one kind of a thin layer of material attached on the surface of another kind of bulk material, has been investigated for many years. Although some of the studies were conducted in respect of oxide scales on metals or thin solid films, they also apply to ceramic coating systems. In this section, the experimental and theoretical aspects of mechanical integrity failure of the bimaterials are reviewed. For consistence and convenience, the thin layer is termed as 'coating', although it is sometimes termed as 'oxide scale' or 'thin solid film' in the original references; the bulk material is termed as 'substrate', although it is sometimes termed as 'metal' in the original references.

Ceramic coating systems may fail by a number of different forms, including mud cracking, (through-thickness cracking), mud cracking followed by delamination, delamination followed by coating buckling, and delamination initiating from a free surface [95, 96], as shown in Fig.2.9.

Delamination occurring at the coating/substrate interface is usually referred to as adhesive failure, while that occurring within the coating is referred to as cohesive failure [97-99]. Normally coating systems fail adhesively when coating/substrate interface adhesion strength is lower than the coating cohesion strength, otherwise cohesively. Delamination of coating may lead ultimately to coating spalling.

The type of coating failure depends mainly on stresses in coating systems. It should be noted that due to the complications arising at the edges of specimens, the effects of stress are usually analysed based on a semi-infinite model, as reviewed in this section. The semi-infinite model is valid for most coating failure forms except delamination from free edges.
Fig. 2.9 Schematic diagrams showing basic coating failure forms [95]. (a) mud-cracking, (b) mud-cracking followed by delamination, (c) delamination followed by buckling, and (d) delamination initiating from a free edge.
2.4.1 Failure under Tensile Stress

When a coating is subjected to biaxial tensile stress, the most common failure form is mud cracking. Occasionally, delamination and spalling may occur [98,99].

**Mud Cracking**

Under tension, through-thickness cracks can be induced when the tensile stress is beyond the tensile strength of a coating. The cracks are likely to develop by propagation of pre-existing defects either within or, more likely, at the surface of a coating. It was found that thicker coating layers failed at lower levels of applied stress than did the thin ones. This is thought due to a higher probability of finding larger defects in the thicker coating. Once a through-thickness crack has developed, the stress state changes significantly. First, stress normal to the crack surface drops to zero and an elastic relaxation of stress occurs in the vicinity of the crack. In addition, shear stresses develop along the coating-substrate interface (Fig.2.10), where there was no stress originally except at the edges [99]. Through-thickness cracking may not necessarily be detrimental and also may have the beneficial effect of arresting cracks [73].

**Spalling**

Once a through-thickness crack forms, shear stress develops along the coating-substrate interface and reaches a maximum adjacent to the crack (Fig.2.10), although the result obtained by Tien and David is different from that obtained by Nicholls et al. in the stress magnitude. Two shear spalling mechanisms were proposed. One is brittle shear fracture, the other is non-elastic slippage of the coating over the substrate. According to the first mechanism, the high shear stress which develops at coating/substrate interface at a position adjacent to the through-thickness tensile crack
Fig. 2.10 Stress state change after mud-cracking under tensile stress [99].
(a) formation of mud-cracks, (b) normal tensile stress at crack surface reduces to zero, and (c) shear stress at coating/substrate interface rises with maximum value adjacent to the cracks.
itself initiates a shear crack. This nucleation occurs when the maximum shear stress exceeds the shear strength of the coating-substrate interface. Once nucleation occurs, propagation will follow and spalling will result. If brittle shear fracture in the interface does not occur, non-elastic slippage of the coating over the substrate may possibly lead to damage at the interface when the creep strength in shear of the interface is low. In practice, however, coatings under tensile stress seldom spall and tend to remain adherent to substrates.

2.4.2 Failure under Compressive stress

Under compression, a coating system normally fails by spalling. Spalling can occur by one of two processes, depending on the relative fracture strength of the coating and the coating/substrate interface [98, 99].

Route I

When the coating/substrate interface is stronger than the compressive fracture strength of the coating, the Route I process arises (Fig.2.11a). The coating develops compressive shear cracks firstly through its thickness before the interface fails. The formation of these shear cracks results in a geometry which permits tensile cracks to be wedged open along the coating-substrate interface and causes spalling. As shown in Fig.2.11b, increased stress, for example due to continued cooling, can then drive a wedge of adherent coating into the interfacial region of the block defined by the two shear cracks by sliding of the adherent coating on either side of the shear cracks. This wedging action nucleates a tensile crack which then propagates along the interface region of the block. As a result, the coating block will slide upward along the shear crack faces assisted by wedging of the adherent coating.
Fig. 2.11. Route I spalling under compressive stress.
(a) formation of shear cracks and followed spalling [98],
(b) formation of coating/substrate interfacial crack due to wedging effect [99].
Route II

By contrast, a relatively weak interface leads to the Route II process. As shown in Fig.2.12, localized decohesion of the film occurs first. The presence of such a decohesion can result in buckling of the coating when the compressive stress in the coating exceeds a critical value, which can be expressed as [100]:

\[ s = \frac{k E_c}{12} \left( \frac{H_c}{c} \right)^2 \]

where \( c \) is the radius of separation between the oxide and the metal and \( k \) is a constant. The buckling leads to stress concentrations at the crack tips and hence a crack driving force. As the result of coalescence of the buckles by the interfacial tensile crack propagation, coating spalling occurs.

2.4.3 Edge Effect

In the semi-infinite model used in the above analysis, shear stresses do not exist in the interface before coating damage by tensile or compressive stress occurs. However, in practice, all specimens have finite dimensions, where shear stress is distributed along the coating/substrate interface as a function of distance from the free edge. It is the shear action in the interface that keeps the coating and the substrate identical in their dimension and to achieve dimensional compatibility required by the composite structure. In addition, the stress in the coating at the edges is different from that in other areas. Stress distributions in Fig.2.10 show the edge effect.
Fig. 2.12 Route II spalling under compressing stress [98].
3.1 GENERAL

This chapter is devoted to details of the experimental work, including coating systems used in the present research in §3.2, thermal cycle test techniques in §3.3 and §3.4, specimen examination in §3.5; thermomechanical and thermogravimetric analysis in §3.6. A summary of this chapter is given in §3.7.

3.2 SPECIMENS

3.2.1 Specimen Configuration

In the present research, a disc shape was adopted as the specimen configuration to simplify the analysis and fabrication of the specimens. The disc diameter and thickness were 31.5mm and 3mm respectively. Ceramic coatings were deposited on both sides of each disc, therefore effectively two coating samples were obtained in each disc specimen, and tests for each disc specimen showed the performance of two coating samples.

3.2.2 Substrate Materials

The substrate is an essential part of a coating system and plays an important role in the overall performance of the coating system. For example, the thermal expansion
coefficient of the substrate has a significant effect on thermal expansion mismatch between the coating and the substrate. This mismatch is believed to be a limiting factor in the life of ceramic coating systems exposed to high temperatures or temperature variations. In addition, the bonding nature, which determines the coating adhesion, may also depend on substrate type.

In the present research, three types of substrate were used: an austenitic stainless steel (AISI316), copper and a carbon steel with composition shown in Table 3.1.

**Table 3.1 Composition of the carbon steel**

<table>
<thead>
<tr>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>0.016</td>
<td>0.51</td>
<td>0.21</td>
<td>0.018</td>
<td>0.03</td>
<td>0.077</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Austenitic stainless steels comprise a group of iron-base alloys that contain 16% to 25% Cr and up to 20% Ni, and most of them are used extensively at elevated temperatures. Austenitic stainless steels may be one of potential substrates for coating systems for high temperature applications. Carbon steels are widely used and their performance as substrates for C-ramic coatings is of special interest to the manufacturer of the C-ramic coatings. Copper is usually very difficult to coat with AX coatings cured at 540°C. In the present research, copper was used to study the coatability and related thermal shock performance of the substrate with CZ type coatings cured at 400°C.

### 3.2.3 Coating Types

C-ramic coatings are applied onto a substrate in two stages, viz., deposition of a base coating consisting of filler particles and a binder/densifier, and subsequent densification by impregnation of a binder/densifier. The C-ramic coatings thus can be classified into different categories according to the type of base coatings and the
binder/densifiers. Four types of coatings were involved in the present research: two CZ type coatings, one AX type coating, and one hybrid CiX type coating. In the codes of coating types, the first letter represents the base coating type, the second letter represents binder/densifier type. The starting materials of the coatings are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Type</th>
<th>Base coating</th>
<th>Binder/densifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CiZ1</td>
<td>C1 (cured at 400°C)</td>
<td>Z1 (cured at 400°C)</td>
</tr>
<tr>
<td></td>
<td>Filler: SiO2, Al2O3, ZnO</td>
<td>CrO3, H3PO4, H2O, urea</td>
</tr>
<tr>
<td></td>
<td>Binder/densifier: CrO3, H3PO4, H2O, urea</td>
<td></td>
</tr>
<tr>
<td>C2Z2</td>
<td>C2 (cured at 400°C)</td>
<td>Z2 (cured at 400°C)</td>
</tr>
<tr>
<td></td>
<td>Filler: SiO2, Al2O3, ZnO</td>
<td>CrO3, H3PO4, H2O</td>
</tr>
<tr>
<td></td>
<td>Binder/densifier: CrO3, H3PO4, H2O</td>
<td></td>
</tr>
<tr>
<td>AX</td>
<td>A (cured at 540°C)</td>
<td>X (cured at 540°C)</td>
</tr>
<tr>
<td></td>
<td>Filler: SiO2, Al2O3, ZnO</td>
<td>CrO3, H2O</td>
</tr>
<tr>
<td></td>
<td>Binder/densifier: CrO3, H2O</td>
<td></td>
</tr>
<tr>
<td>CiX</td>
<td>C1 (cured at 400°C)</td>
<td>X (cured at 540°C)</td>
</tr>
<tr>
<td></td>
<td>Filler: SiO2, Al2O3, ZnO</td>
<td>CrO3, H2O</td>
</tr>
<tr>
<td></td>
<td>Binder/densifier: CrO3, H3PO4, H2O, urea</td>
<td></td>
</tr>
</tbody>
</table>

Basically, all the base coatings consist of silica (about 50% (wt)), alumina (about 2-5%) and trace amounts of zinc oxide (about 1-2%) as fillers. The binder/densifier in C and A base coatings are similar to Z and X types of binder/densifiers respectively in their ingredients. All binder/densifiers contain chromic acid, but the Z types contain phosphoric acid in addition. Also, Z1 has small amount of urea (about 2%), which is added in an attempt to stop fuming of CrO3 during curing. The CZ type coatings are cured at 400°C, the AX type coating is cured at 540°C, and the CiX type coating is cured at 400°C for the base coating and 540°C for densification.
The AX type coating was developed directly from the recipes of Kaman Science Cooperation [18, 19], while the CZ and CiX coatings have been developed by Ceramic Australia Pty Ltd. Details of the coating ingredients were covered by the expertise of Ceramic Australia Pty Ltd. Due to the commercial sensitivity of the coatings' formulation, the manufacturer did not release the exact composition of the coatings. Also, the coating types were selected by the manufacturer and the author had no control over them.

### 3.2.4 Coating Systems

A coating system includes a coating and a substrate. In the present research, eight types of coating systems were investigated (Table 3.3). Each coating system is given a code to specify the type of substrate and the coating. The stainless steel, carbon steel and copper are represented by SS, CS and CU respectively. All four types of coatings were applied to the stainless steel substrate, allowing the performance of the four types of coatings to be compared directly. C\textsubscript{2}Z\textsubscript{2} and AX were applied on the carbon steel substrate, and C\textsubscript{1}Z\textsubscript{1} and C\textsubscript{2}Z\textsubscript{2} were applied on the copper substrate. The effects of substrate can be compared between the coating systems with the same types of coatings but different substrates.

<table>
<thead>
<tr>
<th>Table 3.3 The Specimens Used in the Research</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coating—</strong></td>
</tr>
<tr>
<td>C\textsubscript{1}Z\textsubscript{1}</td>
</tr>
<tr>
<td>C\textsubscript{2}Z\textsubscript{2}</td>
</tr>
<tr>
<td>AX</td>
</tr>
<tr>
<td>C\textsubscript{1}X</td>
</tr>
</tbody>
</table>
3.2.5 Specimen Preparation

Specimen preparation includes preparation of the substrate discs and deposition of coatings. The substrate discs were made by sawing and machining commercially available rods with diameter of 31.5mm of the substrate metals. The finished discs were 3mm±0.05mm in thickness. A hole of 1.5 mm in diameter leading to the centre of the disc was drilled from the circumference to the centre of each disc. This hole was used for holding the discs during the process of applying the coatings, and for embedding a thermocouple to monitor the temperatures during thermal cycle tests.

Prior to deposition of coatings, the substrate discs were subjected to a surface pretreatment in which the surface was degreased by solvent cleaning and grit blasted using alumina grit. The stainless steel substrate discs were also fired at 500°C in an attempt to aid the formation of surface oxide film. During the coating process, water based slurries of raw materials were prepared by ball milling to assure thorough mixing. The slurries were sprayed on both sides of the substrate discs by a manually operated compressed air spray gun. The specimens were then fired slowly, from ambient temperature to 400°C or 540°C to form the base coatings. The specimens were then sprayed with binder/densifiers and then heated to 400°C or 540°C. Since a fully-densified coating is not preferred for tolerance of thermal stresses generated under thermal shock, the densification process was repeated only six times on each specimen to produce the coatings with a certain level of porosity. The coating thickness was controlled in the range of 70±10µm. The coating process was conducted by one operator in C-Ramic Australia Pty Ltd.

3.3 TEST PIECES

3.3.1 Assembling of Test Pieces

A test piece consists of a specimen and a thermocouple embedded in the specimen. The thermocouples, which were standard K-type with metal sheath 1.5mm in
diameter, were used to monitor temperature and to suspend the specimen in a vertical tube furnace during thermal cycle tests.

In order to embed the thermocouples into specimens, a 10BA thread was cut on the thermocouple shield for about 20mm in length. Cutting threads is helpful for tapping the thermocouples into specimens. In thermal cycle tests (See §3.4), thermocouples were required to fit specimen holes tightly to bear the specimen weight and to suspend specimens in a furnace during heating. However, it is very difficult to find a suitable cement to fix thermocouples in the specimen holes, and in order to overcome this difficulty, the diameter of the holes in the specimens was selected to be the same as the diameter of the thermocouple metal shield. Threads were cut on thermocouple metal shield (Fig.3.1) and thermocouples were tapped into specimens. During tapping, the threads touched the hole walls and deformed to allow thermocouples to fit specimen holes tightly (Fig.3.2).

3.3.2 Location of Thermocouples

To measure specimen temperature accurately, the thermocouple bead was required to touch the end of a specimen hole. Since the length of the hole is known, the location of the bead was judged by the length of the thermocouple inserted into the hole. The bead was in touch with the end of the hole when the length of inserted thermocouple was equal to the length of the hole.

3.4 THERMAL CYCLE TESTS

The thermal cycle tests were carried out to study the performance of various coating systems under thermal shock. The principal purpose was to investigate when and how coating failure occurs.
Fig. 3.1 A schematic diagram showing threads cut in the thermocouple sheath.

Fig. 3.2 A schematic diagram showing tapping of a thermocouple in a specimen.
3.4.1 Design of Thermal Cycle Modes

To study the thermal shock performance of the coating systems and to investigate failure mechanisms, five modes of thermal cycle tests, A, B, C, D and E, as designed in Table 3.4, were used.

3.4.1.1 Mode A and mode C tests

Mode A and C tests are thermal cycles with an identical rapid cooling environment but different heating rates. They were designed to show the effect of different heating histories on the performance of the coating systems under cooling thermal shock. Water quenching was used for the thermal shock. Due to the experimental arrangement, the coating failure cannot be observed in these tests, and thus the following tests were designed.

3.4.1.2 Mode B and mode D tests

Mode B and mode D tests are thermal cycles with the same heating as A and C tests but involving slow cooling in air instead of rapid cooling by water quenching. The purpose of conducting the slow cooling tests was to analyse the thermal shock failure mechanism of the coating systems subjected to A and C cycles. The reasons for conducting the comparison are as follows.

In the water quenching test, the severity of thermal shock is increased by increasing the specimen temperature before quenching, (the peak temperature of a thermal cycle). For a homogeneous specimen, quenching damage is normally attributed only to the stresses caused by rapid cooling, which is termed 'cooling-rate-related stresses' here. The cooling-rate-related stresses are usually considered a function of peak temperature: the higher the peak temperature, the more severe the stresses. For
Table 3.4 Scheme of Thermal Cycle Tests

<table>
<thead>
<tr>
<th>Mode</th>
<th>Schematic Presentation of the Procedure</th>
<th>Objective of Investigation</th>
<th>Test Procedure</th>
</tr>
</thead>
</table>
| A    | ![Graph](image)                         | Response to thermal shock correlated to slow heat history | * heating at 20°C/min to peak temperature  
* stabilising 30 sec.  
* quenching into water |
| B    | ![Graph](image)                         | 1. Response to slow cool correlated to slow heat history  
2. Thermal shock failure mechanisms correlated to slow heat history | * heating at 20°C/min to peak temperature  
* stabilising 30 sec.  
* cooling in air |
| C    | ![Graph](image)                         | Response to thermal shock correlated to rapid heat history | * heating at 250°C/min to peak temperature  
* stabilising 30 sec.  
* quenching into water |
| D    | ![Graph](image)                         | 1. Response to slow cool correlated to rapid heat history  
2. Thermal shock failure mechanisms correlated to rapid heat history | * heating at 250°C/min to peak temperature  
* stabilising 30 sec.  
* cooling in air |
| E    | ![Graph](image)                         | Influence of time-at-high temperature on thermal shock performance | * heating at 250°C/min to peak temperature  
* holding for certain time  
* quenching into water |
a coating system, however, the situation is far more complex. Due to the mismatch of thermal expansion coefficients between the coating and the substrate, stresses will be induced in a coating system at any temperature that is different from the fabrication temperature of the coating systems, as described in §2.3.1.2. Therefore, in a thermal cycle, stresses due to thermal expansion mismatch arise firstly at the heating up stage. If the peak temperature is sufficiently high, the stresses may damage the coating directly, or may be relieved by material inelastic deformation. This stress relaxation may increase the mismatch between the coating and the substrate dimensions during the subsequent cooling [40], regardless of cooling rate. Consequently, coating failure observed from a quenching test cannot be attributed solely to cooling-rate-related stresses. Stresses related to heating, which are termed 'heating-related stresses' here, may also contribute.

To investigate the contribution of cooling-rate-related stresses and heating-related stresses to coating failure under thermal shock, when damage occurs during water quenching, say test A, a parallel test B with the same heating history but air cooling, which is much slower than water quenching, was conducted. During the air cooling procedure, a specimen was taken out of a furnace at the same peak temperature used in mode A and visually inspected while it cooled down. If failure was not observed in test B, the failure in test A is due to cooling-rate-related stresses caused by thermal shock. Otherwise, failure in test A may be attributed to heating-related stresses, instead of thermal shock.

3.4.1.3 Mode E test

In the mode E test, a specimen was heated up as in the mode C test to a predetermined temperature, and then kept in the furnace at this temperature for a predetermined time before quenching.
The mode E test was used to study the effect of time-at-temperature. At high temperature, various thermally-activated events which are time-dependent may occur, such as diffusion, chemical reaction, inelastic deformation, and sintering. All those events may affect the thermal shock performance of a coating system. Since either positive or negative effects may be induced from the thermally-activated events, the overall influence from the events can be very complex, depending on both the time and the temperature level. Clearly, a comprehensive investigation of the time-at-temperature behaviour of a coating system is a large research subject and cannot be covered by the present work. The mode E test was therefore used only for a preliminary study of the influence of time at high temperature on thermal shock performance of some selected coating systems.

3.4.2 Test Program

The details of the thermal cycle test program are as follows. In all thermal cycle tests, to exclude the effect of fatigue on the observed critical peak temperature (defined in §3.4.2.1), each specimen was used only once, (i.e. exposed to one thermal cycle).

3.4.2.1 Mode A and C tests

In the thermal shock tests, the peak temperature ($T_p$) was raised in intervals of 50°C to increase the severity of the test condition. The $T_p$ of a thermal cycle upon which failure (see §3.4.5 for the definition of the failure) occurs in more than one out of four coating surfaces in two disc specimens is defined as the critical peak temperature ($T_{cp}$). Since the increment in $T_p$ is 50°C in the thermal cycle tests, a value of $T_{cp}$ actually represents a temperature range of 50°C, between ($T_{cp} - 50^\circ C$) to $T_{cp}$.

The value of $T_{cp}$ for each type of the coating systems under the thermal shock tests was determined in a series of cycles. The tests were conducted firstly from an
arbitrary initial $T_p$. If the coating system did not fail, $T_p$ for the next specimen was increased by 50°C until the coating system failed; otherwise, decreased by 50°C until the coating system did not fail. Then, the current cycle and the previous cycle were duplicated to confirm the result. In the quenching tests conducted in the early stages of the research using SS/CiZ1, the initial $T_p$ was chosen as 500°C. Since the tests showed that this temperature was far below the critical peak temperature of the SS/CiZ1, the initial $T_p$ for the other coating systems with stainless steel substrate was raised to 800°C. The initial $T_p$ for the coating systems with the carbon steel substrate was chosen as 700°C.

3.4.2.2 Mode B and D tests

When a coating system failed under thermal shock, say mode A, with a critical peak temperature $T_{cp}$, a parallel test B with the same heating history but air cooling was conducted for the same coating system. If the coating system did not fail, the peak temperature of the mode B test was raised to $T_{cp}+50$°C. If the coating system still did not fail, then the effect of cooling rate on thermal shock behaviour of the coating systems was considered significant and the air cooling tests were usually terminated.

3.4.2.3 Mode E test

In mode E test, the selected coating systems were held for 30min at a temperature which was lower by 50°C than the related $T_{cp}$ under mode C test.

3.4.2.4 Definition of code representing test and specimen

In this thesis, for convenience, each test is given a code indentifying the specimen and the test condition. The code consists of three parts: specimen, peak temperature and test mode. For example, the code SS/CiZ1-800A indicates the test of coating
system SS/CiZi subjected to a mode A thermal cycle defined in Table 3.4 with $T_p=800^\circ C$.

### 3.4.3 Test Equipment

The equipment used in the thermal cycle tests consists of an vertical tube furnace, a water bath and a temperature monitoring system. The arrangement of this apparatus is shown schematically in Fig.3.3.

During the heating procedure, a specimen was suspended in the hot zone of the furnace by a thermocouple and a steel guide shaft. The water bath, at room temperature, was used to cool the specimens rapidly during quenching. In order to quench, the steel guide shaft was released from a clip and the specimen was allowed to drop 10cm into the water. The temperature monitoring equipment was used to monitor the temperature of the specimen by means of a K-type thermocouple embedded in the centre of the specimen and a computer controlled digital data acquisition facility.

The error in temperature values obtained using the K-type thermocouple was estimated to be $\pm 5^\circ C$. The temperature readings from the computer digital data acquisition facility are within an error of $\pm 5.5^\circ C$. Thus the error of temperature readings is approximately $\pm 10^\circ C$.

### 3.4.4 Reproducibility of the Quenching Test

Reproducibility of the quenching procedure was judged from cooling curves measured from the centre of a stainless steel disc during repeated quenching. Fig.3.4 shows the cooling curves obtained from four successive quenching tests on the same
Computer-controlled data acquisition subsystem

Water bath

Fig. 3.3 A schematic diagram of the test apparatus
Fig. 3.4  Cooling curves from a series of water quenching tests on the same sample.
stainless steel disc test piece. The similarity of the cooling curves suggests that the quenching procedure is reasonably reproducible.

3.4.5 Definition of Failure

Failure was defined as the visible spalling of the coating from the top or bottom side of the disc specimens. Spalling from the circumference was not considered, because this region was not deliberately coated due to the technical inconvenience of controlling coating quality and thus coatings in this region are unrepresentative.

3.5 SPECIMEN EXAMINATION

To characterise the coating systems, investigate the influence of thermal shock on microstructure, and analyse failure type, the pre-test and post-test specimens were examined using a scanning electron microscope (SEM) and an X-ray diffractometer (XRD).

3.5.1 Coating Microstructure Study

3.5.1.1 Surface morphology

The surface morphology of the four types of coatings, represented by the coating systems with stainless steel substrates, before and after thermal cycle tests, was examined using a SEM. The specimen surface was inspected using disc specimens directly after carbon coating.

3.5.1.2 Cross-section morphology

The cross-section morphology of the four types of coatings, also represented by the coating systems with stainless steel substrates, before and after thermal cycle tests, was examined using the SEM.
To prepare cross-section samples, the specimens were cut carefully and then cold mounted, as shown in Fig.3.5. The cross-section sample of spalled coating fragments was prepared by gluing the fragments onto a flat metal piece and then mounting the metal piece as shown in Fig.3.6. The cross-section samples were then ground and polished carefully. During grinding and polishing, special care was taken to minimise artifacts due to particle pull-out, which is very difficult to eliminate in grinding and polishing of ceramics with multi-particle structures, such as the coatings involved in the present research. Effective cutting during grinding and using napless or short napped cloths in polishing can reduce the risk of particle pulled-out [101]. To avoid particle pull-out as much as possible under the present research condition, the specimens were initially ground carefully with a series of silicon carbide (SiC) papers: 240, 400, 600 and 1200 grit. During grinding, abrasive papers were changed frequently to maintain effective cutting. After grinding, the specimens were polished on short napped cloths charged with 6μm diamond and with 1μm diamond paste respectively.

3.5.1.3 Interfacial region

Interfacial regions of the eight coating systems were examined in cross-sections of the specimens using SEM. The purpose of the examination was to investigate the formation of the conversion coating layer, which was believed to have an important contribution to coating adhesion.

3.5.1.4 X-ray diffraction analysis

To investigate the microstructural stability of the coating material and the related influence on coating spalling, X-ray diffraction analysis of the coatings prior to and after thermal cycle tests was carried out using an X-ray diffractometer with Cu Kα radiation. Pre-test and unfailed specimens were examined directly by using the disc
Fig. 3.5 Preparation of a cross-section sample.

Fig. 3.6 Preparation of a cross-section sample of spalled coating fragments.
specimens, while the failed specimens were analysed using the spalled coating fragments, which were ground into powder using an agate mortar and pestle.

3.5.2 Investigation of Failure Form

In thermal cycle tests, the coating systems failed by coating spalling. Generally speaking, coating spalling may occur either adhesively or cohesively, depending mainly on the ratio of adhesive strength to cohesive strength of the coating system. If adhesive strength is stronger than cohesive strength, spalling may occur cohesively, and vice-versa.

To analyse the failure modes, surfaces of the substrates after spalling and the inner surfaces of the spalled coating fragments were analysed in terms of surface morphology and composition, using SEM in conjunction with energy dispersive spectrum analysis (EDS). The substrate surfaces were examined by using the disc specimens directly. The spalled coating fragments were inspected after glueing the coating fragments with the inner surface up on standard aluminium stubs.

3.6 THERMAL ANALYSIS OF COATING MATERIALS

To study the thermal stability of the coatings, thermomechanical analysis and thermogravimetric analysis were conducted. Coatings free of substrates were used. The samples were prepared by depositing the coatings on porcelain plates. The coatings have almost no adhesion on the porcelain plates and can thus be removed from the plates easily.

3.6.1 Thermomechanical Analysis

Thermomechanical analysis was conducted to study the thermal stability of the coating materials by monitoring volumetric change using a dilatometer attached to a
Mettler TA 3000 System. The samples used in the analysis were about 1cm$^2$ in area and 150µm in thickness. The specimens were heated from room temperature to 900°C at 20°C/min, and the specimen thickness change was recorded as a function of temperature.

### 3.6.2 Thermogravimetric Analysis

The analysis was conducted in conjunction with the thermomechanical analysis to study the relationship between coating volumetric change and coating thermogravimetric change. A Perkin-Elmer 7 Series Thermogravimetric Analyser was employed. The samples, about 0.05g, were heated from room temperature to 900°C at 20°C/min, and the sample weight change was recorded as a function of temperature.

### 3.7 SUMMARY

Eight types of coating systems were studied in the present research. The performance of coating systems under thermal shock was investigated by using five modes of thermal cycle tests. The coating system performance under thermal cycles was evaluated mainly by a 'critical peak temperature' that is related to the failure of mechanical integrity of coating systems. A scanning electron microscope (SEM) and a X-ray diffractometer (XRD) were used for characterization and failure analysis of the coating systems. Thermal stability of the coatings was studied by thermomechanical analysis and thermogravimetric analysis.
CHAPTER FOUR

CHARACTERISTICS OF THE COATINGS

4.1 GENERAL

This chapter presents characteristics of the coatings as received, including the coating surface and cross-section morphology, coating/substrate interfacial region morphology, and coating X-ray diffraction patterns. The characteristics are described in §4.2, §4.3, §4.4 and §4.5 respectively for C1Z1, C2Z2, AX, and C1X coatings. A summary and concluding remarks of this chapter are given in §4.6.

4.2 C1Z1 COATING

4.2.1 Surface

As shown in Fig.4.1a the surface of the C1Z1 type coating has a featureless non-crystalline appearance, and is covered with microcracks distributed randomly in a network pattern. The amorphous appearance is a consequence of the Z1 densifier, which results in the formation of an amorphous compound between chromic acid and phosphoric acid, as will be shown in §4.2.4. The width of the cracks is about 0.5 to 1μm; the length of the cracks varies. Vertical cracks penetrating to the substrate are not observed in the cross-section of the coatings (Fig.4.2a), which indicates that these cracks are very shallow. The cracks might result from the densification procedure due to shrinkage of the binder/densifier during drying. In addition to the microcracks, there are some spalling-like defects, as indicated by the arrow in Fig.4.1a. The EDS of the normal area and the defect area are shown in Fig.4.1b and Fig.4.1c. The two spectra are similar, mainly consisting of P and Cr, which are
Fig. 4.1 Surface morphology of C1Z1 coating.  
(a) general morphology (× 500), (b) EDS of the surface, (c) EDS of the spalling-like defect indicated by the arrow in (a).
constituent elements of the Z1 bonder/densifier. In addition, the spectrum from the defect area shows a significant peak of Si from the base coating.

4.2.2 Cross-section

The backscattered electron micrographs of the coating cross-section (polished-unetched) are shown in Fig.4.2a and Fig.4.2b. Since the atomic numbers of Si and Al in the filler particles (SiO₂, Al₂O₃) are lower than those of P and Cr in the matrix formed from the Z1 binder/densifier, the filler particles appear darker than the matrix. As can be seen, the coating microstructure consists of discrete filler particles dispersed randomly in the matrix. Their size varies from a few microns to tens of microns. In addition, pores of various size are distributed in the coating randomly and non-uniformly. It should be noted that not all the pores are genuine: the pores with granular shape may result from particle pull-out during specimen preparation. Genuine pores in the coating may be generated mainly due to evaporation of water from the base coating slurry and densifier solutions during the curing cycles.

4.2.3 Interfacial Region

The C₁Z₁ coating was applied to stainless steel and copper substrates. The interfacial region of the SS/C₁Z₁ in Fig.4.3a shows that the coating and the substrate are distinguished clearly by a wavy line and no conversion coating layer was detected. The dark particles in the substrate near the interface are alumina particles trapped in the substrate during grit blasting.

The interfacial region of CU/C₁Z₁ is shown in Fig.4.3b. An intermediate layer, which is an order of microns in thickness, exists between the coating and the substrate. EDS obtained from point analysis of the white layer shows mainly Cu with a trace amount of Cr. Since the content of Cr is very low, this layer is likely to be a copper oxide layer which was formed during the coating process. Significant
Fig. 4.2 Cross-section morphology of C1Z1 coating. 
(a) × 500, (b) × 1000.

A: filler particle, B: binder matrix, C: pore.
Fig. 4.3 Interfacial region.
(a) SS/C1Z1 (x 1500), (b) CU/C1Z1 (x 1500), (c) EDS of the intermediate layer in (b).
oxidation of the substrate could have resulted during curing of the coating at 400°C due to oxygen diffusion from atmosphere, or by oxygen released from CrO₃ when Cr⁶⁺ is reduced to Cr³⁺.

4.2.4 X-ray Diffraction Pattern

The X-ray diffraction pattern of the coating is shown in Fig.4.4. The main diffraction peaks are from the α-quartz. Faint diffraction peaks from α-Al₂O₃ were also detected. Since no diffraction peaks from P or Cr compounds were detected, any compound formed from chromic acid and phosphoric acid in the Z₁ binder/densifier, which forms the coating surface and matrix, must be in an amorphous state.

4.3 C₂Z₂ COATING

4.3.1 Surface

As shown in Fig.4.5a, the surface morphology of the C₂Z₂ coating is similar to that of the C₁Z₁ coating. The surface has a featureless amorphous appearance, and is covered with microcracks distributed randomly in a network pattern, and also contains micro-spalling defects. The featureless appearance is a result of the Z₂ densifier, which produces an amorphous compound from chromic acid and phosphoric acid, as will be shown in §4.3.4. No penetrating vertical cracks were observed in the cross-section of the coatings (Fig.4.6a), which indicates that the microcracks were very shallow. The EDS of the coating surface in Fig.4.5b shows mainly P and Cr from the Z₂ binder/densifier.

4.3.2 Cross-section

The backscattered electron micrographs of the coating cross-section (polished-unetched) are shown in Fig.4.6a and Fig.4.6b. The microstructure consists of
A: SiO$_2$ (α-quartz)
B: α-Al$_2$O$_3$

Fig. 4.4 X-ray diffraction pattern of C1Z1 coating.
Fig. 4.5 Surface morphology of C2Z2 coating.
(a) general morphology (x 500), (b) EDS of the surface.
Fig. 4.6 Cross-section morphology of CzZ2 coating. (a) × 500, (b) × 1000.
discrete silica and alumina particles dispersed randomly in a matrix formed from Z2 densifier, together with genuine pores and holes resulting from particle pull-out. The structure is very similar to that of the C1Z1 coating.

4.3.3 Interfacial Region

The C2Z2 coating was applied to all three types of substrate used in the present research. The interfacial regions of SS/C2Z2 and CU/C2Z2 are similar to those of SS/C1Z1 and CU/C1Z1 respectively. The interfacial region of the coating with a carbon steel substrate, CS/C2Z2 is shown in Fig.4.7. As with the coating on stainless steel substrates, the coating and the substrate are separated clearly by a wavy line, and no conversion coating layer was detected.

4.3.4 X-ray Diffraction Pattern

The X-ray diffraction pattern of the coating is shown in Fig.4.8. It is very similar to the pattern of C1Z1. Since no diffraction peaks related to P or Cr could be detected, any compounds from chromic acid and phosphoric acid in Z2 binder/densifier must also be in an amorphous state.

4.4 AX COATING

4.4.1 Surface

A typical coating surface morphology is shown in Fig.4.9a. The coating surface is covered with agglomerated particles formed from X type binder/densifier which results in the formation of Cr2O3 particles in crystalline form, as will be shown in §4.4.4. Defects consisting of microcracks in network patterns (Fig.4.9b) also exist in some areas. Penetrating vertical cracks are not observed in the cross-section of the
Fig. 4.7 Interfacial region of CS/C2Z2 (x 1500).
A: SiO$_2$ (α-quartz)
B: α-Al$_2$O$_3$

Fig. 4.8 X-ray diffraction pattern of C$_2$Z$_2$ coating.
Fig. 4.9 Surface morphology of AX coating.
(a) general morphology (×500), (b) microcracking defects (×2000), (c) EDS of the surface.
coatings (Fig. 4.10a), which indicates that the microcracks are very shallow. The EDS of the surface is shown in Fig. 4.9c, which shows mainly Cr from the top binder/densifier, and Si and Al from the base coating.

### 4.4.2 Cross-section

The backscattered electron micrographs of the coating cross-section (polished-uncharged) are shown in Fig. 4.10a and Fig. 4.10b. The microstructure consists of filler (SiO₂, Al₂O₃) particles dispersed in a matrix formed from X type binder/densifier. As has been shown from the coating surface morphology, agglomerated Cr₂O₃ particles are formed from the X binder/densifier, and thus the matrix in the AX coating is made of agglomerated Cr₂O₃ particles. In addition, pores of various size are distributed in the coating randomly and non-uniformly. As with the CZ coatings, some pores are not genuine and are probably caused by particle pull-out during grinding and polishing. In comparison with backscattered electron image of CZ coatings, the contrast between the discrete filler particles and the matrix in the AX image is much stronger. This is due to the difference between the CZ coatings and AX coatings in their matrix composition. The matrix of CZ coatings is composed of compounds of chromic acid and phosphoric acid, while the matrix of AX coatings is Cr₂O₃. The atomic number of P is 15, which is very close to those of Si (14) and Al (13), while the atomic number of Cr is 24. Therefore, the contrast between the filler particles and the Cr₂O₃ matrix in the AX coating is much stronger than that between the filler particles and the matrix from chromic acid and phosphoric acid in CZ coatings.

### 4.4.3 Interfacial Region

The AX coating was applied on both stainless steel and carbon steel substrates. The interfacial region of SS/AX is similar to that of SS/C₁Z₁, i.e. the coating and the
Fig. 4.10 Cross-section morphology of AX coating. (a) $\times 500$, (b) $\times 1000$. 
substrate are distinguished clearly by a wavy line (Fig. 4.11a). However, the interfacial region of CS/AX (Fig. 4.11b) is different from that of SS/AX. An intermediate layer, which is a few microns in thickness and envelopes the contours of the substrate, was found between the coating and the substrate. This intermediate layer is distinguished from the coating in two aspects in its appearance. Firstly, the layer is denser than the coating; there are almost no pores. Secondly, the amount of filler particles in the intermediate layer is less, and particle size is smaller. An EDS spectrum from point analysis of the intermediate layer matrix shows Fe and Cr (Fig. 4.11c).

4.4.4 X-ray Diffraction Pattern

Fig. 4.12 shows the X-ray diffraction pattern of the coating. The main diffraction peaks are from the α-quartz and Cr₂O₃. Also, faint diffraction peaks from α-Al₂O₃ were identified. In addition, the X type of binder/densifier, which forms the coating surface and matrix, leads to the formation of crystallised Cr₂O₃.

4.5 CiX COATING

4.5.1 Surface

As shown in Fig. 4.13a, the coating surface is covered with agglomerated particles formed from X densifier, which results in the formation of Cr₂O₃ particles in crystalline form, as will be shown in §4.5.4. Microcracks in network patterns exist in some areas. Penetrating vertical cracks were not observed in the cross-section of the coating (Fig. 4.14a), which indicates that the intrinsic cracks are very shallow. All the features are similar to those of AX coatings. The EDS of the surface is shown in Fig. 4.13b, which shows mainly Cr from the top binder/densifier, and Si, P and Al from the base coating.
Fig. 4.11 Interfacial region. 
(a) SS/AX (×1500), (b) CS/AX (×1500), (c) EDS of the conversion coating layer in (b).
A: SiO₂ (α-quartz)
B: α-Al₂O₃.
C: Cr₂O₃.

Fig. 4.12 X-ray diffraction pattern of AX coating.
Fig. 4.13  Surface morphology of ClX coating.
(a) general morphology (× 500), (b) microcracking defects (×2000), (c) EDS of the surface.
4.5.2 Cross-section

The backscattered electron micrographs of coating cross-section view (polished-unetched) are given in Fig.4.14a and Fig.4.14b. The microstructure consists of discrete silica and alumina particles dispersed in a matrix formed from chromic acid and phosphoric acid in the C1 type base coating. The X densifier fills the pores of the base coating. The microstructure also contains genuine pores and holes resulting from particle pull-out.

For the hybrid C1X type, since the binder/densifier used for densification is different from that in the base coating, the penetration of the binder/densifier is clearly demonstrated in the coating microstructure, which cannot be observed in the CZ and AX type coatings.

4.5.3 Interfacial Region

The C1X coating was applied only to stainless steel substrates. As can be seen from Fig.4.15, similar to other coating systems with stainless steel substrates, the coating and substrate are distinguished clearly from each other by a wavy line, and no conversion coating layer was detected.

4.5.4 X-ray Diffraction Pattern

Fig.4.16 shows the X-ray diffraction pattern of C1X. The main diffraction peaks are from the α-quartz and Cr2O3. Faint diffraction peaks from α-Al2O3 were also identified. Also, the compound of chromic acid and phosphoric acid from the C1 base coating is in the amorphous state, the Cr2O3 from the X densifier is in a crystalline form.
Fig. 4.14 Cross-section morphology of C1X coating.
(a) $\times 500$, (b) $\times 1000$. 
Fig. 4.15 Interfacial region of SS/CtX (×1500).
A: SiO$_2$ (α-quartz)  
B: α-Al$_2$O$_3$  
C: Cr$_2$O$_3$

Fig. 4.16 X-ray diffraction pattern of C1X coating.
4.6 SUMMARY AND CONCLUDING REMARKS

The coating surface morphology is determined by the binder/densifier type. For coatings with Z types densifiers, the coating surface is amorphous and covered with microcracks accommodated in the top surface. For coatings with X types densifiers, the surface is covered with agglomerated Cr$_2$O$_3$ particles.

It is seen from the cross-section morphology that the typical microstructure of the coatings consists of discrete filler particles randomly dispersed in a matrix formed from binder/densifiers in base coatings and densifiers. Also, since the coatings used in the present research had been subjected to only six cycles of densification, pores also exist.

X-ray diffraction patterns of the coatings show that α-quartz is the main crystalline phase for all coatings, with α-Al$_2$O$_3$ in smaller amount. The compound formed from chromic acid and phosphoric acid in CZ coatings is in an amorphous state. The chromic acid used in AX coating results in the formation of crystalline Cr$_2$O$_3$.

For the eight types of coating systems with the four types of coatings and the three types of substrates, a conversion coating layer was detected only in the coating system with the AX coating on the carbon steel substrate.
CHAPTER FIVE

BEHAVIOUR OF THE COATING SYSTEMS UNDER THERMAL CYCLE TESTS

5.1 GENERAL

This chapter presents the results of thermal cycle tests in a phenomenological sense. Interpretation of the results will be covered in Chapter 9.

§5.2 to §5.5 describe the performance of the coating systems under various thermal cycle conditions. The performance is evaluated mainly in terms of 'critical peak temperature' ($T_{cp}$) that represents, as mentioned in §3.4.2, a temperature range between ($T_{cp} - 50^\circ C$) to $T_{cp}$. In §5.6 the forms of coating failure and the progress of the failure are presented. Finally, the common performance features of the C-ramic coating systems and the influence of coating type and substrate material on performance are highlighted in §5.7.

5.2 RESPONSE TO HEATING

Heating is part of any thermal cycle and may induce coating damage before thermal shock due to cooling. The response of coating systems to heating was observed through mode B and mode D tests. The typical heating histories for the slow heating and rapid heating are given in Fig.5.1. Once the temperature reached a critical peak temperature in corresponding to mode A and mode C test, a coating system was removed from the furnace for visual inspection. No visual cracking or spalling was detected in either of the mode B and mode D tests for all the coating systems when the
Fig. 5.1 Typical heating histories of mode A and mode C thermal cycles.
specimens were initially removed from the furnace. This fact indicates that stresses induced by heating alone do not cause failure. Therefore, the failures of the coating systems in the thermal cycle tests are due mainly to the stresses induced in the cooling stage.

5.3 RESPONSE TO THERMAL SHOCK

5.3.1 Effect of Coating Type

The rank of the coatings in their thermal shock resistance was investigated by comparing the performance of different coatings deposited on the same type of substrate under cooling thermal shock. The substrate materials selected for this investigation included stainless steel, carbon steel and copper, with emphasis on the stainless steel.

5.3.1.1 Stainless steel substrate

The values of the critical peak temperature ($T_{cp}$) for the four types of coating systems with stainless steel substrates, SS/C1Z1, SS/C2Z2, SS/AX and SS/C1X, under mode A and mode C tests, are given in Fig.5.2.

The critical peak temperatures ($T_{cp}$) for different coating systems vary from 850°C to 1000°C. The $T_{cp}$ of C1Z1 and C2Z2 are affected slightly by heating history. Under mode A (slow heating) cycles, the $T_{cp}$ of C1Z1 and C2Z2 are 850°C and 900°C respectively. While under mode C (rapid heating) cycles, values of the $T_{cp}$ of the both coatings increase by one temperature increment, reaching 900°C and 950°C respectively. The $T_{cp}$ of AX is 850°C and is not affected by heating history. Of the four types of coatings, only the $T_{cp}$ of C1X is independent of heating history and reaches 1000°C.
Fig. 5.2 Effect of coating type on $T_{cp}$ under thermal shock.
5.3.1.2 Other substrates

For the two coating systems on carbon steel substrates, CS/C2Z2 and CS/AX, there is no significant difference between the C2Z2 and the AX coatings in their Tcp. Coating spalling occurred during quenching from 750°C independent of heating history.

For the two coating systems with copper substrates (CU/C1Z1 and CU/C2Z2), tests were conducted under the slow heating condition only. The value of Tcp for both C1Z1 and C2Z2 is 550°C.

5.3.2 Effect of Substrate Type

The effect of substrate material on coating system performance under thermal shock was investigated mainly by comparing the performance of the coating systems with the same C2Z2 coating but different substrates. In addition, C1Z1 type and AX type coatings were also used to confirm the effects.

5.3.2.1 C2Z2 coating

C2Z2 coatings were applied to all the three types of the substrates involved in the present research. Fig. 5.3 shows values of the Tcp of the three coating systems, SS/C2Z2, CS/C2Z2, CU/C2Z2, under mode A test (slow heating and rapid cooling). The Tcp of SS/C2Z2, CS/C2Z2, CU/C2Z2 are 900°C, 750°C and 550°C respectively. It is apparent that the coating system with stainless steel substrate has better thermal shock resistance than for the other substrates.
Fig. 5.3  Effect of substrate type on $T_{cp}$ under thermal shock.
5.3.2.2 Other coatings

The C1Z1 coating was applied to stainless steel and copper substrates. The $T_{cp}$ of SS/C1Z1 and CU/C1Z1 under mode A test, are 850°C and 550°C respectively. The results are similar to those obtained from C2Z2 coating.

The AX coating was applied to stainless steel and carbon steel substrates. Under mode A test, $T_{cp}$ of SS/AX and CS/AX are 850°C and 750°C respectively. The results are similar to those obtained from C2Z2 coating.

5.4 EFFECT OF COOLING RATE

To study the reasons for coating failure under thermal shock, the coating systems were also subjected to air cooling with much slower cooling rates than water quenching. Typical cooling curves for the two cooling modes represented by SS/C1X–1000C and SS/C1X–1000D are shown in Fig.5.4a. Cooling rates for the two cooling modes are significantly different. For water quenching, the temperature dropped from 1000°C to 200°C within 2sec. For air cooling, the temperature dropped by the same amount in about 3min. The average cooling rates are approximately 400°C/sec and 4°C/sec respectively.

The $T_{cp}$ of the eight types of coating systems under water quenching and air cooling are given in Fig.5.4b and Fig.5.4c for slow heating and rapid heating history respectively. As it is seen, the effects of cooling mode on $T_{cp}$ depend mainly on substrate type. For most of the coating systems with stainless steel substrate, i.e., SS/C2Z2, SS/AX and SS/C1X, the $T_{cp}$ are not affected by cooling rates under either rapid heating or slow heating, only the $T_{cp}$ of SS/C1Z1 under water quenching is lower than that under air cooling by one temperature interval (50°C). For coating systems with copper substrates, i.e., CU/C1Z1 and CU/C2Z2, $T_{cp}$ is not affected by
Fig. 5.4 Effect of cooling rates.
(a) typical cooling curves corresponding to water quenching and air cooling,
(b) $T_{cp}$ under water quenching and air cooling corresponding to slow heating,
(c) $T_{cp}$ under water quenching and air cooling corresponding to rapid heating.
cooling rate. The results suggest that for the coating systems with stainless steel substrate and copper substrates, coating spalling induced by thermal shock may be closely related to heating-related stresses. For coating systems with carbon steel substrate, i.e. CS/C2Z2 and CS/AX, coating spalling did not occur under air cooling even with \( T_p \) 100°C higher than the corresponding \( T_{cp} \) under water quenching, as indicated by arrows on related bars in Fig.5.4b and Fig.5.4c. Coating spalling for CS/AX occurred in a further Mode D test with \( T_p \) increased to 900°C, which is 150°C higher than the corresponding \( T_{cp} \) under mode C test. The results indicate that for coating systems with carbon steel substrates, cooling-rate-related stresses made a significant contribution to coating spalling under thermal shock.

5.5 EFFECT OF TIME AT HIGH TEMPERATURE

The influence of time at high temperature on thermal shock performance of SS/C1Z1 and SS/C1X was investigated in mode E tests. The specimens were heated in the same style as in mode C cycle to peak temperatures which are lower than the critical peak temperatures of the specimens in mode C test by 50°C. The specimens were then held at the peak temperature for 30min. For SS/C1Z1, the mode E test was conducted with \( T_p=850°C \). For SS/C1X, the mode E test was conducted with \( T_p=950°C \). Failure did not occur for either of the coating systems.

5.6 OBSERVATION OF FAILURE

5.6.1 Failure Form

In the present research, visible mud-cracking was not found. Visible spalling occurred for all coating systems under critical conditions. The results indicate that the coatings are probably under compressive stress when failure occurs.
5.6.2 Observation of Spalling Under Thermal Shock

During rapid cooling, the temperature dropped from $T_{cp}$ to room temperature within ten seconds. When the specimens were removed from the water bath, spalling had stopped. Although the spalling process could not be inspected directly under these conditions, some information can be inferred from the spalling patterns on the specimens. Three typical kinds of spalling patterns were observed (Fig. 5.5). In the first pattern (PI), coatings spalled completely from the substrates (Fig. 5.5a). This spalling pattern gave no obvious clues about the spalling process. In the second pattern (PII), the spalled areas are connected and located at the edges of the specimen (Fig. 5.5b). This spalling pattern indicates that the spalling may initiate at the edges. In the third pattern (PIII), the spalled areas are located randomly (Fig. 5.5c). This spalling pattern indicates that the spalling initiated from individual areas instead of preferentially at the edges.

As mentioned in §3.4.2, the coating performance was determined from the four surfaces of the two specimens in duplicated tests. Coating systems with stainless steel substrate showed both PI and PII spalling patterns. Coating systems with carbon steel substrates had the PI spalling pattern. Coating systems with copper substrates had the PIII spalling pattern.

5.6.3 Observation of Coating Spalling Under Slow Cooling

5.6.3.1 Spalling temperature

When the specimens were taken out of the furnace at the critical peak temperatures, there was no visible cracking nor spalling on the specimens. The specimens were observed visually until they cooled down to room temperature. It was found that visible spalling started when the temperature in the specimens decreased to some particular level depending mainly on the type of the substrate. With stainless steel
Fig. 5.5 Three typical patterns of coating spalling under rapid cooling. (a) complete spalling (PI), (b) spalling from edge area (PII), (c) spalling from spots (PIII).
substrates, spalling occurred at temperatures around 200°C; with copper substrates, spalling occurred at temperatures below 300°C; while for carbon steel substrates, coating spalling occurred at around 600°C.

5.6.3.2 Spalling process

Under slow cooling, the spalling process in terms of spalling area and spalling speed appeared to depend mainly on the substrate material.

With stainless steel substrates, spalling initiated from the edge of the specimen surface and gradually progressed to the centre with flaking of the coating piece by piece. The spalling progress was not uniform, being sometimes fast and sometimes slow. The process could last for 10 to 20 minutes until the coating spalled completely from the whole surface area of the substrate or stopped flaking with some coating remaining on the substrate. Fig.5.6 is a group of photographs taken for SS/CiZ1 during the spalling process. The spalled coating chips detached from the substrate explosively. With a carbon steel substrate, coating spalling was much quicker. The coating flaked in a violently explosive style within a second, and therefore spalling progress could not be followed visually. With a copper substrate, coating buckling in the area away from surface edge appeared first and then the buckled coating flaked off, as shown schematically in Fig.5.7. This behaviour indicates that the coating is under compression.

5.6.3.3 Spalling front

The spalling front of SS/CiZ1 during the spalling progress was observed using optical microscopy. Fig.5.8 shows the spalling front from above: the area out of focus is the spalled area. The spalling front did not appear to follow pre-existing cracks. This result gives the impression that the coating spalling was not caused by
Fig. 5.6 Spalling process observed during air cooling of SS/ClZ1

(a) $t=1$ min, (b) $t=3$ min, (c) $t=5$ min, (d) $t=7$ min.
Fig. 5.7 Spalling process observed during cooling of coatings with copper substrate.
Fig. 5.8  A micrograph showing spalling front which did not follow the pre-existing surface cracks (×300).
biaxial tensile stress, otherwise the cracking through coating thickness would prefer to follow the pre-existing surface cracks due to stress concentration effects.

5.7 SPALLING MODES ANALYSIS

5.7.1 Substrate Surface before Deposition of Coatings

Analysis of the substrate surfaces after coating spalling is one of the main approaches for analysing the spalling mode. It is necessary to understand the substrate surfaces before deposition of coatings to understand the morphology of the substrate surface after coating spalling.

The substrate surfaces were grit-blasted before applying the coatings. Fig.5.9 shows the typical appearance of the substrate surfaces, which is randomly wavy due to the plastic deformation of metal caused by the force of the grit during the blasting procedure.

5.7.2 Basic Spalling Modes

From examination of substrate surfaces after spalling, inner surfaces of the spalled chips, and cross-sections of substrate after spalling, four spalling modes classified according to the decohesion locations were observed (Fig.5.10):

- mode I: total decohesion along the coating (including a conversion coating if there is any) and substrate interface,
- mode II: decohesion along substrate peaks,
- mode III: decohesion within the coating, and
- mode IV: decohesion within the substrate.

The spalling mode depends mainly on the type of the coating system. For a particular coating system, the coating may spall in either one or a mixture of the four modes.
Fig. 5.9  A substrate surface after grit blasting (×500).
Fig. 5.10 Schematic diagrams showing the four spalling modes. (a) mode I: decohesion at the coating-substrate interface, (b) mode II: decohesion along substrate peaks, (c) mode III: decohesion within the coating, (d) mode IV: decohesion within the substrate.
Details of the correlations between coating system types and the spalling modes are presented in the following subsections.

5.7.3 Coatings with Stainless Steel Substrates

The spalling modes I, II and III were observed in specimens with stainless steel substrates. There is a close correlation between coating type and spalling modes.

5.7.3.1 CZ coatings

For CZ type coatings, spalling occurred in a mixture of mode I and mode II. It was noted that the contribution from each of the two modes was affected by the values of critical peak temperature. As mentioned previously, the critical peak temperatures of CZ coatings were influenced slightly by the heating rates and cooling rates. It appeared that higher critical peak temperature resulted in much more coating retention.

Fig. 5.11a and Fig. 5.11b show the morphology and the related EDS of the substrate associated with SS/CtZt-850A, with which mode I spalling is a majority. It can be seen that a very small amount of coating material is retained on substrate surfaces. Fig. 5.11c and Fig. 5.11d show the morphology and EDS of the inner surface of the spalled coating fragment. The inner surface has a wavy morphology that is similar to that of the substrate. Also, a very slight amount of Fe was detected. Spalling in mode I indicates that the coating cohesive strength is higher than its adhesive strength.

Fig. 5.12a and Fig. 5.12b show the surface micrograph and related EDS result of the substrate surface from SS/CtZt-900C, in which mode II spalling is the majority. It is seen that there is more coating material remaining on the substrate surface than SS/CtZt-850A. Fig. 5.12c shows the cross-section of the substrate, which illustrates that the remaining coating is mainly in the valleys of the substrate surface. The above
Fig. 5.11 The substrate surface and spalled coating fragment inner face of SS/C1Z1-850A, showing spalling occurred mainly in mode I.
(a) a micrograph of the substrate surface (×500), (b) EDS of the substrate surface, (c) a micrograph of the inner surface of a spalled coating fragment (×500), (d) EDS of the inner surface of a spalled coating fragment.
Fig. 5.12 The substrate surface and cross-section of SS/CiZ1-900C, showing spalling occurred mainly in mode II.
(a) a micrograph of the substrate surface (×500), (b) EDS of the substrate surface, (c) cross-section view of the substrate showing the remaining coating in the valleys of the wavy substrate surface (×240).
results indicate that when the coatings experienced higher temperature, either their adhesive strength increased or the cohesive strength decreased.

5.7.3.2 AX and CiX coatings

For AX type and CiX type coatings, spalling occurred mainly in mode I. Fig.5.13a and 5.13b show the surface morphology and cross-section morphology of the substrate from SS/AX-850C. Fig.5.14a and 5.14b show the surface morphology, and cross-section of the substrate from SS/CiX-1000C. As shown, coating spalling occurred cohesively within the coating. The results indicate that the coating adhesive strength was significantly higher than cohesive strength when coating spalling occurred.

5.7.4 Coatings with Carbon Steel Substrates

For coating systems with carbon steel substrates, spalling occurred mainly in mode I. Fig.5.15a and 5.15b show the substrate surface morphology and EDS result of CS/C2Z2-750A. The morphology does not show significant amounts of coating. The EDS shows that the dominant component of the surface is Fe. Fig.5.15c and 5.15d show the morphology and EDS of the inner surface of spalled coating fragments. The morphology is similar to that of the substrate. The EDS shows that the composition of the inner surface contains substantial amounts of Fe compared to the coating elements, Cr, Si, P and Al. A cross-section view of the coating fragment in Fig.5.15e shows Fe rich areas near the interface.

Fig.5.16a and 5.16b show the substrate surface and EDS of CS/AX-750A. As with CS/C2Z2-750A, almost no coating material remained on the substrate. Fig.5.16c and 5.16d show the morphology and EDS of the inner surface of spalled coating fragments. Fig.5.16e shows the cross-section view of the fragments. The inner surface morphology is similar to that of the substrate. The EDS shows mainly Cr and
Fig. 5.13 The substrate surface and cross-section of SS/AX-850C, showing spalling occurred in mode III. (a) a micrograph of the substrate surface (×500), (b) cross-section view of the substrate showing the remaining coating layer.
Fig. 5.14 The substrate surface and cross-section of SS/C1X-950C, showing spalling occurred in mode III.
(a) a micrograph of the substrate surface (x300), (b) cross-section view of the substrate showing the remaining coating layer (x500).
Fig. 5.15 The substrate surface and spalled coating fragment inner face of CS/CzZ2-750A, showing spalling occurred in mode I.
(a) a micrograph of substrate surface (×500), (b) EDS of substrate surface, (c) a micrograph of inner surface of a spalled coating fragment (×500), (d) EDS of inner surface of a spalled coating fragment, (e) cross-section view of the spalled coating fragment (×750).
Fig. 5.16 The substrate surface and spalled coating fragment inner face of CS/AX-750A, showing spalling occurred in mode I.
(a) a micrograph of the substrate surface (×500), (b) EDS of the substrate surface, (c) a micrograph of inner surface of a spalled coating fragment (×500), (d) EDS of inner surface of the spalled coating fragment, (e) cross-section view of the spalled coating fragment (×750).
Fe, which are the components of the conversion coating layer (see §4.3.5.1). The cross-section view in Fig.5.16e clearly demonstrates the conversion coating attached on the spalled fragment. The above results indicate that the spalling occurred in the interface between the conversion coating and the substrate.

It is clear that for the coating systems with carbon steel substrates, the coating spalled adhesively under thermal shock. However, it may not be 'absolute adhesive', i.e., exactly from the coating/substrate interface. Since substantial amounts of Fe were detected from the inner surface of the spalled coating fragment, it is possible that spalling occurred within the substrate just adjacent to the interface.

**5.7.5 Coatings with Copper Substrates**

For the coatings with copper substrates, spalling occurred mainly in mode IV. Fig.5.17a and 5.17b show the morphology and EDS of the substrate surface corresponding to CU/C2Z2–550A. The morphology shows that particles covered the surface. The EDS shows no coating element remained in the surface. Fig.5.17c and 5.17d show the morphology and EDS of the spalled coating fragments, which are similar to those of the substrate surface. Fig.5.17e is a cross-section view of a spalled coating fragment showing a white layer attached on the fragment. The above results indicate that spalling occurred within the copper oxide layer between the coating and the substrate. The copper oxide appears red in visual inspection, which is the colour of cuprite (Cu₂O) formed under low oxygen pressure [102].

**5.7.6 The Size of Spalled Coating Fragments**

The size of spalled coating fragments provides information about crack propagation. The bigger the coating fragments, the longer the cracking propagated along or parallel to the interface. It appears that the fragment size depends mainly on the type of the coating system, especially the type of substrate material.
Fig. 5.17 The substrate surface and spalled coating fragment inner face of Cu/C2Z2-550A, showing spalling occurred in mode IV.
(a) a micrograph of the substrate surface (×500), (b) EDS of the substrate surface, (c) a micrograph of inner surface of a spalled coating fragment (×500), (d) EDS of inner surface of the spalled coating fragment, (e) cross-section view of the spalled coating fragment (×750).
With a stainless steel substrate, the dimension of the spalled coating chips is related to coating type. The fragments from CZ types (Fig. 5.18a) are larger than those from AX and CX types (Fig. 5.18b). With a carbon steel substrate, coating fragments from CZ and AX types are not significantly different in their size, and are much larger than those from stainless steel substrates (Fig. 5.18c). With a copper substrate, the fragment size appears to be between of those with stainless steel substrates and carbon steel substrates.

The information about cracking propagation revealed by coating fragments is consistent with the information obtained from spalling mode analysis, especially for mode I and mode III spalling, which are two extreme cases and thus the contrast is obvious. For mode I spalling with carbon steel substrates, since cracking propagation along the interface between the coating and the substrate is preferable, cracking was able to propagate long distances along the interface, which results in large fragments. For mode III spalling of AX and CiX types with stainless steel substrates, since there is not a easier path within the coating for cracking propagation, cracking cannot propagate a long distance parallel to the interface, therefore the spalled fragments in mode III spalling are significantly smaller.

5.8 SUMMARY AND CONCLUDING REMARKS

The thermal shock performance of eight types of coating systems with four types of coatings and three types of substrates was investigated. The coating systems failed by spalling during cooling when the peak temperature of the thermal cycles reached a particular level, depending on the type of the coating system.

In quenching, the coating systems with stainless steel substrates showed the best thermal shock resistance. The critical peak temperatures of the four types of coatings fall in a range of 850°C to 1000°C. For the two coating systems on carbon steel substrates, coating spalling occurred with critical peak temperature of 750°C. For the
Fig. 5.18 Size of spalled coating fragments
(a) CZ coatings with stainless steel substrates, (b) AX and C1X coatings with stainless steel substrates, (c) coatings with carbon steel substrates.
two coatings on copper substrate, spalling occurred with a critical peak temperature of 550°C.

For coatings on stainless steel and copper substrates, thermal shock failure may be correlated closely to the heating-related stresses, while for coatings with carbon steel substrates, coating spalling is related to cooling-rate-related stresses.

Four modes of spalling were observed. Similar to critical peak temperature, the spalling mode also depends on substrate type. Coating cohesive fracture occurred only for coating systems with stainless steel substrates. For coating systems with carbon steel and copper substrates, spalling occurred in the coating/substrate interface or within the substrates.
CHAPTER SIX

EFFECTS OF THERMAL SHOCK ON COATING MICROSTRUCTURE

6.1 GENERAL

This chapter describes the effects of thermal shock on coating microstructure, including coating surface morphology, cross-section morphology and X-ray diffraction patterns, represented by the coating systems with stainless steel substrates. The results are presented in §6.2 to §6.6 for the four types of coating respectively. Summary and concluding remarks are given in §6.7.

6.2 C1Z1 COATING

6.2.1 Surface

Under thermal shock test, SS/C1Z1 survived quenching with Tcp=800°C and Tcp=850°C for mode A and mode C tests respectively. The surface morphologies of SS/C1Z1-800A and SS/C1Z1-850C, are given in Fig.6.1a, Fig.6.1b respectively. Generally speaking, there is no significant damage to the coating surface. However, in comparison with the as-received specimen (Fig.4.1), the top densifier disappeared in some areas, and thus the peak of Si in EDS detected from coating surface becomes stronger (Fig.6.1c). Surface microcracks also seem wider, and are not well linked to each other due to the disappearance of the top densifier.
Fig. 6.1 Surface morphology of C1Z1 survived from thermal shock. (a) SS/C1Z1-800A (x500), (b) SS/C1Z1-850C (x500), (c) EDS of surface in (a).
6.2.2 Cross-section

Fig. 6.2a and Fig. 6.2b show the cross-section microstructure of SS/C1Z1-800A and SS/C1Z1-850C, which survived quenching. Although no through-thickness cracking appears, the coating structure appears shattered in comparison with the as-received sample (Fig. 4.2) and thus compositional contrast of the backscattered electron images cannot be obtained. The shattered appearance may not be genuine, but rather damage caused from grinding and polishing of the samples, although the samples were prepared carefully by the same technique used for the as-received specimen. The shattered appearance may be due to increased residual stress in the coating after thermal shock. The residual stress may lead to enhanced matrix material drop-out and filler particle pull-out during grinding and polishing. This explanation is supported by the appearance of spalled coating fragments of SS/C1Z1-850A in Fig. 6.2c. Since the fragment is free of substrate and thus is not subjected to severe residual stress, the coating structure is not so shattered.

As seen from the structure of the spalled coating fragment in Fig. 6.2c, in comparison with the as-received specimen, the continuity of the matrix is degraded due to small particles and voids generated in the matrix. Generation of the small particles may be the result of crystallization of the matrix material. X-ray diffraction of the coating shows that crystallized Cr₄(P₂O₇)₃ formed after thermal shock tests, as will be seen in §6.2.3. Generation of the voids probably can be attributed to three reasons. Firstly, the matrix crystallization may lead to material shrinkage and in turn generation of voids. Secondly, since the coating has been subjected to tensile stress at high temperature due to the mismatch between the coating and the substrate in their thermal expansion coefficients, the coating might undergo inelastic deformation accompanied by void generation. Thirdly, grinding and polishing of the sample may also induce matrix material drop-out and thus void generation if the cohesive strength of the matrix decreases after being subjected to the thermal shock test.
Fig. 6.2 Cross-section morphology of C1Z1 after thermal shock. 
(a) survived from SS/C1Z1-800A (×1000), (b) survived from SS/C1Z1-850C (×1000), (c) spalled after SS/C1Z1-850A (×1000).
6.2.3 X-ray Diffraction

X-ray diffraction patterns of the coating pre-test and after thermal shock test, SS/C1Z1–850A and SS/C1Z1–850C, are given in Fig.6.3a, Fig.6.3b and Fig.6.3c. The pattern of the coating pre-test is included here for convenience of comparison.

In comparison with the coating pre-test, diffraction peaks from Cr4(P2O7)3 were identified in the coatings after thermal shock. The result indicates that the compound of chromic acid and phosphoric acid is crystallized after being exposed to high temperature. Because Cr4(P2O7)3 is detected in both SS/C1Z1–850A which failed in thermal shock, and SS/C1Z1–850C which survived from thermal shock, it appears that coating spalling is not closely related to the formation of the Cr4(P2O7)3.

6.3 C2Z2 COATING

6.3.1 Surface

SS/C2Z2 survived from thermal shock with Tcp=850°C and Tcp=900°C for mode A and mode C tests respectively. The surface morphologies of SS/C2Z2-850A and SS/C2Z2-900C are given in Fig.6.4a and Fig.6.4b respectively. In comparison with the as-received sample (Fig.4.4), there is no significant damage to the coating surface. Unlike the C1Z1 sample, areas showing disappearance of the densifier are rare. This result indicates that the Z2 densifier is more stable than the Z1 densifier.

6.3.2 Cross-section

The cross-section morphologies of SS/C2Z2-850A and SS/C2Z2-900C, which survived from thermal shock, are shown in Fig.6.5a and Fig.6.5b respectively. The specimens appear shattered, although not as severely as the C1Z1 coating. The cross-
Fig. 6.3  X-ray diffraction patterns of C1Z1 coating.
(a) as-received, (b) after SS/C1Z1-850A test, (b) after SS/C1Z1-850C test.
Fig. 6.4 Surface morphology of C2Z2 survived from thermal shock.
(a) SS/C2Z2-850A test (×500), (b) SS/C2Z2-900C test (×500).
Fig. 6.5  Cross-section morphology of C2Z2 after thermal shock. 
(a) survived from SS/C2Z2-850A (×1000), (b) survived from SS/C2Z2-900C (×1000), (c) spalled after SS/C2Z2-900A (×1000).
section morphology of spalled coating fragment from SS/C2Z2-900A is given in Fig.6.5c. As with SS/C1Z1, small particles and voids have been generated in the coating matrix. Compared with SS/C1Z1, the generation of the small particles may be correlated with the formation not only of Cr\(_4\)(P\(_2\)O\(_7\))\(_3\), but also of some unidentified crystallized phases, as will be shown in §6.3.3.

6.3.3 X-ray Diffraction

The X-ray diffraction patterns of the coating pre-test and after quenching, SS/C2Z2-900A and SS/C2Z2-900C, are given in Fig.6.6a, Fig 6.6b and Fig.6.6c.

As in C1Z1, Cr\(_4\)(P\(_2\)O\(_7\))\(_3\) is formed after thermal shock. There are also some peaks labeled with '?' in Fig.6.6b and Fig.6.6c, which have not been identified. These peaks are attributed to the formation of some unknown crystalline phases. Because there is not significant difference between the failed SS/C2Z2-900A and unfailed SS/C2Z2-900C in their X-ray diffraction patterns, the coating spalling is apparently not closely related to the formation of the Cr\(_4\)(P\(_2\)O\(_7\))\(_3\) and the unidentified phases.

6.4 AX COATING

6.4.1 Surface

Under the thermal shock test, SS/AX survived quenching with Tcp=800°C for both mode A and mode C tests. In comparison with the as-received specimen (Fig.4.9), no significant microstructural change can be detected in the coating surface which survived thermal shock, as represented by SS/AX-800C in Fig.6.7.

6.4.2 Cross-section

The cross-section morphology of SS/AX-800C which survived thermal shock is given in Fig.6.8. In comparison with the as-received condition (Fig.4.10), matrix
A: SiO$_2$ (α-quartz)
B: α-Al$_2$O$_3$
D: Cr$_6$(P$_2$O$_7$)$_3$
?: unidentified phases

Fig.6.6 X-ray diffraction patterns of C$_2$Z$_2$ coating.
(a) as-received, (b) after SS/C$_2$Z$_2$-900A test, (b) after SS/C$_2$Z$_2$-900C test.
Fig. 6.7  Surface morphology of AX survived from thermal shock with \( T_{cp}=800^\circ C \) (\( \times 500 \)).

Fig. 6.8  Cross-section morphology of AX after thermal shock with \( T_{cp}=800^\circ C \) (\( \times 1000 \)).
drop-out occurs, which is probably caused by polishing and grinding of the specimen, thus the matrix is not as continuous as before the test, and the filler particles are not enveloped by the matrix as completely as before the test. The cross-section specimen after quenching was prepared by the same procedure as the specimen before testing. The occurrence of matrix drop-out may indicate either the cohesive bonding of the coating is weakened after thermal shock testing, or the coating is under severe residual stress.

6.4.3 X-ray Diffraction

The X-ray diffraction patterns of the coating pre-test and after thermal shock test SS/AX–850C, are given in Fig 6.9a, Fig 6.9b.

The coating material is thermally stable. The diffraction pattern of the coating spalled in thermal shock test SS/AX–850C is the same as the diffraction pattern of the as-received coating. The result indicates that no chemical reaction and phase change occurred in the coating after thermal shock, and that coating spalling is not related to the formation of any new phase or phase change.

6.5 CiX COATING

6.5.1 Surface

Under thermal shock testing, SS/CiX survived with Tcp from 800°C to 950°C in both mode A and mode C tests. In comparison with the as-received condition, no significant change in coating surface morphology can be detected when the peak temperature is increased up to 850°C, as shown in Fig.6.10a. Although microcracks appear after thermal shock from 900°C as shown in Fig.6.10b and Fig.6.10c, the
A: SiO$_2$ (α-quartz)
B: α-Al$_2$O$_3$
C: Cr$_2$O$_3$

Fig. 6.9 X-ray diffraction patterns of AX coating.
(a) as-received; (b) after SS/AX-850°C test.
Fig. 6.10 Surface morphology of C1X survived from thermal shock.
(a) SS/C1X-850C test (×500), (b) SS/C1X-900C test (×500),
(c) SS/C1X-900C test (×2000).
microcracks do not penetrate through the coating thickness according to the cross-section morphology examination (Fig. 6.11a).

### 6.5.2 Cross-section

The cross-section morphologies of SS/CiX-900C and SS/CiX-950C, which survived thermal shock, are given in Fig. 6.11a, Fig. 6.11b, Fig. 6.11c. Although CiX has the base coating matrix formed from chromic acid and phosphoric acid, which is similar to CiZi, the CiX structure does not have the shattered appearance of CiZi. In comparison with the pre-test morphology, the coating structure appears more porous in the base coating matrix. However, this is not necessarily a genuine feature of the coating. Grinding and polishing may also lead to the cavity generation if drop-out of matrix material occurred. In SS/CiX-950C (Fig. 6.11c), lateral cracks within the coating are also observed, which indicates that the coating is subjected to compressive stress.

### 6.5.3 X-ray Diffraction

The X-ray diffraction patterns of the coating pre-test and after thermal shock SS/CiX-1000C, are given in Fig 6.12a and Fig 6.12b.

In comparison with the as-received coating, two new diffraction peaks, which are labeled D, were detected. The two peaks have values of d-space the same as the first and second strongest diffraction peaks of Cr$_4$(P$_2$O$_7$)$_3$ respectively. Although the other peaks of Cr$_4$(P$_2$O$_7$)$_3$ are absent from the diffraction pattern, it is possible that Cr$_4$(P$_2$O$_7$)$_3$ is also formed in CiX. The absence of the other peaks of Cr$_4$(P$_2$O$_7$)$_3$ can be attributed to the low content of Cr$_4$(P$_2$O$_7$)$_3$. In comparison with CZ coatings, the CiX coating only has the compound from the chromic acid and phosphoric acid in the
Fig. 6.11 Cross-section morphology of C1X after thermal shock.
(a) survived from SS/C1X-900C (×500), (b) survived from SS/C1X-900C (×1000), (c) survived from SS/C1X-950C (×1000).
A: SiO$_2$ (α-quartz)
B: α-Al$_2$O$_3$
C: Cr$_2$O$_3$
D: Cr$_4$(P$_2$O$_7$)$_3$

Fig. 6.12 X-ray diffraction patterns of C:X coating.
(a) as-received, (b) after SS/C:X-1000C test.
base coating binder/densifier. Therefore, the content of \( \text{Cr}_4(\text{P}_2\text{O}_7)_3 \) in \( \text{C}_1\text{X} \) must be lower than that in CZ coatings.

Since \( \text{Cr}_4(\text{P}_2\text{O}_7)_3 \) is trivial in amount, the coating spalling in SS/\( \text{C}_1\text{X} \) may not be related to the formation of \( \text{Cr}_4(\text{P}_2\text{O}_7)_3 \), as in SS/\( \text{C}_1\text{Z}_1 \) and SS/\( \text{C}_2\text{Z}_2 \).

### 6.6 SUMMARY AND CONCLUDING REMARKS

For CZ and AX type coatings, no significant change in surface morphology can be detected in the coatings which survived thermal shock with peak temperatures from 750°C to 850°C. For the \( \text{C}_1\text{X} \) type coating, no significant change in surface morphology can be found from the specimens which survived thermal shock with peak temperature lower than 900°C, but microcracks were induced in the specimens which survived thermal shock when the peak temperature rose to 900°C. However, these microcracks do not penetrate through the coating thickness.

For CZ type coatings, cross-section morphology of the coatings which survived from thermal shock with peak temperature from 800°C to 900°C is shattered probably due to increased residual stress in the coatings. The shattered appearance is not observed from the cross-section morphology of spalled coating fragments, which shows the generation of small particles from binder matrix after thermal shock. The particles may be related to the formation of \( \text{Cr}_4(\text{P}_2\text{O}_7)_3 \) and some unidentified crystalline phases, as confirmed by X-ray diffraction patterns of the coatings. For the AX type, matrix drop-out is observed from the cross-section morphology of the specimen which survived the thermal shock test. The occurrence of matrix drop-out may indicate either the cohesive bonding of the coating is weakened by the thermal shock test, or that the coating is under severe residual stress. X-ray diffraction patterns of these coatings show that they are thermally stable and there are no new crystalline phases formed after thermal shock. For the \( \text{C}_1\text{X} \) type coating, lateral cracks are
detected from the coating after thermal shock tests when the peak temperature is increased to 950°C. X-ray diffraction patterns of these coatings after thermal shock show that less \( \text{Cr}_4(\text{P}_2\text{O}_7)_3 \) is formed in C\(_1\)X than in CZ coatings, because the compound from the chromic acid and phosphoric acid is involved only in the base coating for the C\(_1\)X type coating.
CHAPTER SEVEN

INVESTIGATION OF COATING THERMAL STABILITY

7.1 GENERAL

The main experimental work, including the characteristics and performance of the coating systems under thermal cycle tests, has been described in the previous chapters. This chapter is devoted to thermal analysis, including thermomechanical analysis in §7.2, and thermogravimetric analysis in §7.3. Scale changes of the thermal analysis plots presented in the related subsections should be noted. Summary and concluding remarks of this chapter are presented in §7.4.

7.2 THERMOMECHANICAL ANALYSIS (TMA)

7.2.1 CiZ1 Coating

Fig.7.1a and Fig.7.1b show the TMA plots from two specimens. In both plots, an abrupt expansion occurred around 500°C followed by a slight shrinkage.

Values of the temperature of the abrupt expansion were obtained by step analysis completed by the computer systems of the TMA equipment. In Fig.7.1a, the start temperature of the abrupt expansion is 482°C, and the peak temperature is 554°C. The expansion value is about 5%. In Fig.7.1b, values of the start temperature and peak temperature are 499°C and 556°C respectively, which are very close to the...
Fig. 7.1  TMA results of C1Z1 coatings.
(a) and (b) TMA curves in duplicated tests,
(c) the curve obtained by re-heating the sample used for (a).
values measured in Fig.7.1a. However, the expansion value is smaller than 1%. Although the expansion values for the two samples are not duplicated well, which may be caused by heterogeneity of the samples, the phenomenon of abrupt volume change and the related temperature are duplicated. The results indicate that at temperatures around 480°C and 560°C, some reactions occurred which induced abrupt expansion.

Fig.7.1c shows the TMA plot obtained by reheating the sample used for the curve in Fig.7.1a. During the reheating process, the abrupt expansion did not occur. This result suggests that the reactions finished during the first heating cycle.

7.2.2 C₂Z₂ Coating

Fig.7.2a and Fig.7.2b show the TMA plots from samples of C₂Z₂. In both curves, an abrupt expansion also occurred. However, in comparison with C₁Z₁, C₂Z₂ has more obvious shrinkage following the abrupt expansion.

In Fig.7.2a, the start temperature of the abrupt expansion is 476°C, and the peak temperature is 506°C. The value of expansion is about 5%. After 506°C, an obvious shrinkage occurs and the curve decreases to the level before the expansion. In Fig.7.2b, the start temperature and peak temperature are 439°C and 512°C respectively. The value of expansion is about 15%, which is about 3 times of the value in Fig.7.2a. After 512°C, an obvious shrinkage occurs and thus the curve decreases to the level before the expansion. The results from the two samples are not duplicated well both for values of related temperature and expansion value, which may be caused by heterogeneity of the samples. However, the phenomena of abrupt expansion and subsequent shrinkage are duplicated well, which indicates that some reactions occurred at temperatures around 440°C to 520°C.
Fig. 7.2 TMA results of C\textsubscript{2}Z\textsubscript{2} coatings. 
(a) and (b) TMA curves in duplicated tests, 
(c) the curve obtained by re-heating the sample used for (a).
Fig. 7.2c shows the TMA plot obtained by reheating the sample used for the plot in Fig. 7.2a. During the reheating process, the abrupt expansion did not occur. The results suggest that the reactions were completed during the first heating cycle.

7.2.3 AX Coating

Fig. 7.3 shows the plot for AX. The curve shows only the usual thermal expansion and no abrupt expansion occurred. This result indicates that the reactions occurring in CZ types did not occur in the AX type.

7.2.4 CiX Coating

Fig. 7.4a shows the plot for a sample of CiX coating. During heating, the coating started to shrink slightly at 326°C. As temperature increased further, a slight expansion started at 446°C and reached a maximum at 576°C. The abrupt expansion amount is smaller than 1%. During the reheating process, the abrupt volumetric change was not detected, as shown in Fig. 7.4b.

7.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

7.3.1 CiZ1 Coating

Fig. 7.5 shows the TGA curve of CiZ1. During heating from room temperature to about 530°C, the specimen weight reduced about 1.5% gradually, which may be related to the loss of moisture and organic contaminants absorbed by the sample. At about 530°C, coating weight began to reduce dramatically. The weight loss reached 10% when the sample was heated to 900°C. It should be noted that the temperature at which the specimen began to lose weight dramatically is around the same level as the
Fig. 7.3  TMA curves of AX coating.

Fig. 7.4  TMA results of C1X coatings.
(a) a TMA curve,
(b) the curve obtained by re-heating the sample used for (a).
Fig. 7.5  TGA curve of CrZr coating.
abrupt expansion found in TMA, and thus the dramatic weight loss is probably related to the reactions inducing the abrupt expansion.

7.3.2 C2Z2 Coating

Fig. 7.6 shows the TGA curve of C2Z2. During heating from room temperature to about 520°C, the sample weight reduced about 1% gradually. At about 520°C, coating weight began to reduce dramatically. The weight loss reached 4% when the sample was heated to 900°C. The temperature at which the specimen began to loss weight dramatically is also around the same level as the abrupt expansion in TMA, and thus the dramatic weight loss is again related to the reactions inducing the abrupt expansion.

7.3.3 AX Coating

Fig. 7.7 shows the TGA curve of AX. During heating up from room temperature to about 900°C, the sample weight reduced about 0.7% gradually, which is not significant. The result is consistent with the result from TMA that the coating is thermally stable.

7.3.4 CiX Coating

Fig. 7.8 shows the TGA curve of CiX. During heating from room temperature to about 650°C, the sample weight reduced about 1% gradually. At about 650°C, the coating weight loss began to increase. The weight loss reached about 3% when the sample was heated to 900°C. The weight loss of CiX is less than CZ coatings, which is consistent with the TMA results that the abrupt expansion of the CiX is far less significant than that of CZ coatings.
Fig. 7.6 TGA curve of Cz coating.
Fig. 7.7 TGA curve of AX coating.
7.4 SUMMARY AND CONCLUDING REMARKS

TMA results showed that the CZ coatings were not fully cured, some reactions, which induce abrupt expansion, occurring when the coatings were heated up to around 500°C. Such an abrupt expansion did not occur for AX coating, and was not significant for C1X. The TGA results confirmed that the CZ coatings were not thermally stable, and weight loss of up to 10% occurred. The weight loss of AX coatings was not significant. The weight loss of C1X coatings was about 3%, which was far less than for CZ coatings.
CHAPTER EIGHT

THEORETICAL ANALYSIS OF
TRANSIENT TEMPERATURE PROFILES AND
UNCONSTRAINED STRAIN MISMATCH UNDER
THERMAL SHOCK

8.1 GENERAL

The characteristics and performance of the C-ramic coatings have been investigated experimentally and presented in Chapter 4 to Chapter 7. This chapter is devoted to an analysis of the effects of temperature gradient on coating failure tendency under thermal shock. Due to a lack of relevant data, such as thermal and physical properties of C-ramic coatings and heat transfer coefficients, the present analysis is not for the purpose of simulating the real thermal shock procedure in the experimental work, but is aimed at a preliminary investigation of spalling mechanisms and effects of temperature gradient caused by rapid cooling on spalling tendency, based on assumed coating systems and thermal shock conditions.

In the following section, an analysis of the coating spalling mechanism is presented. Based on this analysis, a parameter referred to as "Unconstrained Strain Mismatch (USM)" is proposed as a principal indicator of coating spalling tendency. For slow rates of temperature change, the temperature profile in a coating system is approximately uniform and consequently the value of USM can be evaluated simply by eq.(8.1). However under rapid temperature change, such as the case of thermal shock induced by water quenching, the temperature profile in the system is non-uniform and the USM depends on the transient temperature profile in the coating.
system. Hence, in §8.3 a numerical procedure for the calculation of transient temperature profiles is presented. Formulae for calculation of the USM based on the transient temperature profile are then given in §8.4. Finally, in §8.5, a parametric study is conducted to investigate the influence of material thermal physical properties on temperature profiles, and in turn the USM. The effect of coating thickness is also considered.

8.2 MECHANISM OF COATING SPALLING AND CONCEPTS OF USM

Coating spalling is attributed mainly to stresses induced by the mismatch in the stress-free dimension between the coating and the substrate. Normally, the dimensions of the coating and substrate are identical at the fabrication temperature at which the coating is applied on the substrate. When the temperature is changed, the coating and the substrate tend to deform different amounts due to the difference in thermal expansion coefficients and the non-uniform temperature distribution caused by thermal transients. The difference in their deformation tendency is referred to as 'unconstrained strain mismatch' (USM) in the present work. Due to the USM, stresses are induced in the coating, in the substrate and in the coating/substrate interface to achieve the dimensional compatibility required by the composite structure. The more severe the USM, the greater the stresses, and once the magnitude of the stresses exceeds the related strengths of the coating systems, spalling will occur. Therefore, the USM reflects the tendency for coating failure.

For the case in which the temperature distribution in the coating system is uniform, the USM can be simply expressed as,

$$\Delta \varepsilon = (\alpha_s - \alpha_c)(T - T_0)$$

(8.1)
where $\alpha_s$ and $\alpha_c$ are the thermal expansion coefficients of the substrate and the coating respectively, $T$ is the coating system temperature, and $T_0$ is the temperature at which the coating was applied. When $T=T_0$, $\Delta e$ is zero. Obviously, this expression is applicable to a slow temperature change procedure only. Under thermal shock, eq. (8.1) may not be applicable, since it does not consider the effect of transient non-uniform temperature distribution under thermal shock. The transient non-uniform temperature distribution depends on the materials' thermal diffusivity and thermal conductivity, which are not taken into account in the above expressions. Since the calculation of transient temperature for coating systems under thermal shock is complex and can hardly be expressed analytically, there is no existing formula for the calculation of USM under thermal shock. Consequently, the influence of non-uniform temperature distribution on the USM under thermal shock is not yet clear. Since the USM depends on the transient temperature profile, a numerical procedure for the calculation of transient temperature profiles is first presented in the following section.

8.3 NUMERICAL METHOD FOR THE ANALYSIS OF TRANSIENT TEMPERATURE PROFILE

The problem addressed in this section is to determine the transient temperature profile in coating systems subjected to thermal shock. The geometry of the coating system considered in the calculation is selected to be similar to the specimens used in the present research, which consists of a disc-shaped metal substrate and a ceramic coating deposited on the top and bottom surfaces of the substrate disc (Fig.8.1). The diameter and thickness of the substrate disc are taken to be 32mm and 3mm respectively, and the thickness of the coating layer varies from 50$\mu$m to 100$\mu$m. The thermal shock environment is produced by immersing the coating systems with initial temperature $T_i$ into water at room temperature.
Fig. 8.1 Configuration of the coating systems.
8.3.1 Governing Equations

The fundamental equations governing the transient temperature profiles in the coating systems during quenching consist of a Fourier heat conduction equation, an initial condition and a convective boundary condition. The equations, referred to the cylindrical coordinate system $(r, z)$ (Fig. 8.1) under an axially-symmetrical condition at time $t$ can be expressed as:

$$
\rho c \frac{\partial T}{\partial t} - k \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) - k \frac{\partial^2 T}{\partial z^2} = 0, \quad \text{in } \Omega \quad (a)
$$

$$
T(r, z, 0) = T_i \quad \text{in } \Omega \quad (b)
$$

$$
k \left( \frac{\partial T}{\partial r} n_r + \frac{\partial T}{\partial z} n_z \right) = -h_T(T - T_\infty), \quad \text{on } \Gamma \quad (c)
$$

where $\Omega$ and $\Gamma$ are the domain and the boundary of the coating system respectively, $T = T(r, z, t)$ denotes temperature, $\rho$, $c$, and $k$ are density, specific heat and thermal conductivity respectively. $h_T$ is the surface heat transfer coefficient between the specimen and quenching water, and $T_i$ and $T_\infty$ are the initial temperature of the specimen and the quenching water temperature respectively.

8.3.2 Weak Form of the Governing Equations

In order to solve the heat conduction problem (8.2) numerically by the finite element method, the first step, which leads to the weak form of equation (8.2), is to convert the equation (8.2a) from the local description (or pointwise description) to a global form. To do this, equation (8.2a) is multiplied by an arbitrary function $\psi$ and integrated over the domain $\Omega$, thus
\[ \int_{\Omega} \left( \rho c \frac{\partial T}{\partial t} - k \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) - k \frac{\partial^2 T}{\partial z^2} \right) \psi \, d\Omega = 0 \]  
\quad (8.3)

Using Green's theorem, we have:

\[ \int_{\Omega} \left( k \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right) \psi \, d\Omega = \int_{\Gamma} k \left( \frac{\partial T}{\partial n_r} + \frac{\partial T}{\partial n_z} \right) \psi \, d\Gamma - \int_{\Omega} k \left( \frac{\partial \psi}{\partial r} \frac{\partial T}{\partial r} + \frac{\partial \psi}{\partial z} \frac{\partial T}{\partial z} \right) d\Omega \]  
\quad (8.4)

Substitution of eq. (8.4) into eq. (8.3) yields:

\[ \int_{\Omega} \rho c \frac{\partial T}{\partial t} \psi \, d\Omega = \int_{\Gamma} k \left( \frac{\partial T}{\partial n_r} + \frac{\partial T}{\partial n_z} \right) \psi \, d\Gamma - \int_{\Omega} k \left( \frac{\partial \psi}{\partial r} \frac{\partial T}{\partial r} + \frac{\partial \psi}{\partial z} \frac{\partial T}{\partial z} \right) d\Omega \]  
\quad (8.5)

Further substitution of eq. (8.2c) into eq. (8.5) produces:

\[ \int_{\Omega} \rho c \frac{\partial T}{\partial t} \psi \, d\Omega + \int_{\Omega} k \left( \frac{\partial \psi}{\partial r} \frac{\partial T}{\partial r} + \frac{\partial \psi}{\partial z} \frac{\partial T}{\partial z} \right) d\Omega + \int_{\Gamma} h T \psi \, d\Gamma = \int_{\Gamma} h T \omega \psi \, d\Gamma . \]  
\quad (8.6)

Using Cartesian tensor notation with summation over repeated indices, equation (8.6) can be rewritten as:

\[ \int_{\Omega} \rho c \frac{\partial T}{\partial t} \psi \, d\Omega + \int_{\Omega} k T \cdot \psi \, d\Omega + \int_{\Gamma} h T \psi \, d\Gamma = \int_{\Gamma} h T \omega \psi \, d\Gamma , \]  
\quad (8.7)

where \( i = r, z \). Equation (8.7) is the weak form of eq. (8.2), and forms the basis of the finite element approximation.
8.3.3 Finite Element Discretization

To solve the initial boundary value problem described in the previous section, the domain $\Omega$ is divided into a finite number of four noded regions $\Omega_e (e = 1, N)$ called elements, each having uniform properties. Consequently the boundary $\Gamma$ of the domain $\Omega$ is divided into a finite number of segments $\Gamma_b (b = 1, B)$. Thus, by replacing the integral on the whole domain by the sum of the integral on each element, we have:

$$\sum_{e=1}^{N} \int_{\Omega_{e}} \rho c T \psi \, d\Omega + \sum_{e=1}^{N} \int_{\Gamma_{b}} k T_{,i} \psi_{,i} \, d\Omega + \sum_{e=1}^{N} \int_{\Gamma_{e}} h T \psi \, d\Gamma = \sum_{e=1}^{N} \int_{\Gamma_{b}} h T_{f} \psi \, d\Gamma$$  \hspace{1cm} (8.8)

Within each element, the coordinate-dependent variables $T$ and $\psi$ are interpolated by functions of compatible order, in terms of values to be determined at a set of nodal points, that is:

$$T (r,z) = N^T T_e, \quad \psi (r,z) = \psi_e^T N$$  \hspace{1cm} (8.9)

where $T_e$ and $\psi_e$ denote the column vectors of the element nodal point values of $T$ and $\psi$ respectively, and $N$ is the interpolation functions. For example for 4 nodal isoparametric element,

$$T_e = (T_1, T_2, T_3, T_4)^T, \quad \psi_e = (\psi_1, \psi_2, \psi_3, \psi_4)^T,$$

$$N = (N_1, N_2, N_3, N_4)^T.$$  \hspace{1cm} (8.10)

By applying the weighted residual technique in a single element $\Omega_e$, we obtain a corresponding equation to eq.(8.7) with $\Omega$ submitted by $\Omega_e$, which on using eq.(8.10) produces
where $C_e$, $K_e$, $H_b$ and $F_b$ are defined by

$$
C_e = \int_{\Omega_e} \rho c N N^T d\Omega, \quad K_e = \int_{\Omega_e} k N \nabla N N^T d\Omega, \quad H_b = \int_{\Gamma_b} h N N^T d\Gamma, \quad F_b = \int_{\Gamma_b} h N T_\infty d\Gamma.
$$

On eliminating $\psi_e$, eq.(8.11) becomes

$$
\psi_e \begin{bmatrix} T_e \end{bmatrix} = \begin{bmatrix} C_e \frac{\partial T_e}{\partial t} + K_e T_e + H_b T_b \end{bmatrix} = \psi_e F_b \quad (8.13)
$$

Eq.(8.13) is the finite element formula for a single element and the finite element formulae for the whole body can be obtained by summing the finite elements (8.13) for each individual element in the whole regimes at the common nodes, thus a set of simultaneous equation can be obtained:

$$
C \frac{\partial T}{\partial t} + K T = F \quad (8.14)
$$

where $C$ and $K$ are the assembled heat capacity matrix and conductivity matrix respectively, $T$ is the nodal temperature vector at all nodes. The matrices are determined by:

$$
C_{ij} = \sum_{\Omega} C_{e_{ij}}, \quad K_{ij} = \sum_{\Omega} K_{e_{ij}} \sum_{\Gamma} H_{b_{ij}}, \quad F_i = \sum_{\Gamma} F_{b_i} \quad (8.15)
$$

where $\sum_{\Omega}$ denotes summation over all the elements with both nodes $i$ and $j$, and $\sum_{\Gamma}$ is summation over all the boundary segments with both nodes $i$ and $j$. 
8.3.4 Solution Procedure

At an instant of time $t^{n+1}$, eq.(8.14) becomes:

$$C \left( \frac{\partial T}{\partial t} \right)^{n+1} + KT^{n+1} = F^{n+1}. \quad (8.16)$$

To solve the above equations, referring to Fig. 8.2, the following approximation is used:

$$T^{n+1} = T^n + \left( \beta \frac{\partial T}{\partial t}^{n+1} + (1-\beta) \frac{\partial T}{\partial t}^n \right) \Delta t, \quad (8.17)$$

where $\beta$ is a parameter with value between 0 and 1, and the magnitude of $\beta$ determines the weight contribution of $\frac{\partial T}{\partial t}^n$ and $\frac{\partial T}{\partial t}^{n+1}$ to $T^{n+1}$. $\beta=0$ corresponds to the forward difference scheme while $\beta=1$ corresponds to the backward-difference scheme. Now, from eqs.(8.16) and (8.17), we can deduce that

$$T^{n+1} = \frac{1}{C+\beta K \Delta t} \left\{ (C-K(1-\beta)\Delta t) T^n + (\beta F^{n+1} + (1-\beta) F^n) \Delta t \right\}. \quad (8.18)$$

Thus, starting with an initial temperature field $T(r, z)$, we can calculate the temperature field $T^1(r, z)$ at a new instant of time $t_1 = t_0 + \Delta t$. By repeating this process, we can calculate the temperature field at any instant during thermal shock.

Based on the formulae presented above, a computer program has been developed for the calculation of the transient temperature profiles. Fig.8.3 shows the flow chart of the program.
Fig. 8.2 A schematic diagram showing the approximation of $T^{n+1}$ by $T^n$. 

\[
\frac{\partial T^{n+1}}{\partial t} = \beta \Delta t \frac{\partial T^n}{\partial t} + (1-\beta) \Delta t \frac{\partial T^{n+1}}{\partial t}
\]
Start

Data Input

Mesh Generation

\( i=0, T_i = T_{in} \)

\( t_{i+1} = t_i + \Delta t \)

Form K and C

\( LDL^T \)

Form F

Solve Eqs for \( T_{i+1} \)

Output?

Yes  Print

No  \( i = i + 1 \)

Yes  \( T_{i+1} > T_f \)

No  Print

Stop

Fig. 8.3 Flow chart of the FEM computer program
8.3.5 *Convergence Analysis*

Convergence analysis of the FEM computer program was conducted on a model coating system. The relevant data used in the calculation are listed in Table 8.1. It is assumed that all of the physical parameters are independent of temperature. The coating thickness is 100μm.

<table>
<thead>
<tr>
<th></th>
<th>Diameter (m)</th>
<th>Thickness (m)</th>
<th>Density (kg/m³)</th>
<th>Thermal conductivity (W/m²°C)</th>
<th>Heat capacity (J/kg °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>0.032</td>
<td>0.003</td>
<td>8000</td>
<td>21.5</td>
<td>500</td>
</tr>
<tr>
<td>Coating</td>
<td>0.032</td>
<td>0.0001</td>
<td>3650</td>
<td>11</td>
<td>480</td>
</tr>
</tbody>
</table>

The surface heat transfer coefficient in water from Fletcher [68] (Fig.2.5) is used in the calculation for the assumed thermal shock condition in the analysis. The following expressions were proposed to describe the variation of heat transfer coefficient with temperature \( T \):

\[
 h(T) = \begin{cases} 
 792 + 6.2T + 3.0 \times 10^{-2}T^2 + 2.1 \times 10^{-4}T^3 & 100 < T < 250 \\
 -7.9 \times 10^4 + 633.9T - 1.5T^2 - 1.4 \times 10^{-3}T^3 - 4.8 \times 10^{-7}T^4 + 8.7 \times 10^{-12}T^5 & 250 \leq T \leq 850 
\end{cases}
\]

(8.19)

Since the geometry of the model system is symmetrical about the z-axis and the plane \( z=0 \), the calculation was conducted only in one quarter of the specimen. Five different finite element meshes were used in the convergence analysis. The number of elements and nodal points for each type of mesh are listed in Table 8.2.
### Table 8.2 The Meshes Used in Convergence Analysis

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Number of elements</th>
<th>Number of nodal point</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>II</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>III</td>
<td>60</td>
<td>77</td>
</tr>
<tr>
<td>IV</td>
<td>90</td>
<td>117</td>
</tr>
<tr>
<td>V</td>
<td>180</td>
<td>210</td>
</tr>
</tbody>
</table>

The temperature profiles at the centre with coordinates \((r, z) = (0, 0)\), interface \((0, 1.5\text{mm})\), surface \((0, 1.6\text{mm})\) and edge \((16\text{mm}, 1.6\text{mm})\) of the disc obtained by using the five types of mesh are shown in Fig.8.4a to Fig.8.4d. It can be seen that when the element number of the mesh increased, the values of temperature have a tendency to converge.

### 8.3.6 Verification of the FEM Scheme

Normally, the procedure to verify a finite element scheme is to solve a problem using the scheme and another acceptable method, and then to compare the results obtained from both methods. In the present research, the finite element scheme was verified using Heisler's charts for a typical simple problem. It should be noted that Heisler's method in general is not applicable to two dimensional problems with temperature-dependent surface heat transfer coefficients.

It has been proved that the solution for certain two dimensional transient conduction problems can be obtained by using a 'product super-position principle' procedure [87]. With this procedure, the solution for a disc can be obtained as the product of the solution for an infinite slab and the solution for a solid circular cylinder of infinite
Fig. 8.4 Relationship of temperature and mesh type showing the results of convergence analysis.
(a) at location $r=16\text{mm}$, $z=1.6\text{mm}$; (b) at location $r=0$, $z=0$; (c) at location $r=0$, $z=1.5\text{mm}$; (d) at location $r=0$, $z=1.6\text{mm}$.
length. Normally, the numerical value of temperature for either the infinite slab or the
infinite cylinder, which has a uniform initial temperature \( T_i \) and is suddenly
immersed into a medium at \( T_\infty \), is calculated by using Heisler's charts [87]. In
Heisler's charts, the dimensionless temperature \( \theta \) is plotted versus the dimensionless
time \( Fo \) (Fourier's number) for different dimensionless surface heat transfer
coefficient \( Bi \) (Biot number). Definitions of the variables are described in Table 8.3.

### Table 8.3. Definitions of the Variables Used in Heisler's Charts

\[
\theta = \frac{T - T_\infty}{T_i - T_\infty} \quad \quad \quad \quad Fo = \frac{d \cdot t}{A^2} \quad \quad \quad \quad Bi = \frac{hA}{k}
\]

where:

- \( t \) time
- \( T \) instantaneous temperature
- \( T_i \) initial temperature
- \( T_\infty \) final temperature (equal to the ambient temperature)
- \( d \) thermal diffusivity of the material
- \( A \) characteristic dimension of the object
  - for a infinite slab, \( A \) is the half thickness of the slab
  - for a infinite cylinder, \( A \) is the radius of the cylinder
- \( h \) surface heat transfer coefficient
- \( k \) heat conductivity of the material

In the verification, the calculations are conducted for a stainless steel disc without
coating. In addition, since Heisler's charts are restricted to values of the Fourier
number greater than 0.2 [103], the disc is modified into a cylinder which is 0.003m
in both of its diameter and length to satisfy this requirement. It is assumed in the
verification that the cylinder is initially at a uniform temperature \( T_i = 700^\circ C \) and
suddenly immersed into a medium at temperature \( T_\infty = 20^\circ C \). The surface heat
transfer coefficient is assumed to be 1000W/m²°C. Values of relevant parameters are listed in the table 8.4.

**Table 8.4. Parameters Used in the Calculation with Heisler's Chart**

<table>
<thead>
<tr>
<th></th>
<th>$A$ (m)</th>
<th>$d$ (m²/sec)</th>
<th>$Fo$</th>
<th>$Bi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>infinite slab</td>
<td>0.0015</td>
<td>5.38e-6</td>
<td>2.39t</td>
<td>6.98e-2</td>
</tr>
<tr>
<td>infinite cylinder</td>
<td>0.0015</td>
<td>5.38e-6</td>
<td>2.39t</td>
<td>6.98e-2</td>
</tr>
</tbody>
</table>

Temperature profiles in the centre and edge of the cylinder under above conditions were calculated using both Heisler's charts and the FEM scheme. A comparison of the results is given in Fig.8.5. It can be seen that the results from the two methods are in a good agreement. Therefore, the algorithm of the FEM scheme is correct.

### 8.4 MATHEMATICAL EXPRESSIONS FOR THE USM

The unconstrained strain mismatch is evaluated from the temperature distribution resulting from the above calculation. Since the specimen configuration is a thin disc, the temperature variation along radial direction of coating systems during quenching is negligible, as will be seen in Fig.8.6, while distribution along $z$ axis is approximately linear in the coating layer and symmetrical about the $z=0$ plane in the substrate, as will be seen in Fig.8.7.

Under the above conditions, if the coating and the substrate are free of constraint, the substrate will deform uniformly, termed pure expansion, and the coating will undergo a deformation termed pure bending[104]. The expression of unconstrained strain for the substrate ($\varepsilon_s$) and the coating ($\varepsilon_c$) in the coating/substrate interface can be derived according to thermal stress theory [104] as:

$$\varepsilon_s = (T - T_0) \alpha_s , \quad \varepsilon_c = (T_{int} - T_0) \alpha_c . \quad (8.20)$$
Fig. 8.5 Comparison of the temperature profiles obtained from the FEM scheme and from Heisler's Chart.
where $\bar{T}$ is the mean temperature across the thickness of the substrate, $T_{int}$ is the temperature in the interface, $T_o$ is the temperature at which the coating is applied, $\alpha$ is the thermal expansion coefficient, and subscript 's' and 'c' denote substrate and coating respectively. Thus, the unconstrained strain mismatch in the interface can be expressed as:

$$\Delta \varepsilon = \varepsilon_s - \varepsilon_c = (\bar{T} - T_o) \alpha_s - (T_{int} - T_o) \alpha_c .$$

(8.21)

### 8.5 RESULTS

Practically, it is difficult to apply the above theoretical calculation procedure to the quenching tests conducted in the experiment, because not all the parameters related to the experiment are available, including the thermal physical properties of the C-ramic coatings and heat transfer coefficient in water. Measurement of the parameters is a vast subject and therefore cannot be covered in the present work. Therefore, the present calculation is presented solely as a preliminary investigation of the effects of temperature gradient on the USM based on assumed coating systems and assumed thermal shock condition as described below.

#### 8.5.1 Assumed Coating Systems and Thermal Shock Condition

##### 8.5.1.1 Coating systems

Since the temperature profiles of a coating systems depend on the thermal diffusivity and thermal conductivity of coating and substrate materials, the calculation is conducted for assumed coating systems with extreme values of thermal diffusivity and thermal conductivity for common oxide ceramics and metals.

Three sets of parameters (Table 8.5) were used in the analysis. Set number 1 (S1) consists of a substrate with low thermal diffusivity and thermal conductivity as for
metals such as stainless steel AISI316 [86], and a coating with a high thermal diffusivity and thermal conductivity for ceramics such as Al₂O₃ [49]; set number 2 (S2) consists of a substrate with a high thermal diffusivity and thermal conductivity for metals as copper [105], and a coating as Al₂O₃; set number 3 (S3) consists of a substrate as stainless steel, and a coating with a smaller thermal diffusivity and thermal conductivity such as vitreous silica [49]. Thus, by comparing the results between S1 and S2, or S1 and S3, the effects of substrate or coating thermal physical properties on temperature profiles and in turn the USM of coating systems during thermal shock can be deduced. It is assumed that the material properties are independent of temperature.

Table 8.5 Material Data Used in Temperature Profile Analysis

<table>
<thead>
<tr>
<th>Coating system</th>
<th>Substrate metals</th>
<th>Coating ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ρ (kg/m³)</td>
<td>c (J/kg°C)</td>
</tr>
<tr>
<td>S1</td>
<td>8000</td>
<td>500</td>
</tr>
<tr>
<td>S2</td>
<td>8940</td>
<td>385</td>
</tr>
<tr>
<td>S3</td>
<td>8000</td>
<td>500</td>
</tr>
</tbody>
</table>

As long as the temperature profile across the thickness of a coating system is known, the unconstrained strain mismatch depends on the thermal expansion coefficient of the coating and the substrate materials. In the present analysis, the values of thermal expansion coefficient for substrate materials is taken as 17.5 μm/m°C, which is the value for stainless steel at 500°C. The thermal expansion coefficient for coating materials is taken as 7.5 μm/m°C, which is the value of C-ramic coatings given by Nomura et al. [17].
8.5.1.2 Thermal shock condition

Thermal shock induced by water quenching is one of the most severe cooling thermal shock conditions. Usually, the heat transfer coefficient in water depends on details of the quenched body, such as temperature, geometrical configuration, and surface condition. In the present analysis, the assumed thermal shock condition is water quenching with the heat transfer coefficient expressed by eq.(8.19) from Fletcher [68].

8.5.2 Transient Temperature Profiles

8.5.2.1 Temperature distribution along r-axis

To illustrate the effects of material thermal diffusivities and conductivities on transient temperature profiles in coating systems during quenching, temperature profiles along the r-axis and z-axis of the model coating systems with coating thickness of 100μm and corresponding to initial temperature $T_i=850^\circ C$ are presented.

Fig.8.6a and Fig.8.6b show temperature distributions along the radial direction, at location $z=0$, for coating systems $S_1$ and $S_2$ respectively. For $S_1$, the temperature distribution is uniform along most of the radius, varying only at the edge part. For $S_2$, although the area involving non uniform temperature distribution is larger in comparison with $S_1$, the steepness of the curves are not significant. According to the above results, the temperature variation along the radial direction can be neglected in the analysis of the USM to simplify the analysis.

8.5.2.2 Temperature distribution along z-axis

Fig.8.7a, 8.7b, and 8.7c show temperature distribution along the z-axis for material parameter data $S_1$, $S_2$ and $S_3$ respectively. The profiles depend on both coating and
Fig. 8.6  Temperature variation along radial direction of the coating systems.
(a) for S1, (b) for S2.
Fig. 8.7 Temperature variation along z-axis of the coating systems.
(a) for S1,
(b) for S2,
(c) for S3.
substrate materials. The temperature distribution in the substrate of S2 is almost uniform (Fig.8.7b) due to the high thermal diffusivity and thermal conductivity of the substrate, while for substrates S1 and S3 it is parabolic (Fig.8.7a, 8.7c). The steepness of the temperature gradient can be represented by the temperatures difference between \( z=0 \) and \( z=1.5 \text{mm} \). The maximum gradient in S1 and S3 is approximately \( 130^\circ \text{C/mm} \) and \( 120^\circ \text{C/mm} \) respectively.

The temperature distribution in the coatings is essentially linear. The steepness of the temperature gradient in the coatings is not affected significantly by the substrate thermal physical properties, while it is affected significantly by the coating thermal physical properties. The steepness of temperature gradient can be represented by temperature difference between \( z=1.5 \text{mm} \) and \( z=1.6 \text{mm} \). The maximum gradients in S1 and S3, which occurs at 0.4sec and 0.1sec respectively, are approximately \( 550^\circ \text{C/mm} \) and \( 2760^\circ \text{C/mm} \) respectively. The effect of coating thermal physical properties on the temperature gradients in the coatings is related not only to heat conduction in the coatings, but also to the surface heat transfer coefficient in water. At the early stages of quenching, the surface heat transfer coefficient increases dramatically with decrease of specimen surface temperature. Lower thermal conductivity and thermal diffusivity of the coating produce a lower surface temperature and thus faster heat transfer between coating surface and water, and in turn a steeper temperature gradient.

### 8.5.3 Unconstrained Strain Mismatch

The transient USM (\( \Delta \varepsilon \)) is calculated by eq.(8.21) from the temperature profiles along the z-axis at location \( r=0 \), for initial specimen temperatures \( T_i=600^\circ \text{C}, 700^\circ \text{C}, 800^\circ \text{C} \) and \( 850^\circ \text{C} \). Fig. 8.8a, 8.8b, and 8.8c show the \( \Delta \varepsilon \) as a function of mean temperature across specimen transverse during quenching for S1, S2 and S3 respectively. By using the mean temperature as the independent variable instead of
Fig. 8.8 Unconstrained strain mismatch.
(a) for S1,
(b) for S2,
(c) for S3.
time for the plotting, the $\Delta \varepsilon$ corresponding to slow cooling, calculated according to eq.(8.1), can be plotted into the same figures to illustrate the effect of temperature gradient on $\Delta \varepsilon$.

8.5.3.1 Effects of substrate and coating thermal physical properties

The effect of substrate thermal physical properties is demonstrated by comparing Fig.8.8a and Fig.8.8b for S1 and S2 respectively. For S1, which has a substrate with lower thermal diffusivity and conductivity, the maximum of $\Delta \varepsilon$ during quenching is slightly higher than that under slow cooling, while for S2, which has a substrate with a higher thermal diffusivity and thermal conductivity, the $\Delta \varepsilon$ during quenching is not significantly different from that during slow cooling.

The effect of coating thermal physical properties is demonstrated by comparing Fig.8.8a and Fig.8.8c for S1 and S3 respectively. Lower thermal diffusivity and conductivity of the coating leads to a slight increase in $\Delta \varepsilon$ for higher initial specimen temperatures.

8.5.3.2 Effect of coating thickness

The $\Delta \varepsilon$ for a coating thickness of 50$\mu$m are plotted in Fig.8.8a and 8.8c as small square dots. There is no significant difference in $\Delta \varepsilon$ between coating thicknesses of 100$\mu$m and 50$\mu$m for either of the coating materials.

8.6 SUMMARY AND CONCLUDING REMARKS

In order to understand the effects of temperature gradient on coating spalling tendency under thermal shock, a parameter referred to as 'unconstrained strain mismatch' (USM) is defined and calculated. Under the assumed thermal shock
conditions, the USM depends mainly on thermal physical properties of the substrate materials. For coating systems with substrates having low thermal diffusivity and thermal conductivity such as stainless steel AISI316, the maximum USM under thermal shock is slightly larger than that under slow cooling; for coating systems with substrates having higher thermal diffusivity and thermal conductivity such as copper, the maximum USM under thermal shock is not significantly different from that under slow cooling. The effects of coating thermal physical properties and coating thickness are slight. The analysis in this chapter indicates that the temperature gradient induced by thermal shock is unlikely to be the main cause of coating spalling as one might have expected before a detailed examination. As a result of this conclusion, together with the experimental observation that spalling occurs during the cooling process in the coating after being subjected to a critical peak temperature, it can be further understood that the thermoelastic theory is no longer able to account for the coating spalling as, if only elastic deformation occurs during thermal cycling, then the mismatch of the substrate and coating deformation tendency will be the same as that before being subjected to the thermal cycle and thus spalling will not occur. Thus the analysis indirectly indicates that certain forms of inelastic deformation most likely occur at high temperature. Detailed discussion is presented in Chapter 9. Although the analysis in this chapter is only qualitative and cannot simulate the spalling process, the results obtained help in the understanding of the spalling mechanism.
CHAPTER NINE

DISCUSSION

9.1 GENERAL

The general characteristics and performance of various C-ramic coating systems under thermal cycling have been investigated and presented in Chapters 4 to 7, the theoretical analysis of the coating spalling tendency under thermal shock has been given in Chapter 8. Based on these results, phenomena observed from experiment will be interpreted and discussed in this chapter. Adhesion mechanisms are analysed in §9.2. Performance of the coating systems is discussed in §9.3. In §9.4 and §9.5, the effects of coating types and substrate types are analysed. In §9.6, coating spalling mechanisms are discussed.

9.2 ADHESION MECHANISM OF THE COATINGS

Adhesion usually means the state in which two surfaces are held together by interfacial bonding. Bonding between unlike atoms and materials may be due to Coulomb forces, van der Waals' force, direct chemical bonding of molecules, and mechanical interlocking [106].

The adhesion of the C-ramic coatings to metal substrates has been attributed to a chemical bonding due to the formation of a conversion coating layer in the coating/substrate interface [15, 17]. However, among the eight coating systems examined, a significant conversion coating layer was found only in the coating combination consisting of the AX coating on a carbon steel substrate, i.e. CS/AX.
For coating systems with the stainless steel substrate or C2Z2 on a carbon steel substrate, i.e. SS/C1Z1, SS/C2Z2, SS/AX, SS/C1X, CS/C2Z2, the interfacial regions are characterized by an abrupt change from the coating to the substrate. For coatings with copper substrates, i.e. CU/C1Z1, CU/C2Z2, although an intermediate layer was detected in the interfacial region, the layer is likely to be a copper oxide. The results suggest that the formation of conversion coating layers is restricted only to the combination of AX coatings and the carbon steel substrates.

The conversion coating layer in CS/AX consists mainly of Fe from the substrate and Cr from the coating, and is believed to be some type of ferric chromate formed by chemical interaction between chromic acid and metal oxide [15]. The constituents of the conversion coating layer may explain why such a layer is not found in coating systems without the combination of the AX coating and carbon steel substrate. For stainless steel AISI316, the surface oxide film contains mainly Cr2O3 [107]. The Cr2O3 film may act as a barrier to chemical reactions associated with formation of the conversion coating layer. For CZ coatings, chromic acid is probably consumed by phosphoric acid to form a compound, and thus there may not be enough free chromic acid to form the conversion coating layer.

Although the conversion coating layer was detected only in CS/AX, this does not necessarily mean that the adhesion of other coating systems is not associated with chemical bonding at all. It may be that the chemical bonding layers are too thin to be detected from the cross-sectional view of the interfacial region. In addition, mechanical interlocking must contribute to the coating adhesion, since all the substrate surfaces were roughened by grit blasting before application of the coatings.

It should be noted that the conversion coating layer in CS/AX may not be significantly beneficial to coating adhesion. Experimental results show that CS/AX did not perform better than CS/C2Z2 under thermal shock, and coating spalling
occurred by decohesion of the coating from the interface between the conversion coating layer and the substrate, and therefore the junction between the conversion coating layer and the substrate may be critical to coating adhesion.

9.3 BEHAVIOUR OF THE COATING SYSTEMS

In the present research, all coating systems failed by spalling during cooling independent of cooling mode. This behaviour suggests that the coating failures were not caused by biaxial tensile stress, which usually causes coating failure by mud cracking, and the cracked coatings seldom spall and tend to remain adherent to the substrate [98, 99].

Coating spalling is a very common failure form in burner rig tests [40, 41, 55, 73-75, 79, 80], where the extent of thermal shock is not as severe as that during water quenching. Stresses inducing spalling are mainly attributed to the unconstrained strain mismatch due to differences in thermal expansion coefficients between the coating and the substrate. According to the theoretical analysis in Chapter 8, for coating systems with similar geometry to that used in the present research and under thermal shock even as severe as that with heat transfer coefficients of 2 to 16 kW/m²°C given by Fletcher [68], the effect of temperature gradient on the unconstrained strain mismatch may not be significant, regardless of the thermal and physical properties of the coating and the substrate.

Failure with significant mud cracking was not observed in the present water quenching tests as reported by other researchers [22, 40]. During quenching, the tensile stress inducing mud cracking usually is the sum of the stress caused by temperature gradient in the coating ($\sigma_{tem}$) and the stress caused by unconstrained strain mismatch between the coating and the substrate ($\sigma_{mis}$). Performance of the C-ramic coating systems during quenching suggests that the C-ramic coatings have
good resistance to thermal shock tensile cracking, which is related to the coating thermal physical properties, mechanical properties and microstructure, as described in §2.3.6. Details of the effects of coating thermal and physical properties and mechanical properties can be analysed as long as the data are available, which will be suggested for the further work. In terms of microstructure, C-ramic coatings studied in the present research contain pores and amorphous phases (as matrix or in boundaries between oxide particles). Pores can increase material toughness and thus lead to good thermal shock resistance [79, 81, 82]. Viscous flow of amorphous phases can reduce $\sigma_{\text{mix}}$ by stress relaxation at high temperature [49, 84], and thus reduce the overall tensile stress at an early stage of quenching.

9.4 EFFECTS OF COATING TYPE

9.4.1 Comparison of C1Z1 with C2Z2

C1Z1 and C2Z2 coatings are slightly different in the constituents of the starting material in their binder/densifiers: C1Z1 contains about 2% (wt) of urea, while C2Z2 does not.

The two CZ coatings are very similar in their microstructure (§4.2 and §4.3) and their behaviour under thermal cycle tests (§5.2). The only significant difference is in their thermal stability. The results of TMA and TGA of the two coatings showed that an abrupt volumetric change and weight loss occurred when the CZ coatings are heated up to 500°C, which may result from further chemical or physical changes occurring at temperatures higher than the fabrication temperature (400°C). In comparison with C1Z1, C2Z2 has a larger abrupt expansion but a smaller weight loss (§7.2).

The volumetric and weight changes are more likely to be associated mainly with coating matrices rather than the filler particles. $\alpha$-Al$_2$O$_3$ is thermally stable until the
melting point of $\alpha$-Al$_2$O$_3$ which is higher than 2000°C [29]. $\alpha$-quartz would change into $\beta$-quartz accompanied by approximately 5% volumetric expansion according to the density change of $\alpha$-quartz to $\beta$-quartz [28]. However, the transformation temperature is 573°C, which is more than 70°C higher than the start temperature of the abrupt expansion detected by TMA. Therefore, it is likely that the coating matrix contributes to the abrupt expansion detected from TMA and the weight loss detected from TGA.

Urea is added in C1Z1 in an attempt to prevent fuming of chromium oxide during the conversion of CrO$_3$ ---$\rightarrow$ Cr$_2$O$_3$. The difference between C1Z1 and C2Z2 in their thermal volumetric change and thermal gravimetric change is probably associated with urea.

The X-ray diffraction patterns of the coatings after thermal shock also show that some unidentified crystallized phases form in C2Z2 in addition to Cr$_4$(P$_2$O$_7$)$_3$ in C1Z1. The formation of the unidentified phases may also be related to the absence of urea in the C2Z2 coating.

**9.4.2 Comparison of CZ Coatings with the AX Coating**

In comparison with the AX coating, CZ coatings contain phosphoric acid, in addition to chromic acid, in their binder/densifiers. It has been found that adding phosphoric acid gives CZ coatings better corrosion resistance and lower curing temperature than the AX coating (the curing temperature of the AX coating is 540°C, which was determined from related patents; while that of CZ coatings is 400°C, which was determined by the experience of the manufacturer). In the present research, the effects of phosphoric acid on coating microstructure, thermal stability and behaviour under thermal cycle tests have been studied.
9.4.2.1 Microstructure

The surface and matrix of AX coating consist of microcrystalline Cr$_2$O$_3$, while the surface and matrix of CZ coatings consist of an amorphous compound formed from phosphoric acid and chromic acid. Chemical details of the compound are not yet clear. Studies of traditional chromium phosphate conversion coatings suggest that the amorphous compound of chromic acid and phosphoric acid in the coatings is comprised of hydrated chromium phosphates [23]. However, the compound in the traditional conversion coatings is formed at temperatures below 100°C, while the compound in the CZ C-ramic coatings is formed at 400°C. Therefore, the amorphous compound in CZ coatings may not be the same as those in the traditional conversion coatings.

9.4.2.2 Thermal stability

In comparison with the AX coating, CZ coatings are not thermally stable. The results of TMA, TGA and X-ray diffraction patterns of the AX coating did not show significant evidence of thermally induced chemical reaction or phase changes. The results of TMA and TGA of CZ coatings indicate further chemical or physical changes happened at temperature higher than the fabrication temperature (400°C). As analysed in §9.4.1, such volume and weight changes are more likely to be associated mainly with coating matrices rather than filler particles. The X-ray diffraction patterns of CZ coatings also showed that crystalline Cr$_4$(P$_2$O$_7$)$_3$ and some unidentified crystallized phases are formed after thermal shock test. All the above facts suggest that although the addition of phosphoric acid can reduce the curing temperature in practice, the coatings are actually not fully cured at 400°C.
9.4.2.3 Behaviour under thermal cycle tests

The effects of phosphoric acid on coating behaviour under thermal cycle tests are discussed here for coatings with stainless steel substrates.

It is interesting that, although the CZ coatings are not thermally stable, their spalling resistance under thermal cycle tests is no worse than that of the AX coating, as mentioned in §5.3. According to the $T_{cp}$ of the CZ coatings which are in the range of 800°C to 950°C, spalling of CZ coatings is not related to their abrupt volume expansion and weight loss detected by TMA and TGA. In addition, since crystallization of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ and some unidentified phases were detected in both failed and unfailed coatings after thermal shock, coating spalling under thermal shock is not closely associated with the formation of the new crystalline phases.

Although the AX and CZ coatings are not significantly different in their $T_{cp}$, they do have different spalling modes (§5.4). Spalling modes of the coatings suggest that adding phosphoric acid reduces the ratio of coating adhesive strength to coating cohesive strength under thermal cycle tests. This means that adding phosphoric acid may either increase the coating cohesive strength or reduce the coating adhesive strength, or may cause both of the above events to happen simultaneously. The change in coating cohesive strength and adhesive strength may be correlated with the change of coating microstructure and bonding nature due to phosphoric acid and decreased curing temperature.

9.4.3 Comparison of the hybrid C1X coating with C1Z1 coating and AX coating

9.4.3.1 Microstructure

The C1X coating has a C1 type of base coating and an X type of binder/densifier. Therefore, the microstructure of C1X has features from both C1 base coating and X
binder/densifier. As shown in §4.5, the coating surface is covered with crystalline Cr$_2$O$_3$ particles, which is the same as AX coating; the coating matrix contains not only compounds from chromic acid and phosphoric acid, but also aggregated crystalline Cr$_2$O$_3$ particles.

9.4.3.2 Thermal stability

Although the results from TMA and TGA showed that the CiX coating is not as thermally stable as the AX coating, the abrupt expansion and thermal weight loss of CiX coating were much less than those of the CiZi coating. The CiX coating contains less of the compound from chromic acid and phosphoric acid than those of CZ coatings, and the CiX coating is heated up to 540°C as is the AX coating during the six densification cycles. Therefore, the results of TMA and TGA of the CiX coating confirm that the abrupt expansion and thermal weight loss in CZ coatings are associated with the compound from chromic acid and phosphoric acid, and the lower fabrication temperature of CZ coatings.

9.4.3.3 Behaviour under thermal cycle tests

Although Tcp of CiX coating reached 1000°C, which is the largest value obtained among the four types of coatings, the difference between either CiX and AX or CiX and CiZi is not very significant (§5.3). As with the AX coating, spalling of the CiX coating occurred within the coating, which indicates that the coating adhesive strength is greater than its cohesive strength. In comparison with CiZi and AX coatings, the CiX coating is close to the AX coating in its ratio of adhesive strength to cohesive strength.
9.5 EFFECT OF SUBSTRATE TYPE

In the present research, three types of substrates were used: stainless steel, carbon steel and copper. The experiments showed that among the three types of substrates, thermal shock resistance of the coating systems with the stainless steel substrate are the best, with the carbon steel the second, and the copper the poorest. Cohesive fracture of the coating is involved only in the coating spalling from the stainless steel substrate. For carbon steel or copper substrates, spalling occurs either in the coating/substrate interface, or within the substrate.

Generally speaking, substrate types may affect the performance of coating systems in several ways, including the level of unconstrained strain mismatch related to substrate thermal physical properties, bonding nature related to substrate material chemical compositions, and debonding tendency related to substrate thermal stabilities. Since the three types of substrates are not significantly different in their thermal expansion coefficients (approximately 18 μm/m°C for stainless steel [86] and copper [105], 15 μm/m°C for carbon steel [85]), and not all coating spalling is related to cooling-rate-related stresses, the effects of substrates on performance of the coating systems may be attributed to their chemical composition and thermal stability. Details about the effects of substrate type will be discussed in the following sections concerning coating spalling mechanisms.

9.6 MECHANISMS OF COATING SPALLING UNDER THERMAL SHOCK

Since the behaviour of the coating systems under thermal cycling, such as critical peak temperatures under rapid cooling and slow cooling tests, spalling pattern, spalling mode, and spalling process, are closely related to substrate types, the mechanisms of coating spalling are discussed in terms of substrate types.
9.6.1 Spalling Process

9.6.1.1 Stainless steel substrate

Under water quenching (mode A, C test), the coating spalling process could not be observed directly. However, the specimens showed spalling pattern II, i.e. some coating remained in the centre of the disc specimens, which suggests that coating spalling might be initiated from the specimen edge. Spalling from the specimen edge was observed clearly under air cooling, which was also observed in other work [55, 71, 74] The spalling process suggests that the coating spalling may be attributed to shear rupture, since shear stress in the coating/substrate interface achieves its maximum value at the specimen edge [99].

9.6.1.2 Copper substrate

Under water quenching (mode A, C test), the specimens have spalling pattern III, i.e. the remaining coating was located randomly, which suggests that coating spalling was not initiated from the specimen edge. Coating spalling after coating buckling away from the specimen edge was observed clearly under air cooling. This spalling process suggests that coating spalling was initiated from coating delamination and that the coating was under compressive stress [98, 99].

9.6.1.3 Carbon steel substrate

Under water quenching (mode A, C test), the coating systems have only spalling pattern I, i.e. no coating remained on the substrate, which did not give any clue to spalling process. Under air cooling, spalling occurred very violently within seconds thus the real process could not be observed.
9.6.2 Causes of Coating Spalling

Logically, for an originally mechanically integrated object, destruction of its mechanical integrity must be attributed to either increase of stress to which the object is subjected, or the decrease in strength of the object for any reasons, or both. In this section, the contributions of stress increase and strength decrease of the coating systems to their behaviour under thermal shock are discussed.

9.6.2.1 Stainless steel substrate

9.6.2.1.1 Consideration of stress

The observation in the research that the coating spalled on cooling from some critical peak temperature which is not influenced significantly by cooling rate, suggests that coating spalling under thermal shock is probably not attributed to cooling-rate-related stresses, but heating-related stresses which are increased after the coating systems have experienced high temperature.

For a coating system which is free of external forces, an increase in stresses in the coating system is usually attributed to the increase in mismatch between the coating and the substrate in their unconstrained strains. In other words, when the extent of the mismatch increases, the stresses in the coating system increase too. The performance of coating systems suggests that the unconstrained strain mismatch in the coating systems may increase after the coating systems experience high temperature, which can be logically related to material deformation due to phase change or material inelasticity at high temperature.
(a) Effect of chemical reactions or phase change

The substrate, stainless steel AISI316, has an austenitic structure, which is stable within the temperature range of the thermal cycle test in the present research. Although the coating materials are not very thermally stable, especially CZ coatings, as discussed in §9.3, coating chemical reactions or phase changes did not attribute to coating spalling directly. Therefore, coating spalling is not related to chemical reactions or phase changes of either of the coatings or the substrate.

(b) Effect of inelastic deformation

During a thermal cycle, the coating and the substrate are always subjected to stresses due to the unconstrained strain mismatch caused by thermal expansion mismatch $(\Delta \varepsilon)$, which can be expressed as:

$$\Delta \varepsilon = (\alpha_s - \alpha_c) (T - T_0)$$  \hspace{1cm} (9.1)

where $\alpha_s$ and $\alpha_c$ are the thermal expansion coefficients of the substrate and coating materials respectively, $T$ is the temperature of the coating systems, and $T_0$ is the fabrication temperature of the coating system, at which the system usually is stress-free. The present experiments showed that the coatings spalled during cooling, which cannot be explained by eq.(9.1). According to eq.(9.1), the $\Delta \varepsilon$ would follow path AB and then BA during a thermal cycle (Fig. 9.1), and thus stresses in the coating systems should not increase dramatically during cooling in comparison with the as-received state. However, if inelastic deformation of the coating occurs at high temperature during heating, $\Delta \varepsilon$ will decrease at high temperature following path BC. During subsequent cooling, the $\Delta \varepsilon$ would follow the path CD. As a result, the $\Delta \varepsilon$ would increase dramatically at low temperature, for example, from OA to OD. Such effects of inelastic deformation have been suggested as one of the factors contributing to coating failure during thermal cycles [40]. The values of $\Delta \varepsilon$ during cooling depends mainly on the peak temperature level of a thermal cycle. The higher the peak
Fig. 9.1 A schematic diagram showing $\Delta \varepsilon$ developed during cooling down due to the inelastic deformation during heating up.
temperature, the more severe $\Delta \varepsilon$ during cooling. For example, $\Delta \varepsilon$ will follow path EF, instead of CD, when the peak temperature is increased further.

Inelastic deformation at high temperature is common for polycrystalline and multiphase ceramic materials with amorphous phases. The basic mechanism of the inelastic deformation of the amorphous phase is viscous flow [49, 84]. For the C-ramic coatings involved in the present research, the microstructure of the coatings determines that the coatings are susceptible to inelastic deformation. The basic feature of the coatings is that oxide particles are dispersed in a matrix. For the CZ type coatings, the matrix itself is amorphous. For the AX coating, although the matrix in general is the aggregation of crystalline particles of $\text{Cr}_2\text{O}_3$, an amorphous phase may exist in particle boundaries. For the CiX coating, amorphous phases may exist as matrix or in particle boundaries.

The observations in this study that the critical peak temperatures are not affected significantly by cooling rates under water quenching and air cooling, and that coating spalling occurred at temperatures around 200°C, suggests that inelastic deformation of the coatings at high temperature might be one contributor to coating spalling. Further research is needed to study the inelastic nature of the C-ramic coating materials to confirm this spalling mechanism.

9.6.2.1.2 Consideration of strength

The adhesion and cohesion of C-ramics are related to some type of chemical bonding. During thermal shock test, since the coating systems experienced temperatures higher than the fabrication temperature of the coatings, the adhesion and cohesion of the coatings might be affected by further chemical reactions or phase transformations, such as those detected by TMA, TGA and X-ray diffraction patterns for CZ coatings.
In addition, coating inelastic deformation via particle sliding at high temperature, if it happens, may also affect the coating cohesion.

Although the effects of thermal cycling on coating adhesive and cohesive strength were not able to be investigated directly in the present research, it should be borne in mind that decrease of strength might occur during the thermal cycle tests and contribute to coating spalling.

9.6.2.2 Copper substrate

9.6.2.2.1 Consideration of stress

As with coating systems with the stainless steel substrates, the critical peak temperature of the coating systems with copper substrates under thermal cycling is not affected significantly by cooling mode. Also, spalling under air cooling occurred when the specimens were cooled below 300°C. Therefore, stresses related to coating inelastic deformation might also contribute to coating spalling. However, the critical peak temperature of the coatings with copper substrates is 550°C, which is much lower that those of the same type of coatings with stainless steel substrates. The lower critical peak temperature may be attributed to poorer adhesion of the coatings due to poor cohesion of copper oxide formed between the coating and the substrate.

9.6.2.2.2 Consideration of strength

During the heating up stage of a thermal cycle, coating adhesion might be affected by further oxidation of the substrate, as well as delamination of copper oxide due to thermal expansion mismatch between copper and copper oxide. Reducing coating adhesion during heating may contribute to coating spalling during cooling.
9.6.2.3 Carbon steel substrate

9.6.2.3.1 Consideration of stress

In contrast with specimens with the other two substrates, the critical peak temperatures of the coatings with carbon steel substrates are affected significantly by the cooling mode. Coating spalling under thermal shock seems closely correlated with cooling rate. The effects of cooling rate under water quenching is commonly attributed to temperature gradients, which could cause coating failure at the initial stage of quenching by mud cracking [40]. However, such failure was not observed in the present work. Instead, the coating spalled completely during thermal shock when peak temperature was increased to 750°C. The value of the critical peak temperature suggests that coating spalling may be related to martensitic transformation of the carbon steel. According to the Fe-C phase equilibrium diagram, pearlite in the carbon steel transforms to austenite at 723°C. Although the phase change during heating did not affect the integrity of the coating systems significantly, it leads to martensitic transformation during water quenching, as suggested by the hardness change (Fig.9.2) and metallograph (Fig.9.3) of the carbon steel before and after thermal shock test CS/AX-750C. Martensitic transformation is normally accompanied by sudden material expansion and surface relief [110], which may induce stresses in coating/substrate interface and thus contribute to coating spalling.

9.6.2.3.2 Consideration of strength

As mentioned in §5.4, a substantial amount of Fe was detected from spalled coating fragments in the region adjacent to the coating/substrate interface after thermal shock. It is not clear yet whether such a phenomenon contributed to coating spalling by weakening the coating adhesion.
Fig. 9.2 Hardness of carbon steel substrate before and after thermal shock test CS/AX-750C.

Fig. 9.3 Metallograph of the carbon steel substrate after thermal shock test CS/AX-750C (×1500).
There is one point that may be addressed here, although it is related to coating spalling under air cooling instead of thermal shock. It was found that when the peak temperature of CS/AX was increased to 900°C, coating spalling under air cooling occurred at about 600°C, which is much higher than the spalling temperature for coating systems with the other substrates. This phenomenon suggests that the coating adhesion was decreased significantly after the coating system experienced 900°C.
CHAPTER TEN

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

10.1 GENERAL

The characteristics and behaviour of C-ramic coating systems under thermal cycling have been investigated in the present research. This research has helped to elucidate the influence of the coating characteristics on the performance of the coating system under thermal shock, including critical peak temperature, spalling modes, spalling mechanisms, etc. The results and conclusions reached are summarized in the following section. Suggestions for further research are given in §10.3

10.2 CONCLUSIONS

10.2.1 Characteristics of the C-ramic Coatings

1. Four types of the C-ramic coatings were examined in the research, viz., C1Z1, C2Z2, AX, and C1X. The coating microstructure depends mainly on the type of binder/densifier used.

2. An amorphous compound is formed for Z types of binder/densifier due to the addition of phosphoric acid into chromic acid, while microcrystalline Cr2O3 particles are formed for the X type of binder/densifier from chromic acid. As a result, CZ coatings have surfaces covered with the amorphous compound and microcracks.
while AX and ClX coatings have surfaces covered with aggregated Cr$_2$O$_3$ particles. The basic feature of the bulk coating microstructure is that SiO$_2$ and Al$_2$O$_3$ particles are distributed randomly in the matrix formed from the amorphous compound for CZ coatings, or from aggregated Cr$_2$O$_3$ particles for the AX coating. The matrix of the ClX coating is a mixture of the amorphous compound and aggregated particles. Six cycles of densification leads to the coatings containing significant porosity.

3. The CZ coatings are not thermally stable and fully cured. Some chemical reactions accompanied by abrupt volumetric change and weight loss occur when the coating systems are heated up to about 500°C. Crystallized Cr$_4$(P$_2$O$_7$)$_3$ and some other unidentified phases formed after thermal cycle tests. The above phenomena are related to an amorphous compound formed between chromic acid and phosphoric acid, and are affected by adding urea to the mixture of chromic acid and phosphoric acid.

4. Formation of the conversion coating layer between the coatings and substrates depends on the combination of coating and substrate type. A significant conversion coating layer was found only in the coating system with the AX coating on the carbon steel substrate. No obvious conversion coating layer was found in any coating systems with stainless steel or copper substrates, and coating systems with CzZ2 coating. Therefore, adhesion of the Cramic coatings to substrates does not rely on the formation of a conversion coating layer.

10.2.2 Thermal Shock Performance of the Coating Systems

1. The thermal shock performance of eight types of coating systems with four types of coatings and three types of substrates were investigated by water quenching. All the coating systems failed by spalling during cooling when the peak temperature of
the thermal cycles reached a critical peak temperature depending on the type of the coating system.

2. The critical peak temperatures ($T_{cp}$) of the four types of the C-ramic coatings with stainless steel substrates are in the range of 850°C to 1000°C. Coating spalling is not affected by the thermal stability of the coating materials in terms of chemical reaction, phase transformation or any change which can be detected from X-ray diffraction patterns of the coating materials. Although the four types of coatings do not differ significantly in their critical peak temperatures, they have different spalling modes. For CZ coatings, spalling occurred by decohesion along the coating/substrate interface or along the peaks of the interface. For AX and C1X coatings, spalling occurred by decohesion within the coatings.

3. The thermal stability of substrate materials plays an important role in the performance of C-ramic coating systems. The performance of the coating systems with stainless steel substrates is better than that of coating systems with carbon steel substrate and copper substrates. The $T_{cp}$ of SS/C2Z2 is in the order of 900°C to 950°C, while the $T_{cp}$ of CS/C2Z2 and CU/C2Z2 are 750°C and 550°C respectively.

4. The substrate type has a significant effect on the coating spalling mode. With stainless steel substrates, coating spalling involved cohesive fracture of coating materials. With the carbon steel substrates, coating spalling did not involve cohesive fracture of coating material, but rather decohesion in the coating/substrate interface. For copper substrates, coating spalling did not involve cohesive fracture of coatings and decohesion occurred within the substrate.

5. The substrate type also has a significant effect on the coating spalling process. With stainless steel substrates, coating spalling initiated at the edge of the specimen
surface due to shear rupture. For copper substrates, coating spalling resulted from delamination by compressive buckling.

6. The effects of substrate on performance of the coating systems under thermal shock is not closely correlated to substrate physical properties such as thermal expansion coefficients, thermal conductivity or thermal diffusivity, which determine the thermal stress level. The substrate chemical composition and thermal stability, which determine the adhesion bonding nature and decohesion tendency, play important roles in the performance of the coating systems under thermal shock.

7. The influence of heating rates (20°C/min and 250°C/min) on thermal shock performance of all coating systems is not significant.

8. Since coating spalling depends on both stresses and strength state, which are difficult to assess in the present research, details of spalling mechanisms are not very clear. However, the values of $T_{cp}$ of coatings with stainless steel substrates and copper substrates are not affected significantly by cooling rates, thus coating spalling is probably related to some process occurring at high temperature, such as inelastic deformation attributed to viscous flow of amorphous phases. The values of $T_{cp}$ of coatings with carbon steel substrates are however affected significantly by cooling rate, and coating spalling may be related to martensitic transformation on rapid cooling. In addition to the possible contributions of increase of stress to coating spalling, the decrease of cohesive or adhesive strength of the coatings due to heating may also contribute to coating spalling.

### 10.2.3 Effect of Temperature Gradient on Coating Spalling Tendency

The effects of temperature gradient during thermal shock on coating failure tendency, in terms of ‘unconstrained strain mismatch’ (USM), has been studied by theoretical
analysis based on assumed typical coating systems and thermal shock conditions. Under the assumed thermal shock conditions, the effects of temperature gradient depend mainly on the thermal physical properties of the substrate materials. For coating systems whose substrates have lower thermal diffusivity and thermal conductivity, such as stainless steel AISI316, the maximum USM under thermal shock is slightly larger than that during slow cooling. For coating systems whose substrates have higher thermal diffusivity and thermal conductivity, such as copper, the maximum USM during quenching is not significantly different from that during slow cooling. The influence of coating thermal physical properties and coating thickness are minor.

10.3 SUGGESTIONS FOR FURTHER WORK

The basic behaviour of the C-ramic coating systems under thermal shock has been studied in the present research. In order to gain a further understanding of thermal shock failure mechanisms through quantitative stress and strength analysis, the following investigations are suggested:

(1) thermal physical properties of the C-ramic coatings and the effect of temperature on those properties, such as thermal expansion coefficient, thermal conductivity, and thermal diffusivity;

(2) mechanical properties of the C-ramics and the effect of temperature on those properties, such as coating elasticity, cohesive strength and adhesive strength.
REFERENCES


