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Development of a copper containing 690 MPa yield strength quenched and tempered steel

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**Development of a Copper Containing 690 MPa Yield
Strength Quenched and Tempered Steel**

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

Honours Masters in Materials Engineering.

From

The University of Wollongong

by

James Alfred Chevis

Department of Materials Engineering 1997

Candidates Certificate

This is to certify that the work presented in this thesis was carried out in the laboratories of the Department of Materials Engineering in the University of Wollongong and at the premises of Bisalloy Steels by the candidate, and has not been submitted to any other university or institution.

James A. Chevis

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Abstract

Demands placed on modern steels mean that higher strengths are being sought while alloy contents, particularly carbon, are decreased. These two conflicting requirements have forced steel designers to consider micro-alloying, heat treatment and precipitation strengthening to meet market demands.

This study concentrated on the use of precipitation hardening by copper to maintain the strength of reduced carbon, quenched and tempered steels. Many studies have concentrated on copper proportions above 1% in as rolled steels. It was the intent of this study to examine the effect of copper levels between 0 and 1% in the development of a low carbon, 690 MPa yield strength quenched and tempered structural steel. The changes in hardness upon tempering, tensile testing, Charpy v-notch impact testing, Jominy hardenability, bead-on-plate weld testing and optical microscopy were used to evaluate the steels. Also covered was the development of empirical descriptions of the response of quenched and tempered steels to heat treatment. Both copper free and copper containing steels were used in the analysis.

In studying the copper containing steels, precipitation hardening was observed in a steel containing 0.4% copper (nominal composition). It was shown that the strength and fracture toughness targets of military and commercial specifications can be met by the steels developed.

As a result of copper based precipitation hardening, Jominy hardenability tests showed a hardenability much higher than would be predicted on the basis of carbon content and the volume fraction of martensite produced as a function of cooling rate. It was demonstrated that the weldability of the low carbon copper steels, as assessed by the bead on plate test, is superior to that of currently used alloys. Therefore, the aim of maintaining strength and increasing weldability by reducing carbon content was clearly achieved.

Definitions

A.S.T.M - American Society for Testing of Materials.

B.H.P S.P.P.D. - Broken Hill Proprietary Limited, Slab and Plate Products Division now known as B.H.P. F. P. D. (Flat Products Division)

CEQ I.I.W. - International Institute for Welding Carbon equivalent.

Pcm - Ito-Bessyo Pcm (a welding index indicating the potential for cold cracking)

H.S.L.A (steels)- High Strength Low Alloy Steels

J.I.S.I- Japanese Iron and Steel Institute.

J.W.E.S - Japanese Welding and Engineering Society

F.R.T. - Finish Rolling Temperature.

HAZ - heat affected zone

GCZ -grain coarsened zone otherwise known as the coarse grained region of the heat affected zone.

Ms - Start temperature of the Martensite transition upon rapid cooling.

A_c - Critical arrest temperature, transformation temperature upon cooling.

CHAPTER 1

Introduction

Demands placed upon the properties of modern steels are influenced by two opposing requirements: that of reducing carbon composition, for weldability improvements, and maintaining or increasing strength, for cost/weight reduction. This is particularly the case with high strength, quenched and tempered steels as they are often used in the most demanding of situations requiring outstanding mechanical properties, coupled with ease of fabrication (weldability, formability) in order to compete with hot rolled steels.

The objectives of this study, which involved Bisalloy Steels Pty. Ltd., were to develop steel alloys capable of meeting the mechanical property requirements of Bisalloy 80, a 690 MPa yield strength, quenched and tempered steel and two U.S. military standards MIL-S-16216(SH), (HY100) and MIL-S-24645(SH), (HSLA100).

The required mechanical property details are shown below in Table 1.1.

Table 1.1 Mechanical Property Requirements for Bis 80¹

- 690 MPa min. Yield strength,
- 790 - 930 MPa Tensile strength,
- 18 % min. elongation (50mm gauge length),
- 45 % min. reduction of area,
- 40 J absorbed energy @ -20 °C (Charpy V- notch),
- 0.95 max. yield to tensile strength ratio, 0.93 Bis 80 pv.

Table 1.2 displays the mechanical property requirements for the military specifications and the combined requirements to satisfy all three specifications.

Table 1.2 Mechanical Property Requirements To Meet HY 100², HSLA100 ³ And Bis 80

	<u>Specifications</u>		
	HY100 >19mm Thick	HSLA100	Combined HY,HSLA BIS80
Yield Strength(MPa)	690-827	690-861	690-827
Tensile Strength(MPa)	-	-	790-930
Min. R.O.A.(%)	45	50	50
Min. Elongation(%) (50mm GL)	18	18	18
Min. Impact Energy Cv (J)	81 (-18°C) 54 (-84°C)	108 (-18°C) 81 (-84°C)	108 (-18°C) 81 (-84°C)
Yield/Tensile ratio (Max.)	-	-	.95 (.93 pv*)

* Note :- pv signifies pressure vessel plate.

Carbon levels in any new alloys had to be significantly lower than existing alloys produced by Bisalloy Steels ($\leq 0.16\%C$). The main reason for this was to provide increased weldability.

In order to maintain the required strength with reduced carbon quantities, copper was added to provide precipitation strengthening.

Development of the required strength at relatively high tempering temperatures was also required from any new alloy. This is an advantage in production as high tempering temperatures aid the relaxation of stresses induced by the quenching process, minimising warpage in the final product and facilitating post fabrication stress relief.

Alloy compositional constraints⁴ existed due to BHP SPPD steelmaking limitations. These constraints (see Table 1.3) are acknowledged and any final alloy for commercial production of plate will be constrained by these boundaries. However these limitations were not imposed on the scope of alloy compositions studied.

Table 1.3. BHP SPPD steelmaking composition constraints

Element	Range %
C	$C < 0.1, C > 0.12$
Mn	$Mn < 1.5$
Ni	$Ni < 0.5$ regular production $Ni < 3.0$ project basis.
Cu	- (see Ni/Cu ratio)
Ni/Cu ratio	1/2

Candidate steels were evaluated through tensile, Charpy V- notch impact, Vickers hardness, Jominy end quench hardenability and bead-on-plate weldability tests. The mean prior

austenite grain size of each candidate steel was also measured.

An additional part of this work was the development of a computer programme as an aid to alloy development. This computer programme allows the prediction of mechanical and physical properties from chemical composition. Empirical models for prediction of tempering behavior were also developed both for copper containing and copper free steels.

CHAPTER 2

Survey of Literature

Historical Perspective

The use of iron and steel in structural applications has a long history. The first iron bridge was built in the mid 1779 by Abraham Darby III⁵ and still stands today in an English town interestingly called Ironbridge.

Cort's puddling process was the method by which most wrought iron for structural uses was produced at the time⁶. This process resulted in a mixture of almost pure iron with inclusions. About 50 kg was the largest ingot that could be formed using this method, severely limiting the size of any component that could be produced without some form of joining such as rivetting or welding.

The next major advance in steel making was the production of crucible steel⁶. This process involved heating pig iron in a sealed crucible with slag forming agents. With practice the crew of a foundry could cast large ingots, one notable achievement being a 2000 kg ingot cast by Krupps foundrymen which was presented at the Great Exhibition of 1851 in London⁶.

In 1856⁶ Henry Bessemer patented a process whereby iron was turned into mild steel by blowing oxygen through the melt in order to remove most of the carbon. This process was sensitive to the level of phosphorus in the iron. Due to the speed at which the reactions proceeded, phosphorus in the iron was not oxidised as it was in the very much slower open hearth process. The open hearth process, invented by William Siemens, could accept iron with a higher phosphorus content than the Bessemer process, however neither could deal with very high phosphorus irons. This problem would not be solved until 1879 by Sydney Thomas.

Thomas' invention⁶, the use of dolomite and tar as a refractory lining for the steel making

vessel allowed basic slags to be used and the phosphorus, oxidised to phosphoric acid in the converter, could be removed in the slag. Thus, the modern Basic Oxygen Steel making process was born.

The large scale production of steel facilitated its economical use in a wide variety of applications. Because of the superior properties of steel over wrought and cast iron, better armour, longer bridge spans and larger structures could be produced. The improvements in properties of steels increased the variety of uses which in turn fuelled demand for further improvements in properties.

Pickering⁷, in his book "Physical Metallurgy and the Design of Steels" gives the following sequence of developments regarding structural steels, beginning with early structural steels and leading to HSLA steels:

1. around the turn of the century, design was based around tensile strength, with carbon being the major strengthening agent, structures were rivetted together and alloy compositions changed little for many years;
2. as welding became a widely used joining method, carbon contents fell and manganese proportions were increased to maintain strength;
3. impact toughness was recognised as an important parameter as brittle fracture of welded structures occurred, yield strength rather than tensile strength was acknowledged as the important factor in structural applications;
4. the significance of grain size was established and the effects of grain refining elements such as nitrogen and aluminium were quantified;
5. precipitation hardening, exploiting niobium, vanadium and titanium additions. was used to further increase the yield strength, but the as rolled grain size was still coarse, and so the fracture toughness poor;

6. the positive effect of Finish Rolling Temperature on as rolled grain size was recognised and consequently the yield strength and the fracture toughness improved; and
7. formability and through thickness ductility improve with improvements in steel cleanliness along with a reduction of the incidence of lamella tearing.

Pickering puts the advances in this field down to systematic metallurgical research and "as such, can be regarded as a good example of how developments are based upon and indeed, often wait upon, the understanding of structure-property relationships, transformations, etc."⁷

Modern Steels

Pickering⁸ states that the driving force for developments in H.S.L.A. steels has stemmed from demand for higher strength, lighter sections, increased weldability, improved fracture toughness and better ductility and formability. This is true, not only for H.S.L.A. steels, but for structural steels in general and it is these considerations that have lead to the development and widespread use of H.S.L.A. steels.

The microstructures of as-rolled H.S.L.A. steels comprise ferrite-pearlite or acicular/lath ferrite (low carbon bainite). Quenching and tempering is also used as a production route for these types of steels and the microstructures produced are generally martensite or bainite depending upon the hardenability of the alloy and the section size.⁸ Ferrite/pearlite and bainitic microstructures are produced via controlled processing, low finish rolling temperatures to refine grain sizes and controlled cooling from the finish rolling temperature. Mechanical properties that are possible via this processing method reach a maximum of around 500 MPa yield strength⁹.

Tensile mechanical properties of quenched and tempered H.S.L.A. steels can reach 1200-1500 MPa yield strength, although, because of fracture toughness concerns, steels of this strength are not normally used in structural applications. Structural steels with yield strengths of 690 MPa are easily produced via quenching and tempering. A family of high strength, quenched and tempered steels is commercially produced in Australia. Yield strengths range from 500 MPa to 690 MPa in structural grades. Wear resistant steels are specified by hardness, which ranges from 320 to 500 Brinell (translating to approximately 1120 to 1750 MPa tensile strength).

Croll,¹⁰ and Haaijer and Beckman¹¹ both point out the advantages of high strength structural steels. Some of these advantages are reduction of plate thickness and thus weight of structures or, alternatively, increases in design stresses utilising the greater strength of such steels.

Components stressed in tension represent the most economical and efficient use of high

strength steels where the increased strength of the steels can be exploited to maximum benefit. In compression the most efficient use of high strength structural steels is in highly stressed members with high aspect ratio, where buckling resistance is not the controlling criterion¹⁰. In Australia, high strength quenched and tempered steels have been used in bridges, mobile cranes (where reduction of dead weight is critical), high rise buildings, pressure vessels (both transportable and stationary), storage tanks and in military applications such as submarines. The pressure hulls of all the Australian built, Collins class submarines are constructed from quenched and tempered high strength structural steel¹⁰.

Many high strength structural steels are produced commercially and many of these are quenched and tempered, particularly for yield strengths greater than 500 MPa particularly in thicker sections. Some examples of the wide-spread manufacture of quenched and tempered structural steels are the Bisplate range manufactured in Australia by Bisalloy Steels¹², RQ steels from the U.S.A. by Bethlehem¹³, River Ace 60, 70, 80 and 100 made by Kawasaki Steel Corporation¹⁴; Welten¹⁵ and NK-Hiten¹⁶ produced by Nippon and Nippon Kokan; and Sumiten produced by Sumitomo Metal Industries¹⁷. These last four companies are Japanese. British Steel¹⁸ and Svenski Stal, Sweden also produce high strength quenched and tempered structural steels.

Rosier and Croll¹⁹, in their review of the use of high strength quenched and tempered steels in structures demonstrate the world-wide acceptance of this type of steel in structural applications. Future developments in high strength structural steels will involve the increasing of strength and the reduction, or more efficient use of alloying elements to improve weldability and toughness^{11,20,21,22}.

Gross, Stout and Czyryca²¹ have described the manufacture of a 900 MPa yield strength steel (HY 130) via controlled rolling and accelerated cooling. The compositions that they used

fell into the following range, 0.04-0.07% C, 0.8% Mn, 0.6% Mo, 0.6% Cr, 5.00% Ni. Strengths of this level can be achieved (and exceeded) with a boron treated, hot rolled and quenched steel with 0.16-0.18 %C, 1.15 %Mn, 0.4 %Si, 0.85 %Cr and 0.2 %Mo.¹² This is a leaner steel, more economical with respect to alloying elements. As well as illustrating the powerful effect of boron, this comparison shows the wide variety of alloy compositions amenable to exploitation via quenching or accelerated cooling.

Gross *et al.*²¹ also provide information on the cooling rates reported for various commercial plate quenching and accelerated cooling operations. The fastest cooling rates are observed in roller quench systems (such as the Drever quench in Bisalloy Steels' Unanderra plant), with the slowest being air cooling. Cooling rates measured in other types of accelerated cooling units fall in-between, providing a variety of cooling efficiencies, possible microstructures and steel strengths.

The impetus for development of stronger steels is also plain. Irving²² reviews the developmental directions, with regard to steel weldability, of several steel companies, in the United States, Europe and Japan. The developments described are reductions in alloy content, particularly carbon, and the use of accelerated cooling and/or controlled rolling to develop stronger steels.

The ASTM A710 and A736 family of steels was developed in the late 1960's²³. This type of steel uses the precipitation of copper to maintain the desired strength, allowing the use of very low carbon contents. The nominal chemical composition for this type of alloy is 0.05-0.06 %C, 1.45 %Mn, 0.72 %Cr, 0.45 % Mo, 0.97 %Ni, 1.25 %Cu, 0.35 %Si²³. Mechanical properties range from 380-585 MPa yield strength depending upon grade and class. Impact toughness is specified to be not less than 27 J @ -45°C for a longitudinal specimen²⁴. Hot rolling and aging seems to be the most widely used production method and Wilson²³ states that 6mm thick plates

of ASTM A710 can be controlled rolled and aged to give 690 MPa yield strength. Increasing Mn and Mo levels increase the thickness of plate in which this strength level can be maintained.

Given the ability of A710 to reach 690 MPa when hot rolled and aged, the increased strength and efficiency of use of alloying elements which is possible when steels are hot rolled, quenched and tempered, particularly using a roller quench system, there appears to be considerable scope for reduction in copper content while still meeting a 690 MPa minimum yield strength requirement. By their nature, copper containing, age hardening alloys are ideally suited to the hot rolled, quench and temper production process.

Due to the high cooling rates in the roller quenching process, (as opposed to air cooling or even accelerated cooling after rolling²¹) much more copper should be retained in solution to precipitate upon aging and increase strength. Thus lower initial copper levels may be possible, reducing the need for nickel to alleviate hot shortness and also reducing the overall alloy cost.

Precipitation Hardening.

The yield strength of a material is the stress at which the material undergoes plastic deformation by dislocation movement throughout the crystal structure. Lloyd²⁵ defines the yield stress of an alloy as the 'stress required to move dislocations large distances through an array of obstacles'. These obstacles could be solute atoms or precipitate particles.

Precipitation hardening is a strengthening mechanism that increases the yield strength by exploiting the decreasing solubility with decreasing temperature to produce a supersaturated solid solution. The precipitates which form, through rapid cooling and subsequent precipitation, provide significant obstacles to dislocation motion.

Lloyd²⁵ examined the simple scenario of a gliding dislocation contacting an array of obstructions.

He derived the following formulae :

$$F=2T\cos(\frac{\phi_c}{2})$$

where : F = the obstacle strength, T = the dislocation line tension, ϕ_c = the breakaway angle.

and

$$\tau=\frac{F}{bL}$$

where : τ = the applied shear stress

b = the Burgers vector

L = the obstacle spacing

This implies that yield strength increases as the particle spacing gets smaller and so the ideal is to have a closely dispersed array of point particles. Of course there exists a practical limit as to how small the particle spacing can become and how small the particle can be.

Lloyd²⁵ makes the point that since commercial alloys contain precipitates of a finite size, then the particle spacing has to be adjusted by accounting for the particle radius.

Precipitation Hardening using Copper as a Strengthening Agent.

Grange, Lambert and Harrington²⁶ studied the effect of copper on the heat treating characteristics of a 0.45% carbon steel. Their focus was concerned with establishing the existence of any detrimental effects of residual copper on the heat treatment characteristics of steels. They used the Jominy end quench test and also quenched cylinders to determine the effect of copper, at levels from 0.06% to 1.5%, on hardenability and the Ms temperature. They also derived an isothermal transformation diagram for the four steels studied. Their findings included the observations that copper increases hardenability, the equilibrium transformation temperatures are lowered slightly, the Ms temperature is depressed by the presence of copper by about 10 degrees for every 0.5% addition, that copper causes precipitation hardening and that the presence of copper increases the ability of an alloy to resist softening on tempering. This effect was attributed to the combined effects of solid solution strengthening and precipitation. No effect on the hardness of martensite due to copper was observed.

Grange *et al*²⁶ state that the precise solubility of copper in austenite is unknown but amounts to several percent. This solubility limit falls to somewhat less than 0.5% in ferrite (and is probably similar in martensite or tempered martensite as these phases are metastable ferrite). It is this change in solid solubility that gives rise to the precipitation or age hardening behaviour²⁷.

Youle and Ralph²⁸ examined the precipitation of copper in an iron-1.7% copper alloy. Samples used in this study were heat treated by first austenitising at 950°C then quenching into water followed by tempering or aging at various temperatures. Hardness results indicated that the peak hardness is developed at an aging time of 7-10 hours when the tempering temperature is 470°C. This time to reach peak hardness reduces to approximately 1 hour at 550 C. An increase of 80°C leads to a ten fold reduction in tempering time to reach peak hardness. Although ten hours is not a commercially viable tempering time, one hour is. The implication of this is that

alloys must be designed so that practical tempering temperature conditions allow the maximum contribution to strength due to copper precipitation. Electron microscopy used in the study by Youle and Ralph²⁸ showed that precipitates formed randomly inside grains as well as on line defects and grain boundaries. They also found that peak hardness occurred when the number of precipitates per unit volume was a maximum. The average size of these precipitates was measured to be approximately 3nm

Goodman, Brenner and Low²⁹ used a field ion microscope atom probe to study the precipitation of copper in an iron 1.4% copper alloy. One of their conclusions was that almost all of the precipitate particles are spherical from the beginning of precipitation. They did observe some rod shaped precipitates and concluded that these may have formed on dislocations. The correspondence of the peak in hardness with the maximum number of precipitate particles per unit volume found by Youle and Ralph²⁸ was confirmed in this study.

Goodman *et al.*²⁹ also attempted to determine the degree of coherency of the copper precipitates. They found that particles larger than 50Å (0.05µm) were incoherent. The authors could not determine the coherency, or otherwise, of smaller particles, but state that they are probably coherent. A mean particle size, in a simple Fe-Cu system, of 50Å is observed after approximately 5-10 hours aging²⁹. Thus, due to the relatively short tempering/aging times, the strengthening due to precipitation in a commercial alloy is probably due to a large number of small, mainly coherent particles. This, however, does not allow for the effect on precipitation of other elements found in commercial alloys, eg molybdenum.

The second part of the work by Goodman, Brenner and Low³⁰ describes atom probe analysis of the precipitate particles. The size of particles for which it is energetically favourable to transform from body centred cubic to face centred cubic (and thus lose coherency) was determined theoretically to be 40Å. This value compares well with the 50Å determined in the first

part of this work. The question that remains unanswered is how the coherency is affected by the morphology of the martensitic microstructure. It is possible that the particles lose coherency much sooner (ie when the particle size is smaller) in a martensitic alloy. Goodman *et al*³⁰ found that the composition of the precipitates in the early stage of precipitation is approximately 50% copper.

This composition remains reasonably constant to the peak strength and then the copper content increases to nearly 100% in the over aged condition, when the particle size is greater than 100Å.

Mechanical Properties of Copper Containing Steels

Much of the work devoted to the development of commercially exploitable, copper precipitation hardening steels has had its primary emphasis on the steels in the 'as rolled' condition. However, when quoted, properties of the same steels in the quenched and tempered condition^{31,32,33,34,35,36,37,38,23} are markedly superior indicating that these types of steels are ideally suited to production by the quenched and tempered route.

Krishnadev and Le May³¹ reported the mechanical properties and microstructure of a low carbon, copper-bearing steel containing 0.05% C, 2.14% Cu and 1.45% Ni. The mechanical properties observed when quenched in water and then aged to give maximum hardness are a yield strength of 894 MPa and a tensile strength of 938 MPa. They found that the time to reach peak hardness during tempering decreased with increasing temperature from greater than ten hours at 425 °C to less than six minutes at 700° C. This agrees well with work by Youle and Ralph³⁸, previously discussed and indicates that low C and Ni in copper steels do not significantly affect the precipitation kinetics. Although ten hours tempering time is not viable commercially, for an aim of 690 MPa yield strength, maximum strength may not need to be developed. Krishnadev and Le May also observed, what they termed 'a loss of work hardening capacity' of the steel occurring after tempering.

This manifested itself as a greater increase in yield strength than tensile strength and thus the ratio of yield to tensile strength increased from approximately 0.8 for the as quenched material to 0.9 to 0.97 for the tempered material. The results of electron microscope work presented by Krishnadev and Le May indicated that at maximum strength few precipitates were visible and thus they concluded that the major strengthening effect arose from small clusters of copper atoms not visible with the electron microscope. Over aging produced many more visible precipitates and as tempering proceeded the inter-particle spacing increased and the strength decreased, supporting

the behaviour described by the formulae presented earlier²⁵.

Abe, Kurihara, Tagawa and Tsukada³² examined aspects of thermo-mechanical processing and accelerated cooling on A.S.T.M. A710 type steels with compositions based on 0.004-0.06%C, 0-0.84% Ni and <0.01-2.83%Cu. They also reported a larger increase in yield strength compared with tensile strength. One of the conclusions of this work was that rapid cooling retarded the precipitation of copper and enhanced the precipitation hardening effect. This was attributed to the propensity of rapid cooling to promote fine, dispersed precipitation. It was also concluded from this study that copper retards the recrystallisation of austenite during hot working. This was attributed to solute drag. Maximum precipitation strengthening was observed to occur at 500-550°C. Mechanical property results presented in this paper for an A710 composition (0.03%C, 0.44%Mn, 1.17%Cu, 0.84%Ni, 0.65%Cr, 0.18%Mo, 0.013%Nb) show a maximum yield strength of 490 MPa and a tensile strength of 640 MPa with a ratio of 0.76 when as rolled and aged at 550°C. In the rolled, quenched and aged condition, a yield strength of approximately 660 MPa and tensile strength of 750 MPa were observed after tempering at 550°C. The yield strength/tensile strength ratio is 0.88.

Controlled rolling, quenching and tempering have quite a dramatic effect, increasing yield and tensile strengths to 760 and 820 MPa respectively with a ratio of 0.92³². The microstructures presented indicate that a finer grain size is developed via controlled rolling and quenching when compared with hot rolling and quenching. Hence, the increase in strength.

Snape³³ reported the mechanical properties of a copper precipitation hardening steel containing niobium (0.05% C, 0.48% Mn, 0.85% Ni, 1.10% Cu 0.025% Nb). The main thrust of this work was to study the effects of warm working on mechanical properties, but some quenched and tempered results are given.

Snape quotes the values of yield strength and tensile strength after quenching and

tempering for 1 hour at 565°C as 650 MPa and 714 MPa respectively. Calculation of the ratio between yield and tensile strength gives the value of 0.91

Krishnadev, Sojka, Le May, Schetky and Banerji³⁴ examined the effect of adding boron to copper precipitation hardening steels. They studied the effect of hot rolling and controlled rolling on steels of various alloy types. The alloys closest to those used in this study have the following general characteristics: 0.039-0.047% C, 1.3-1.5% Mn, 1.79-1.84% Cu, 0-1.04% Ni and 2-9 ppm B. The reported mechanical properties of the hot rolled, quenched and tempered (600 °C, 1hr) steel are 755 MPa yield strength and 784 MPa tensile strength with a ratio of 0.96. Mechanical properties for controlled rolled material are 576 MPa yield strength and 627 MPa Tensile strength. The ratio for the controlled rolled material is 0.92. No as-quenched data was reported to evaluate the effect of tempering on the ratio.

Krishnadev and Galbois³⁵ reported the development of a copper precipitation hardening steel with significant amounts of niobium also added. The steel composition most similar to those used in this study is 0.03% C, 1.78% Mn, 0.1% Nb, 1.57% Ni, 1.86% Cu, 0.3% Mo.

The strengths reported for this steel, after quenching and ageing for 15 min. at 550°C, are 960 MPa yield strength and 999 MPa tensile strength. The ratio of yield to tensile strength is 0.96. These results are for a steel that has been hot rolled with a final rolling temperature of 925°C. Warm working produces a dramatic improvement in strength. The same steel produced with a finish rolling temperature of 650°C displays a yield strength of 1022 MPa and a tensile strength of 1042 MPa. The yield/tensile strength ratio of 0.98 is very unfavourable. The properties developed by this steel upon hot rolling and air cooling are 829 MPa yield strength and 868 MPa tensile strength. These results demonstrate the extent to which quenching to retain copper in solution aids the strengthening effect.

Krishnadev³⁶ has reported mechanical properties for a Cu-Ni-Nb steel (0.020% C, 1.94%

Mn, 1.90% Cu, 1.56% Ni, 0.115% Nb, 0.26% Si) and a Cu-Ti-B steel (0.04% C, 1.52% Mn, 1.8% Cu, 0.25% Si, 0.0009% B, 0.04% Ti, 0.02% Al). The Cu-Ni-Nb alloy displayed a yield strength of 760 MPa and a tensile strength of 795 MPa with a yield to tensile ratio of 0.95. Results presented for the same steel but with a finish rolling temperature of 677°C instead of 843°C displayed an increase in yield and tensile strength to 793 and 819 MPa, respectively. The ratio also increased to 0.97. Room temperature Charpy impact data presented showed this steel to have excellent fracture toughness with an upper shelf energy of 285 J. The copper, titanium, boron steel examined had a yield strength of 755 MPa and a tensile strength of 784 MPa. The ratio was 0.96 and the room temperature impact energy is 118 J.

Krishnadev³⁶ stated that in addition to the strength increase observed with copper precipitation another advantage is that the precipitates stabilise the martensite laths and slow softening during tempering/aging.

All these results indicate that there is a dearth of information concerning the effect on quenched and tempered steels, of copper levels less than 1% and also that a steel with low carbon and substantially less copper than that used by previous authors, has a very good chance of meeting a 690 MPa minimum yield strength target.

Microstructure of Copper Containing Steels

Krishnadev and LeMay³¹ reported the results of microstructural investigations of a steel containing 0.05% C, 0.43%Mn, 1.45% Ni and 2.14% Cu. They report as-quenched microstructures as "massive grains and well defined acicular regions" with a few equiaxed subgrains of ferrite. Transmission electron microscopy indicated that the acicular regions were parallel packets of high dislocation density laths, separated by low angle grain boundaries and the massive regions were also seen to consist of laths. No cooling rate was reported in this work.

On tempering, this structure was found to be very stable with the lath structure still persisting after aging for long times at 700°C. Krishnadev and LeMay do not quantify what they mean by long times, but mention that the structure "recrystallised" after one month at 750°C with precipitates visible via optical microscopy. The stability of the lath structure was attributed to copper precipitates retarding grain boundary migration.

Ohmori, Ohtani and Kunitake³⁹ studied the formation of bainite in steels containing 0.12-0.22% C, 0.3-0.24 % Si, 0.85% Mn, 0.5% Mo, 1% Ni and 0.3% Cu using continuous cooling dilatometry and isothermal techniques. Fast cooling (300°C/sec) produced lath martensite. Slower cooling (1°C/sec) produced "bainitic ferrites" with "low temperature decomposition products between them". Isothermal transformation allowed characterisation of three types of bainite (BI, BII and BIII) by morphology and transformation temperature. All three types have the same habit plane $\langle 111 \rangle_a \{ 110 \}_a$ and for this reason Ohmori and co-workers classify them upper bainite.

Thompson, Colvin and Krauss⁴⁰ studied the continuous cooling behaviour of a steel containing 0.06% C, 1.45% Mn, 0.97% Ni, 0.72% Cr, 0.42% Mo, and 1.25% Cu, a modification of ASTM A710. Their results indicate that cooling rates of around 150°C/sec are required to form 100% martensite. Martensite and AF (acicular ferrite) and GF (granular ferrite) (authors terminology), commonly referred to as bainite, are formed at cooling rates between 150°C/sec and

3°C/sec. Acicular ferrite apparently consists of 1µm thick lath like crystals and granular ferrite is 1µm equiaxed crystals.

Varughese and Howell⁴¹ examined the tempering behaviour of HSLA 100 steel, a version of ASTM A710. The composition of key elements in this steel was 0.04% C, 0.82% Mn, 1.59% Cu, 3.45% Ni, 0.58% Cr, 0.51% Mo. Microstructures observed ranged from 100% lath martensite with interlath retained austenite in the water quenched material to tempered martensite in the aged samples. Aging was carried out at 605°C for 1 and 3 hours. The authors noted that the hardness in the specimens aged at both 1 and 3 hours showed little difference.

Fonda, Spanos and Vandermeer⁴² describe the observation of isolated plates (as opposed to laths) of martensite in HSLA 100 (ASTM A710) containing 0.07% C, 1.61% Cu, 3.49% Ni, 0.8% Mn, 0.58% Mo, 0.57% Cr and 0.37% Si. The steel studied was subjected to a weld thermal cycle simulation and the plate morphology was reproduced in samples quenched in iced brine.

The effect of other elements on the precipitation of Copper

Molybdenum

Krishnadev and Galbois³⁵ have claimed that there is a synergistic effect between copper and molybdenum. "Molybdenum, in addition to delaying the transformation [austenite-ferrite], intensifies the strengthening response of copper." This intensification of the strengthening response is probably due to molybdenum reducing the solid solubility of copper in the ferrite/martensite matrix. The steels that they studied contained 0.3% Mo and approximately 10% improvement in yield strength was observed over similar steels with no molybdenum.

Wilson, cited by Krishnadev and Galbois,³⁵ postulated that segregation of copper to grain boundaries in copper containing maraging steels caused fracture toughness problems. He put forward the idea that addition of molybdenum and niobium might prevent the segregation from occurring. In the study done by Krishnadev and Galbois they concluded that the uniform dispersion of precipitates observed and the acceptable fracture toughness measured, supported Wilson's idea.

Niobium

Krishnadev and Galbois³⁵ concluded from their investigation into steels strengthened by copper and niobium, that the single peak observed in the tempering curves derived for these steels indicates that "strengthening due to niobium is additive to that of copper". From the results presented in this study there is roughly a 4% increase in yield strength with a 0.1% increase in niobium content, from 0.1% Nb to 0.23% Nb.

Boron

Boron is a well known hardenability promoting agent. Krishnadev *et al*³⁴ cite Irvine and co-workers and Pickering as explaining this effect of boron additions as due to retardation of the austenite-ferrite transformation. The same workers proposed that boron has a synergistic effect with molybdenum on transformation dynamics and work by Sojka, Krishnadev and Banerji cited by Krishnadev and co-workers³⁴ suggests that a synergistic effect exists between copper and boron.

Comparison of results presented in reference 6 for steels essentially identical, except for boron content, show a distinct increase in mechanical properties with increasing boron composition, which reaches a plateau at a composition less than, or equal to, 9 ppm (0.0009%) boron. The authors conclude "The strengthening obtained is greater than the sum of the individual strengthening effects from copper and boron".

Krishnadev³⁶ has presented data which shows that copper and boron display a synergism in reducing the A_r temperature range. He points out that the extent to which A_r is depressed in a relatively lean steel is similar to that of more highly alloyed steels.

Problems Associated with Copper Containing steels

Hot Shortness

Hot shortness is a term used to describe cracking or brittleness observed during hot deformation of some steels⁴³. It is thought to be caused by a low melting temperature ϵ -copper phase forming at grain boundaries adjacent to the steel surface. The formation of this phase is due to preferential oxidation of iron at high temperatures, for example during re-heat prior to rolling. Subsequent deformation of the steel leads to surface cracking.

A definition of hot shortness as "brittleness in the hot forging range" is given by Habraken and Lecomte-Beckers⁴⁴. They describe hot shortness as a phenomenon that occurs during hot forging in steels that contain low melting point elements, especially copper. These authors indicate that defects associated with hot shortness (scabs, flakes or slivers) start as small surface cracks in a slab. The cracks are generally at right angles to the surface and upon rolling, rotate until parallel, forming the previously mentioned surface defects.

The occurrence of hot shortness (also described as surface hot shortness) is influenced by residual elements, more soluble in copper than iron, such as tin, antimony and arsenic⁴⁴. Nickel forms complete solutions with copper and nickel also has a high solubility in austenite⁴⁴, thus it has a beneficial effect on hot shortness presumably by increasing the melting point of the copper rich phases involved with the hot short cracking and/or increasing the solubility of the copper phase in austenite.

The effect of elements such as manganese, chromium, antimony and arsenic on hot shortness has also been studied. It has been observed from studies of mild steel-copper-manganese alloys, that manganese has a small effect on hot shortness and seems to cause a minor reduction in the solubility of copper in austenite⁴⁴.

From investigations of mild steel copper-chromium alloys, it has been concluded that

chromium has a small effect on hot shortness and also reduces the solubility of copper in austenite to a minor degree⁴⁴.

Mild steel copper-antimony and mild steel copper-arsenic alloys have been studied and it was found that both antimony and arsenic accentuate hot shortness. Antimony reduces the solubility of copper in austenite (allowing the build up at surfaces and grain boundaries) and arsenic also lowers the solubility of copper in austenite as well as reducing the melting point of the copper phase⁴⁴.

Furnace atmospheres also have an effect on hot shortness. Habraken and Lecomte-Beckers⁴⁴ cite a study by Nicholson and Murray which examined the effect of some common constituents of furnace atmospheres, namely oxygen, water vapour and sulphur dioxide. They found that at 1000°C the incidence of hot shortness increased with oxygen content until about 4% oxygen is reached and then became relatively constant as oxygen content increased. At 1250°C a peak in crack severity occurred after which crack severity decreased with increasing oxygen content. The oxygen content associated with this peak occurs varied with the proportion of other elements in the gas stream, such as nitrogen. Water content of the furnace atmosphere also increased cracking severity. At 1250°C cracking severity roughly doubled with a doubling of the water content.

According to Habraken and Lecomte-Beckers⁴⁴ sulphur dioxide, on the other hand, reduced the incidence of hot shortness provided the oxygen content of the furnace atmosphere was kept low. The suggested reason for this is that between 600 and 1300 °C sulphur has a greater affinity for copper than iron. The copper and sulphur react at the surface to form copper sulphate which is then taken up into the scale, thus preventing the build up of copper rich phases at the surface.

Kohsaka and Ouchi⁴⁵ studied hot shortness of copper containing H.S.L.A. steels. The

compositions that they concentrated on were very similar in range to those examined in this study (0.1%C, 0.25%Si, 1.0%Mn, 0.025% Nb, up to 0.84%Cu and up to 0.41% Ni). Hot shortness was assessed via a hot bending test using a deformation rate of 100mm/min.

Results from this study indicate that both severity of cracking and crack depth reached a maximum at copper levels between 0.6 and 0.8 % when a reheating temperature of 1250°C and bending temperatures of 1000 and 1150°C were used. An important conclusion reached from this work is that a Ni/Cu proportion of 0.5 (ie %Ni = 0.5 %Cu) will reduce cracking severity to zero.

Cox and Winn⁴⁶ examined the scaling behaviour of a 1.8% Cu, 1.7% Si, 1.03% Mn, 0.8% Mo steel when compared with 2.2% and 2.9% plain Cu steels, all containing only trace amounts of Ni. They found that the presence of silicon and molybdenum changed the scaling behaviour such that the copper present in the scale was mixed with iron and molybdenum rather than as lenses of low melting point ϵ -copper (5% Fe/Cu), as found in the plain copper steel.

It appears that silicon and molybdenum aid in the prevention of hot shortness. However, from the results of Kohsaka and Ouchi⁴⁵ who had 0.2-0.3% silicon in all their steels and still observed considerable hot shortness with no nickel present, it would appear that a minimum effective level of silicon exists somewhere between that used by Cox and Winn⁴⁶ (1.7%) and the 0.2% used by Kohsaka and Ouchi⁴⁵. The implication is that unless a relatively high level of silicon is used for protection against hot shortness then the Ni/Cu ratio must be a minimum of 0.5.

Literature used to develop the Steel Design Model.

Commercial development of new steels is an expensive and time consuming business. Part of this cost is in experimental alloys. In order to reduce this cost, the ability to examine prospective alloys and discard poor candidates quickly, easily and cheaply is an attractive proposition. A computer programme that predicts some basic properties is an obvious way to do this and would thus be a useful tool. As part of this development project a computer model was created to predict mechanical properties, a variety of physical properties and welding parameters. A survey of literature was undertaken and a series of mathematical models were found which enabled prediction of these properties. Empirical and theoretical models were used and where appropriate, are noted in the printout generated by the programme. Following are the sources of information used in the development of the steel design model.

The Bisalloy Technical Manual¹² gives the following form of the IIW formula for carbon equivalent (CEQ IIW):

$$C + \frac{Mn}{6} + \frac{Cr+Mo+V}{5} + \frac{Ni+Cu}{15}$$

This formula stems from an International Institute for Welding (IIW) report by IIW Commission IX in 1967⁴⁷

Lin⁴⁸ cites a formula for a carbon equivalent which she calls CEQ (HSLA) apparently more suited to HSLA steels than the IIW formula.

$$C + \frac{Mn}{16} - \frac{Ni}{50} + \frac{Cr}{23} + \frac{Mo}{7} + \frac{Nb}{5} + \frac{V}{9}$$

Other weldability indices that are calculated are the JISI carbon equivalent

$$C + \frac{Mn}{6} + \frac{Ni}{40} + \frac{Si}{24} + \frac{Cr}{5} + \frac{Mo}{4} + \frac{V}{14}$$

and the Ito, Bessyo Pcm⁴⁹

$$C + \frac{Si}{30} + \frac{Mn}{20} + \frac{Cu}{20} + \frac{Ni}{60} + \frac{Cr}{20} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

Yurioka, Oshita and Tamehiro⁵¹ have developed a formula that combines both the IIW carbon equivalent and the Ito-Bessyo Pcm. This formula is apparently suitable⁵⁰ for H.S.L.A. steels and C-Mn alloys and takes into account a wider variety of elements than the other two formulae.

$$CEN(\%) = C + A \left(\frac{Si}{24} + \frac{Mn}{6} + \frac{Cu}{15} + \frac{Ni}{20} + \frac{Cr + Mo + V + Nb}{5} + 5B \right)$$

where

$$A = 0.75 + 0.25 \tanh(20(C - 0.12))$$

Cottrell⁵⁰ has described the derivation of a formula for predicting the heat affected zone hardness of a weld. The implementation of this formula in the programme is for steel with no preheat ie. at 20°C

$$HE=80+800(C+3N+0.29)e^{-(0.25r^{1.5(C+\frac{Mn}{6}+\frac{Cr}{5}+\frac{Mo}{5}+\frac{V}{5}+\frac{Nb}{4C}+\frac{0.0001}{S}+\frac{Ni^2}{Mn})^{-1}}}$$

Data presented by Cottrell⁵⁰ show the value of the CEQ (IIW) at which cracking does not occur(regardless of cooling rate) to be approximately 0.39. Thus "good weldability" will be exhibited by an alloy whose CEQ IIW value is ≤ 0.39.

Since galvanising is often a step in steel fabrication the effect of Si on the coating was taken into account. Notowidjojo⁵² has presented information on silicon and its effect on galvanising alloy growth. A range of silicon content exists, termed the Sandelin range, which promotes rapid growth in the thickness of the zinc layer deposited during galvanising. At the low end of the silicon range the galvanising coating thickness is described in the following way:

$$\text{For the alloy growth to be excessive } Si+2.5(P)>0.09$$

Alloy growth also becomes excessive when the silicon content is higher than 0.3%.

Normalised hardness of a steel can be approximated using the following formula⁵⁶ :

$$NH=42+223(C)-53(Si)+30(Mo)+12.6(Ni)-7(Cr)+19(Mo)+2(10-19(Si)-4(Ni)+8(Cr)+130(V))$$

Reed Hill in his book 'Physical Metallurgy Principles'⁵⁴ provides data in the form of a graph of carbon content and martensite hardness. Data from this graph, and a Mackintosh computer

package called Kaleidograph were used to derive a polynomial to estimate the hardness as a function of carbon content (assuming 100% martensite formation on quenching). This graph provides estimations of as quenched hardness in Vickers diamond pyramid numbers. Wilson conversion charts⁵⁵ were used to convert hardness between Brinell, Vickers and Rockwell. Information was taken from these charts and the same technique described previously to develop polynomials was used to describe the relationship between hardness scales in order that the hardness may be reported in both Vickers and Brinell. All hardness conversions needed throughout the programme were then performed using these polynomials. Once the as quenched hardness is determined, based purely on carbon content, a proportion of hardness can be added as the contribution due to other elements⁵⁶.

Tempered hardness can be calculated from work by Holloman and Jaffe as cited by Semiatin and Stutz⁵⁷. It was demonstrated that both time and temperature can be included in one parameter to model the tempering behaviour of steels.

The parameter that Holloman and Jaffe used has the form:-

$$H = T(C + \log(t))$$

Where:-

H is the Holloman and Jaffe parameter.

T is the temperature in K

C is a material constant

t is the time in hours

Re-arranging, the Holloman and Jaffe relationship can be written as follows;

$$\log 1/t = -H(1/T) + C \quad (y = m(x) + b)$$

It will be seen that if tempering data for a particular steel is plotted on a graph using a semi-log scale ($\log(1/t)$ vs $1/T$) the slope of the line produced will be $-H$ and the point of intercept on the y-axis will be C . Once C is determined then a graph of Hardness Vs H can be produced and from this, a relationship between H and Hardness and thus Hardness and Time and Temperature, can be found.

The steels used in previous studies seem to have been predominantly in the carbon range 0.3-0.4%. In the present work, tempering tests were repeated with a steel with a carbon content of approximately 0.16%.

The constant in the Holloman and Jaffe tempering parameter, C was determined as 16.53 and the relationship between tempered Hardness and H was determined to be :-

$$\text{Hardness} = -0.041 H + 831.21$$

and

$$H = T(16.53 + \ln(t))$$

From this hardness, estimates of yield and tensile strength can be made. The first estimate of yield strength is theoretical and is based on what Ashby and Jones⁵⁸ designate the "true hardness". The theoretical estimate of tensile strength is based on information presented by Dieter⁵⁹. Both these estimates will be slightly inaccurate due to varying degrees of strain hardening occurring in the range of materials likely to be examined.

Empirical data presented in the ASM Metals Handbook⁶⁰ was used to provide alternative estimates of both yield and tensile strength. This information is in the form of graphs of the

relationship between tensile strength and hardness and the relationship between tensile strength and yield strength, for quenched and tempered steels. Because these second estimates are based on empirical data, presumably from a large sample size, strain hardening and other considerations are taken into account and thus these estimates are likely to be more reliable.

The Ac_3 and Ac_1 transformation temperatures⁵³ are calculated and displayed on the printout.

$$Ac_3 = 910 - 203\sqrt{C} - 15.2Ni + 44.7Si + 104V + 31.5Mo + 13.1W$$

$$Ac_1 = 723 - 10.7Mn - 16.9Ni + 29.1Si + 16.9Cr + 290As + 6.38W$$

The programme also estimates the start of the martensite transformation (M_s) temperature⁶¹.

$$M_s = 539 - 423C - 30.4Mn - 17.77Ni - 12.1Cr - 7.5Mo$$

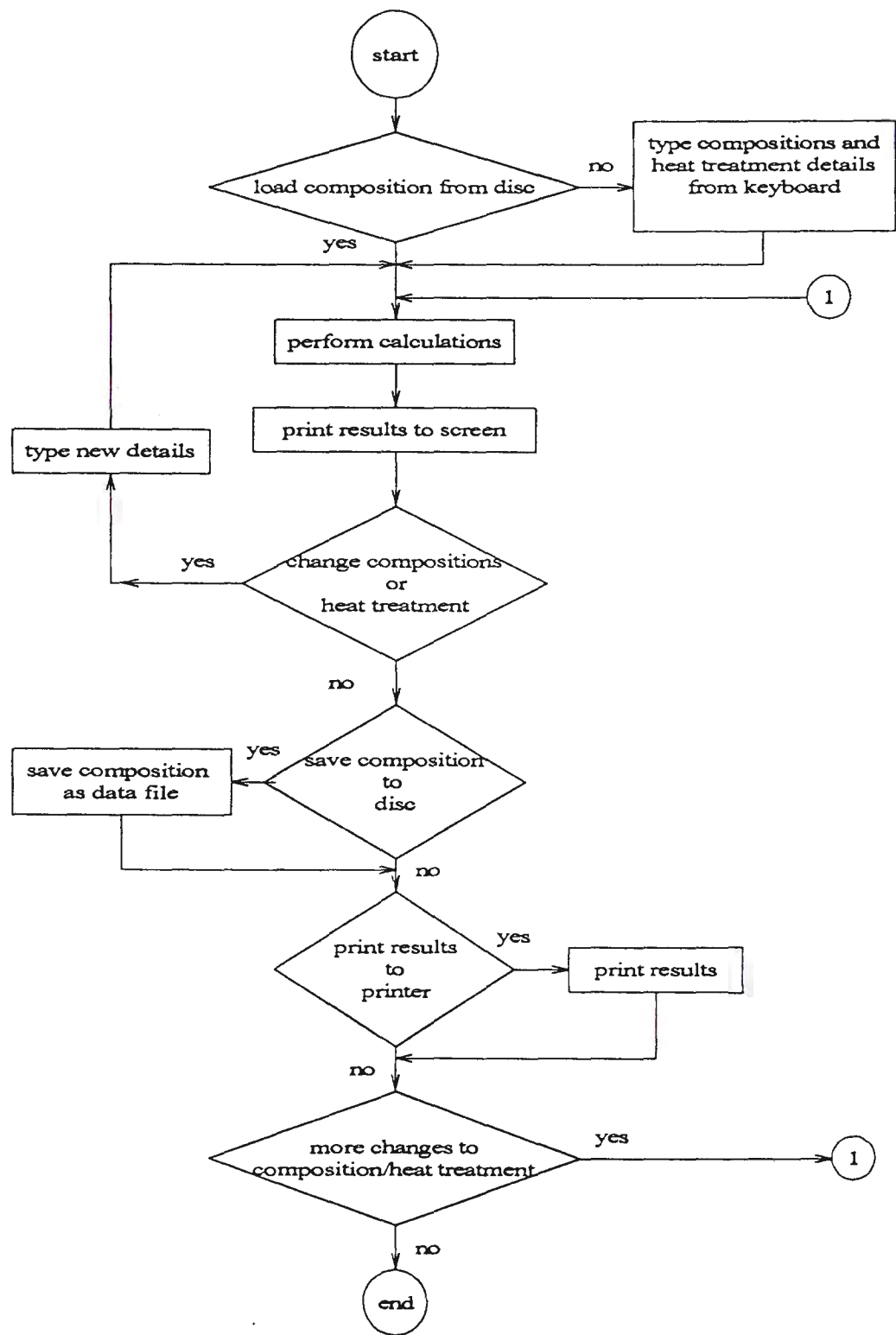
Material presented by Croll⁶² on the cooling rate possible in a roller quench system was used in conjunction with the calculated critical cooling rate for 100% martensite formation⁵⁶ to estimate the maximum thickness that can be fully through hardened.

Empirical hardenability data published by Republic Steel Corp⁶³ allows the Ideal Critical Diameter to be calculated using the alloy chemistry. This Ideal Critical Diameter can be converted to the Jominy distance, using a conversion factor given⁶³ and the theoretical thickness of plate, capable of being through hardened, is then twice the Jominy distance (assuming a complete

quench).

The hardenability information gained through the above calculations allows evaluation of candidate steels in terms of the Jominy distance and also gives an idea of how they might perform in a practical sense when processed as plate through a roller quench system

Flow Chart for the Steel Design Programme



CHAPTER 3

Material Design and Materials Used

Steel Design Concepts

The effect of the major alloying elements must be considered as one of the first steps in alloy development. The following considerations and constraints were taken into account when designing the alloys for investigation.

Carbon

It was considered essential that the carbon proportion be low enough to bestow advantages of increased weldability, when compared with existing Bisalloy alloys and yet not incur production cost penalties from the supplier, B.H.P. Slab and Plate Products Division (S.P.P.D.) Discussions with B.H.P. marketing personnel⁴ indicated that a composition of 0.08% was the lowest practicable carbon level that would not incur any additional cost. This cost increase stems from the additional time required in the steel making vessel to reduce the carbon content below about 0.08%.

Manganese

Manganese is added to heat treatable steels as a hardenability promoter and in non heat treated steels is a solid solution strengthener⁶⁴. It is also a carbide former⁶⁵. Therefore, 1.5% manganese was added to the first alloys as it was thought necessary to ensure that strength levels would be met with such a low carbon level. The manganese content was reduced to 1.2% after the mechanical properties of the first set of alloys were evaluated.

Silicon

Silicon is added to steels, in general, as a deoxidiser. It has a mild positive effect on hardenability and a significant solid solution strengthening effect⁶⁵. Its function in the alloys used in this study is also to provide some additional protection against hot shortness, in conjunction with nickel.

Chromium

Chromium is used to promote hardenability and thus increase through hardening in thick plate sections. Reference 66 places the effect of chromium on hardenability just behind that of manganese and similar to molybdenum. Evaluation of early Charpy impact results indicated that chromium was causing embrittlement for tempering temperatures between 300-400 degrees C. For this reason chromium was not added to later heats.

Molybdenum

Molybdenum has a strong effect on the hardenability of heat treated steel. Its effect is held to be stronger than that of chromium⁶⁵. Molybdenum is also added because it suppresses temper embrittlement. As discussed previously, molybdenum has a synergistic effect on the precipitation of copper. Previous authors reported the use of 0.15-0.3% Mo.^{35,23,67} All of these alloys contained more than 1% copper and so a level of 0.25 % molybdenum was chosen for this work.

Niobium

Niobium acts in conjunction with carbon as a grain refiner⁶⁸ through the formation of niobium carbo-nitrides. A standard level of 0.02% was added to the alloys examined.

Titanium

Titanium is added to steels as a deoxidiser and as protection for boron by reacting with residual nitrogen. A conventional proportion of 0.015% was used in the steels investigated.

Nickel

As mentioned above, nickel is added to copper containing steels mainly to provide protection against hot shortness. The level added to the steels used in this study was between 0.2 and 0.3%. This level was decided upon due to constraints determined by B.H.P. S.P.P.D. Pty. Ltd., the eventual producer of these steels. The constraint placed on the nickel content is that it should be a minimum of approximately half that of the copper content. This condition is supported by results quoted by Kohsaka and Ouchi⁴⁵ mentioned previously.

Boron

Boron has a very strong positive effect on the hardenability of steel. Typical alloy additions are of the order of 0.0005 to 0.0025 wt%. The effect of adding boron is to delay the austenite to ferrite transformation, allowing acicular or lath microstructures to form at comparatively slower cooling rates. One effect of delaying the austenite-ferrite transformation is to increase the solubility of elements more soluble in austenite than ferrite, retarding precipitation and allowing supersaturated solutions to form more easily³⁷. If not tied up with titanium or aluminium, boron can also react with residual nitrogen to form boron nitride and/or complex carbo-nitrides. The aim boron content for this work was 0.0006%.

Copper

Copper is added to steels for various reasons. In weathering steels and steels for sour gas pipelines, copper is added in proportions around 0.1-0.3% as an element to reduce corrosion⁶⁹. It has been reported ^{38,26} that copper contents above approximately 0.6% cause precipitation hardening to occur. Many studies have concentrated on copper levels above 1%. ^{31,33,34,35,36,37,38,23} This study examined steels ranging in copper composition from 0-1%.

Aluminium

Aluminium is used in steels as a deoxidiser and to protect boron by combining with nitrogen. The aim for this study was 0.025%

Materials

The following is a table of compositions of the alloys used in this work.

Table 3.1. Alloys Studied In This Work

Series 1 (B-Cu Steels)		Identification			
	ID code	3588	3589	3590	3591
Elt	Composition (Weight %)				
C		0.09	0.09	0.09	0.09
P		0.018	0.017	0.017	0.015
Mn		1.53	1.53	1.52	1.49
Si		0.42	0.41	0.41	0.40
S		0.003	0.003	0.003	0.003
Ni		0.31	0.21	0.2	0.2
Cr		0.003	0.003	0.003	0.59
Mo		0.27	0.27	0.26	0.26
Cu		1.0	0.77	0.58	0.76
Al(tot)		0.036	0.039	0.037	0.035
Al(sol)		0.035	0.038	0.036	0.032
Ti		0.017	0.018	0.018	0.017
B(tot)		0.0021	0.0013	0.0011	0.0015
B(sol)		0.0007	0.0011	0.0008	0.0009
V		<0.003	<0.003	<0.003	<0.003
Nb		0.022	0.021	0.020	0.022
N		0.0016	0.0013	0.0016	0.0018

Table 3.1 Continued

Series 2 (B-free, Cu Steels)		Identification			
	ID code	3677	3678	3679	3680
Elt	Composition (Weight %)				
C		0.085	0.075	0.044	0.050
P		0.012	0.012	0.013	0.012
Mn		1.58	1.00	1.48	1.48
Si		0.42	0.42	0.42	0.41
S		0.004	0.003	0.004	0.004
Ni		0.020	0.20	0.20	0.20
Cr		0.008	0.005	0.007	0.007
Mo		0.25	0.26	0.25	0.26
Cu		0.38	0.81	0.81	0.38
Al(tot)		0.022	0.024	0.021	0.020
Al(sol)		0.019	0.021	0.018	0.017
Sn		<0.002	<0.002	<0.002	<0.002
Nb		0.021	0.022	0.022	0.022
Ti		0.020	0.017	0.019	0.016
V		<0.003	<0.003	<0.003	<0.003
B(tot)		<0.0003	0.0004	0.0004	<0.0003
B(sol)		<0.0003	<0.0004	<0.0004	<0.0003
N		0.0016	0.0019	0.0017	0.0019

Table 3.1 Continued

Series 3 (B containing, low Cu and B containing, lower Mn Steels)

	Identification	
	MRL code	
	3720	3721
Elt	Composition (Weight %)	
C	0.085	0.080
P	0.019	0.016
Mn	1.5	1.29
Si	0.41	0.41
S	0.004	0.004
Ni	0.17	0.23
Cr	0.007	0.006
Mo	0.21	0.24
Cu	0.003	0.45
Al(tot)	0.033	0.026
Al(sol)	0.030	0.023
Ti	0.014	0.023
B(tot)	0.0012	0.0022
B(sol)	0.0007	0.0015
V	<0.003	<0.003
Nb	0.019	0.021
N	0.0115	0.0078

Table 3.1 Continued

Miscellaneous

Identification				
Bis code	Bis 52	3433	Bis 21	Bis 2
Elt	Composition (Weight %)			
C	0.16	0.08	0.26	0.185
P	0.017	0.004	0.014	0.018
Mn	1.12	1.94	0.52	1.09
Si	0.26	0.27	0.21	0.22
S	0.008	0.003	0.003	0.004
Ni	0.021	0.007	0.026	0.028
Cr	0.016	0.66	0.92	0.79
Mo	0.18	0.21	0.19	0.004
Cu	0.008	1.25	0.01	0.009
Al(tot)	0.028	0.003	0.048	0.039
Al(sol)	0.023	not deter.	not deter.	not deter.
Ti	0.004	0.028	0.023	0.020
B(tot)	0.0007	0.0019	0.0012	0.0012
B(sol)	0.0008	not deter.	not deter.	not deter.
V	0.003	0.003	0.009	0.005
Nb	0.003	0.005	0.003	not deter
N	0.0048	not deter.	not deter.	not deter.

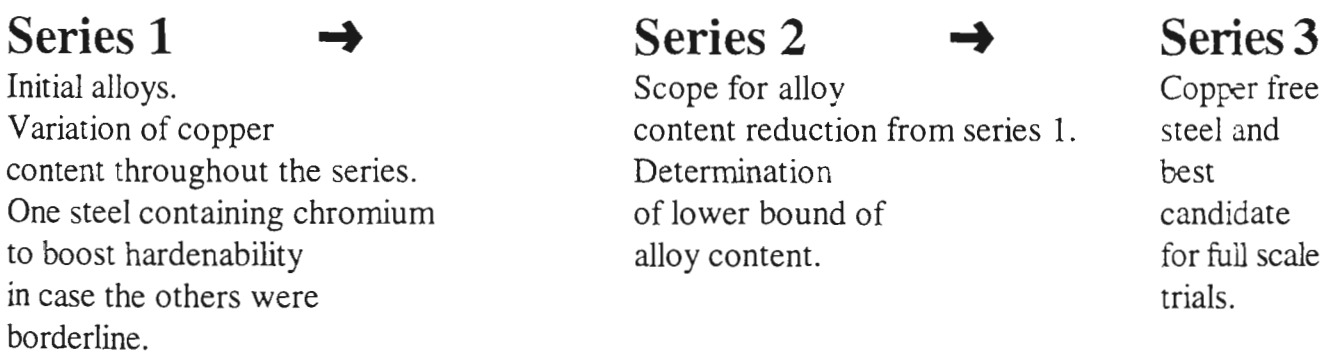
Rationale Behind the Compositions of the Series of Steels Used in this Study

Series 1 comprised a set of alloys whose design was based in information from surveyed literature. It was initially thought that these would span a range of copper contents with the least alloyed failing to achieve the desired mechanical properties thus determining the lower bound of copper content. From this series, one, possibly two of the best candidates would be selected for further development. It was found, with some surprise that all these steels could be made to reach required strength levels and that there was scope for considerable reductions in alloy content.

A second series of steels, Series 2, was designed examining the possibilities of reducing carbon, manganese and copper. The lack of boron in these steels was entirely un-intentional and occurred due to mis-communicaton with the supplier of the test heats.

Based on the results of this investigation the steels of Series 3 were formulated 3720 to provide a baseline 0% copper steel to compare with the other steels, and 3721 as a promising candidate steel that could be tried in full scale production.

The following timeline illustrates the order of development of the series.



CHAPTER 4

Experimental Procedures

Manufacture of Test Heats

Manufacture of test heats was carried out by B.H.P. Research, Melbourne Laboratories using a vacuum furnace capable of producing approximately 70kg of steel to exacting chemical specifications. The test heat was cast into billet form and then rolled using an Hereaus servo controlled rolling mill. The following is a typical rolling schedule for test heats⁷⁰. All test heats used in this study were rolled to 20mm thickness.

- Start at 1200°C
- 15 passes from 130mm thickness to 19.5mm
- Reduction/pass no greater than 10mm
- Air cooled from F.R.T.
- F.R.T. not recorded but generally not below 900°C

Chemical Analysis

Chemical analysis was supplied by B.H.P. Research with the test heats on delivery. Check chemical analysis was carried out by B.H.P. S.P.P.D. In the few instances where the two analyses differed, the S.P.P.D. check analysis was taken to be correct for the following reasons :

1. S.P.P.D. have N.A.T.A. registration for chemical analysis and analyses are issued under a N.A.T.A. seal, whereas B.H.P. Research supply only a typed or hand written note stating chemical composition with no indication as to how the analysis was carried out.

2. S.P.P.D. perform a vast number of analyses and are more experienced in the techniques required to analyse elements like soluble (effective) boron⁷¹. In most cases the S.P.P.D. analysis and the B.H.P. Research analysis did not differ significantly.

Heat Treatment

Heat treatment was carried out in an electrically heated laboratory muffle furnace fitted with a Eurotherm furnace controller. The temperature of the samples was monitored using a MIMS (Mineral Insulated Metal Sheath) thermocouple connected to a digital multimeter. In general, it was found that the temperature of the samples was approximately 5 degrees lower than the temperature indicated by the controller as the feedback thermocouple was positioned halfway up the furnace wall. Thus, if a tempering temperature of say, 500°C was desired then the controller set point was set at 505°C and the temperature of the samples was monitored with the multimeter, to ensure that the temperature of the samples remained within 5°C of the target temperature.

Austenitisation heat treatment for all samples was carried out in air on the basis of 1 hour/inch(25mm) of thickness with a minimum residence time of 20 minutes. Thus the time was adjusted for the thickness of material. Austenitisation temperatures were 925°C +/- 5°C. The temperature was monitored as described above. Samples were quenched in 200 litres of violently agitated water. The water was at supply temperature (generally less than 20°C). The cooling rate of the samples was measured using a thermocouple inserted into a similarly sized piece of steel. The thermocouple was connected to a datalogger allowing the measurement of cooling rate. The cooling rate between 800 - 300°C was calculated from the data collected and for the hardness and microstructural analysis samples was approximately 160°C/second. Samples were also quenched in still water after tempering.

Hardness Tests

All hardness values quoted in this work were determined using a regularly calibrated, NATA registered, Vickers hardness tester. Hardness tests for determination of tempering curves were performed on samples separate to those used for tensile testing. Sectioning of the hardness samples was performed in such a way that the decarburised layer generated during heat treatment was at least 5mm from the hardness impressions. The samples to be tested were sectioned using a water cooled cutter and polished to a 240 grit finish. Three hardness impressions were performed on each sample and the average quoted as the result.

Tensile and Charpy Impact Tests

Tensile properties were measured using a regularly calibrated Tinius Olsen tensile testing machine. Machining and testing was carried out in Bisalloy Steels' NATA registered mechanical testing laboratory. This same laboratory is used for all quality assurance of production material. Tensile tests were carried out in accordance with Australian Standard A.S. 1391-1991⁷².

Charpy V-notch impact testing was conducted in accordance with Australian Standard A.S. 1544.2-1989⁷³, in the same laboratory, using regularly calibrated equipment. All quoted values for Charpy impact energy are an average of three tests. The direction of impact was perpendicular to the rolling direction.

Jominy End Quench Hardenability Tests

Jominy end quench hardenability tests were performed according to Australian Standard AS 1770-1975⁷⁴. All tests were performed on sub size or subsidiary test pieces, the dimensions of which are detailed on page 11 of the Standard. All test pieces for tensile, Charpy and Jominy testing were machined to remove any decarburised layer arising from heat treatment.

Bead On Plate Weld Heat Affected Zone (HAZ) Hardness Tests

Weld heat affected zone hardness was determined using the Bead on Plate test. These tests were performed in accordance with British Standard BS 7363:1990⁷⁵. An additional hardness traverse across the HAZ, perpendicular to the fusion line was performed as detailed in the B.H.P. S.P.P.D. standard procedure for bead on plate tests⁷⁶. The spacing of indentations detailed in Australian Standard AS 2205.6.1-1988⁷⁷ was used. The plates were austenitised at 925°C for 1hour/inch thickness and quenched in the same manner as the hardness samples. However the cooling rate was slower (unmeasured) as the samples were much larger. To maximise the cooling effect the samples were quenched one at a time and were cool to touch (about 50°C) after approximately 20 seconds. The cooling rate was estimated to be about 50°C/second. After quenching the plates were then tempered at the required temperature to give 690Mpa yield strength (270 HV20). In the case of steels incapable of meeting this hardness then the tempering temperature was 600°C to give a tempered microstructure to test.

Prior Austenite(γ) Grain Size Determination

Etching

Several authors have described and reviewed techniques for etching of prior austenite grain boundaries, among them are Barraclough⁷⁸, Brownrigg, Curcio and Boelen⁷⁹, Ginn and Hall⁸⁰ and Wiedermann, Wojtas and Stepien⁸¹. A number of etchants, recommended previously, were tried with mixed success (see results). Three techniques gave similar, usable results, the first, suggested by the B.H.P. S.P.P.D. Metallography Department⁸² consists of a dual stage process starting with light etching with 2% Nital, followed by 20 seconds to 5 minutes (dependant on alloy and heat treatment) at room temperature in 100ml saturated aqueous picric acid + 1.6g CuCl₂ + 0.5ml Teepol. Rubbing with cotton wool under hot water to remove the copper

deposited on the surface is necessary. Best results with this method were observed when the etchant was swabbed on with cotton wool. Reasonably vigorous rubbing was required, to prevent the buildup of copper on the surface. This technique is also mentioned by Ginn and Hall⁸⁰. The second technique that provided reasonable definition of grain boundaries is etching with Vilella's reagent⁷⁸. A third technique is detailed by Wiedermann *et al*⁸¹. This consists of 16g of CrO_3 and 80g of NaOH dissolved in 145 ml of distilled water. The CrO_3 is added to the water and then the NaOH is added slowly (due to the strong exothermic reaction upon dissolution of the NaOH). The whole is brought to boil, the sample preheated to the same temperature as the boiling solution (about 120-130°C).

In all cases tempered material was used for grain size determination due to the poor results encountered when attempting to etch the as quenched steel.

Measurement

Prior Austenite grain size was determined according to Australian Standard A.S. 1733-1976⁸³. The line intercept method was used. A photograph was taken of a representative area, lines scribed, intersections counted and the grain size, in microns, calculated.

Samples for this work were heat treated independently and were sectioned from larger (60 x 20 x 180mm) pieces than those used for the microstructural work.

Microstructural Analysis

Samples for microstructural analysis were sectioned from pieces 60mm long by 10mm thick and 20mm wide. Sections were cut so that they were at least 5mm from the surface, away from any decarburised layer. Rough grinding and polishing were carried out by hand, using the metallographic facilities in Bisalloy Steels laboratory. Samples were etched using 2% nital. Best results were observed when the initial etch was polished off and the sample re-etched, prior to photography.

Glossary of Bisalloy Steel Types

Bisalloy, or Bisplate is a range of quenched and tempered plate produced in Australia by Bisalloy Steels Pty. Ltd. Bisalloy Steels is a wholly owned subsidiary of Email Australia, and forms part of the Metals Distribution Group.

Finished grades produced by Bisalloy Steels and the associated feed alloys are shown in Table 4.1 below.

Table 4.1. Bisalloy Grades¹²

Finished Product	Feed Alloy	Feed Alloy	Mechanical
	(thin plate)	(thick plate)	Properties (min) (MPa)
<i>Structural</i>			
Bisalloy 60	Bis 52	Bis 53	500Y/590T/220HB
Bisalloy 70	Bis 52	Bis 53	600Y/690T/240HB
Bisalloy 80	Bis 52	Bis 53	690Y/790T/255HB
<i>Wear</i>			
Bisalloy 320	Bis 52	Bis 53	320-360HB
Bisalloy 360	Bis 52	Bis 53	360-400HB
Bisalloy 400	Bis 21	Bis 21	400-460HB
Bisalloy 500	Bis 21	Bis 21	477-534HB

Table 4.2 sets out the main composition of Bisalloy Feed alloys.

Table 4.2. Typical Compositions of Bisalloy Feed Alloys¹²

Element%(typ)	C	Mn	Si	Cr	Mo	B
Alloy						
Bis 52	0.16	1.1	0.2	-	0.2	0.001
Bis 53	0.18	1.4	0.2	0.2	0.2	0.001
Bis 21	0.29	0.5	0.2	1.0	0.18	0.001
Bis 2	0.18	1.1	0.2	0.8	-	0.001

CHAPTER 5

Development of a General Model to describe Hardness

Change of non-Precipitation Hardening Steels upon Tempering.

Results

As described before in Chapter 2, techniques developed by Holloman and Jaffe⁵⁷ were used to determine a single parameter to describe tempering behaviour. Once determined, this was to be included in the steel design programme. The chemical composition of the steel used in this section is shown in Chapter 3, and is designated Bis 2. The Bis 2 alloy composition was used to obtain test data, as a quantity of this steel was available and its alloy chemistry is reasonably typical of the alloys used by Bisalloy and many other Q&T steel manufacturers.

The hardness results determined from the quenching and tempering of Bis 2 are contained in Figure 5.1.

Analysis and Discussion of Results

From Figure 5.1, hardness values were selected which were obtained in at least three tempering curves. The time taken to produce a specified hardness for various tempering temperatures were used in the calculation of C, the constant in the Holloman - Jaffe equation. The hardness values selected were 360 HV, 340 HV and 320 HV.

Regression analysis was used to determine the value of the y-intercept constant of the line $\ln(1/t) = \ln(A) + (-Q/RT)$. An example of which is shown in Figure 5.2. It is the y-intercept of this line which forms the constant in the Holloman and Jaffe parameter. This was repeated for

each set of data (time and temperature) for each hardness selected (360 HV, 340 HV and 320 HV).

The information determined from this exercise is contained in Table 5.1

Table 5.1 Constants Determined from Regression Analysis of $\ln 1/t$ vs T Lines

Hardness (HV)	Constant
360	15.66
340	16.70
320	17.26

The average of these values is 16.53.

Now that the value of C has been determined, a direct relationship between the tempered hardness and H can be found. For each data point Temperature (T), time (t) and hardness are known, and H can be calculated from $H=T(C+\ln(t))$.

Figure 5.3, shows the value of H calculated for each data point with C set at 16.53. It is apparent that the tempering temperature has to be above 300 degrees celsius to have any significant effect. The roll off point appears to be about $H = 9500$ and this corresponds to 300 degrees for 75 minutes or 400 degrees for 5 minutes A regression analysis performed upon this part of the curve ($T > 300$) gives the required relationship between H and tempered hardness. It should be noted from this that the model is only valid for $300^{\circ}\text{C} < T < 600^{\circ}\text{C}$ and times up to about 1.5 hours.

The regression line determined has the form :-

$$y = -0.041 x + 831.21$$

Thus:

$$H = T(16.53 + \ln(t))$$

and for

$$H > 9000: \text{Hardness} = -0.041 (H) + 831.21$$

$$H < 9000: \text{Hardness} = 430$$

where :-

H = the Holloman and Jaffe parameter

T = the tempering temperature of the sample, K

t = the residence time in hours

Hardness is the Vickers Hardness number.

The limits of this set of equations are:

$$0 < T < 600 \text{ and}$$

$$t < \text{approximately } 1.5 \text{ hours.}$$

As this work was aimed at constructing a general model predicting tempered hardness the predictive capacity and accuracy of the model was tested. This was carried out using some tempering data for an alloy similar to Bis 2 obtained from work done by Barnett⁸⁴ on Bis 52 (see Chapter 3 for full chemical analysis details). This data, and the predicted hardnesses are shown below in Table 5.2.

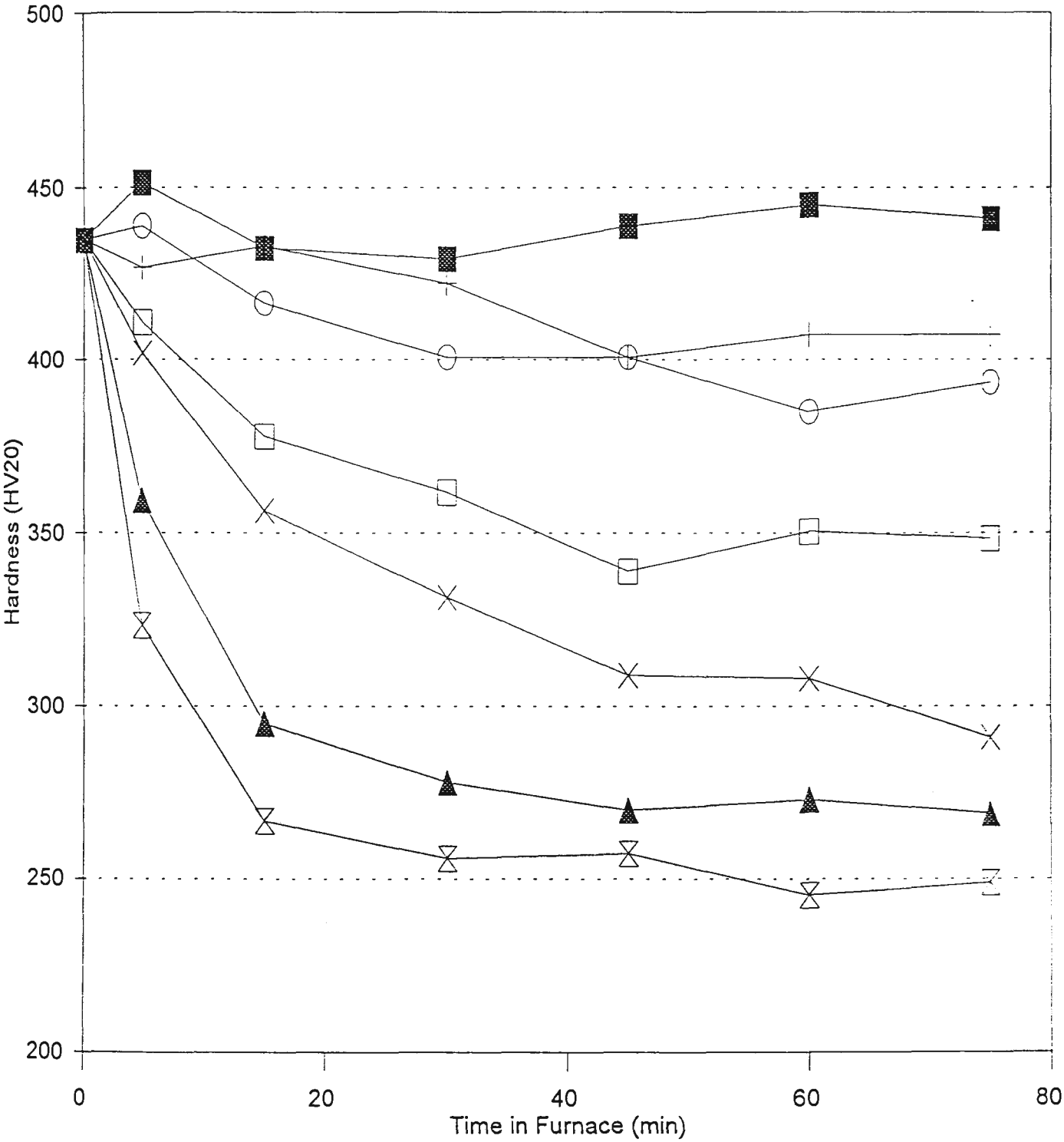
Table 5.2 Comparison of Hardness Results

Temp	Time	Measured	Predicted
		Hardness	Hardness
(°C)	(min)	(HV20)	(HV20)
500	38	320	322
600	38	275	256
650	38	260	223
700	38	255	190
500	47	320	315
600	47	275	248
650	47	255	215
700	47	220	182
500	76	320	300
600	76	270	231
650	76	255	197
700	76	220	162
500	95	300	293
600	95	255	223
650	95	235	188
700	95	210	153
500	118	285	286
600	118	245	215
650	118	235	180
700	118	190	145

From the above table, it appears that for temperatures around 500°C (and presumably lower (although there are no data to show this) the model is reasonably accurate. Once the temperature climbs above 600°C the model becomes inaccurate. This is reasonable as the highest temperature used to generate the model was 600°C. Another possible cause of inaccuracy is the difference in alloy chemistry between the two steels. The table of materials (Table 3.1.) in chapter 3 shows the compositions of the two alloys Bis 2 and Bis 52, although they are similar in carbon and manganese contents Bis 2 contains a significant proportion of chromium and Bis 52 contains molybdenum. At this stage the effects of these compositional differences on this approach to predicting tempering behaviour is unknown.

Figure 5.1

Tempering Curves for Bis 2



■ 200 deg C + 300 deg C ○ 400 deg C □ 450 deg C
× 500 deg C ▲ 550 deg C ⋈ 600 deg C

Figure 5.2

Variation of 1/time and 1/temp
for Bis 2 at 360 HV hardness

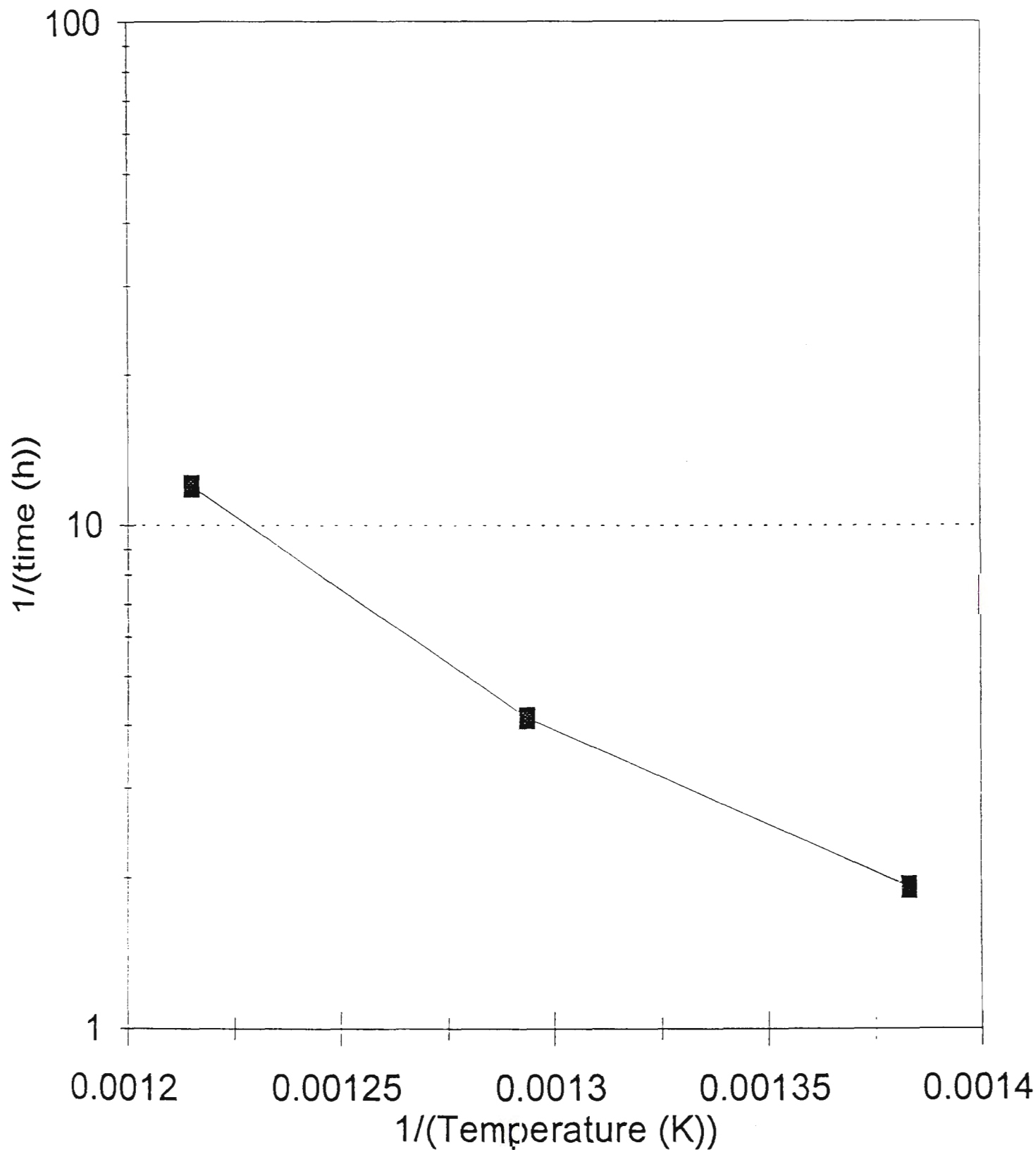
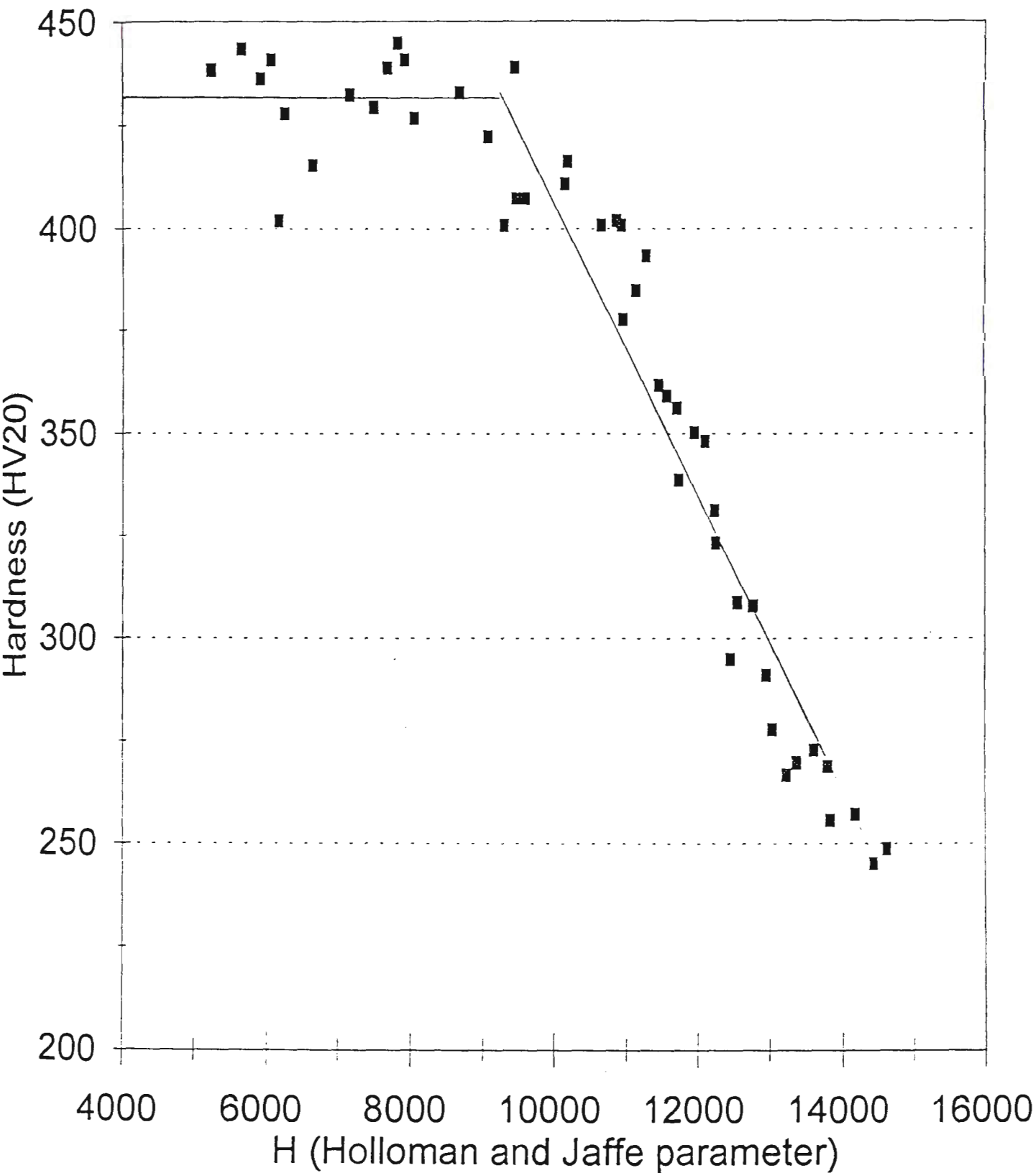


Figure 5.3

Graph of H vs Hardness
For Bis 2 when C=16.53



CHAPTER 6

Hardness Surveys and Tempering Response of Copper

Containing Steels.

Results

The tempering responses of the alloys studied are displayed in graphs in Figures 6.1 to 6.6. Investigation of the heat treatment response indicates appropriate tempering temperatures for performance of tensile and Charpy tests. Chapter 3 contains the heat treatment details.

Analysis and Discussion of Results

As can be seen in Figures 6.1 to 6.6, the Series 1 and 3 steels develop the required hardness for a 690 MPa steel of 255 HB (270HV) after tempering for 30 or more minutes at 650°C. The Series 2 steels fall short of the required hardness when tempered at 650°C. However one of the Series 2 steels, 3677 reached the required hardness at 600°C.

Due to differences in contents of key alloying elements (C, Mn) and the absence of boron, the Series 2 steels differ widely in hardness in the as quenched state. This difference carries on right through the tempering response.

In contrast with the Series 2 steels, the differences in as quenched and tempered hardness of the Series 1 steels are minor until these steels are tempered at a temperature of 700°C. It is only after 15 minutes at this temperature that significant differences in hardness are observed. If Figures 6.5 and 6.6 are compared then it is apparent that the hardnesses of steels 3588 and 3589 are higher when tempered at 700°C than at 650°C. One possible reason for this is rapid precipitation of a relatively large volume fraction of copper precipitates in combination with faster (than that occurring at lower temperature) precipitation of NbC, increasing the hardness over that

resulting from lower tempering temperatures. Another possibility is that tempering at 700°C partially re-austenitises the structure and that martensite has formed after quenching from the tempering temperature. Further investigation of this phenomenon was beyond the scope of this work. These two steels contain 1 and 0.8 % copper respectively and thus, of the alloys studied they are the two most supersaturated in copper. Of the Series 1 steels, the most puzzling behaviour is exhibited by 3591. Tempering at 700°C (Figure. 6.6) shows that for times less than 45 minutes the hardness of 3591 is lower than 3589. However, 3591 differs only insofar as it contains 0.59% Cr whereas the other alloy is Cr free.

Figure 6.7 contains information on the tempering response of some of the alloys studied for furnace times up to 6 hours. This graph is composed of information pertaining to alloys that are essentially the same other than for copper content, although 3677 does not contain boron. Marked on the graph are the heat numbers and the associated copper content. The hardness of 3588 and 3589 remain relatively constant, approximately 295 HV, after about 100 minutes in the furnace. There is an increase in hardness at 60 minutes probably associated with the maximum dispersion hardening of copper precipitates, before the onset of coarsening. This result is supported by work presented by Youle and Ralph²⁸ for precipitation of copper from α -iron during aging at 550°C.

The data in Figure 6.7 seem to indicate that for these combinations of heat treatment and alloy composition there is an optimum level of copper above which further additions make little or no difference. This would appear to be less than 0.8% copper. Results for 3677 show that for short aging times the hardness is little different from that observed in the 0% copper steel, 3720. For longer times, ≥ 180 minutes, the hardness of the 0.4% copper alloy and the 0% copper alloy diverge, since the hardness of the copper steel is maintained while that of the copper-free steel declines.

Statistical analysis of differences between the 0%, 0.4% and 1% copper steels is shown graphically in Figure 6.8. This graph shows the average and standard deviation obtained for hardness tests performed. Table 6.1 shows the results of a one tail t-test($\alpha=0.05$, ie 95% significance) between the hardness of the various alloys at specified tempering times. The test is to determine the validity of the following hypothesis:- hardness of 3588 > hardness of 3677 > hardness of 3720.

Table 6.1. Results of one tail t-test.

Tempering Time (min)	Test			
	3588	>	3677	> 3720
30		✓		✓
120		✓		x
180		x		✓
240		✓		✓
360		✓		✓

where ✓ = significant difference and x = no significant difference.

Thus 3677 is significantly harder than 3720 after more than 120 minutes tempering time. The table also indicates that 3677 is significantly harder than 3720 after 30 minutes. This is so, but if Figure 6.8 is examined closely it can be seen that for times less than 100 minutes 3677 and 3720 swap order several times and are very close to each other in hardness, that is, the difference is significant but very small and thus of little practical importance. It is not until 75 minutes tempering time has elapsed that a clear trend becomes apparent and the hardness differences

become relatively large.

These results also indicate that the hardness of 3677 lies between that of 3588 and 3720 for longer tempering times. For short times, that would be considered appropriate for manufacturing purposes, any copper precipitation effect due to copper levels below 0.4% is relatively minor and that for useful hardening effects to become apparent at this copper content, tempering times greater than 120 minutes need to be used. Thus, the previously mentioned optimum copper content for this type of steel and heat treatment conditions, appears to lie between 0.4 and 0.8%

This effect is much more marked at 650°C, Figure 6.9, with the hardness of the 0% copper steel falling rapidly after 180 minutes aging. The fall in hardness, at 650°C, of the 0.4% copper containing alloy, 3677, is much more gradual as aging time continues. Full statistical analysis was not carried out for these results but the standard deviations are plotted to give an indication of the scatter of results.

The lack of boron in alloy 3677 seems to have manifested itself as lower as quenched hardness than the other two alloys discussed here. However, the difference in hardness between 3677 and 3720 decreases dramatically after 30 minutes tempering. It may be that, apart from the lower initial hardness, the lack of boron in 3677 is having little influence on the tempering and precipitation behaviour, however previously reviewed literature³⁴ suggests a synergy between boron and copper. With boron present, precipitation of copper may be faster in this steel and the difference in hardness between it and 3720 might occur earlier in tempering.

Figure 6.10 shows the effect of copper content on tempered hardness. Hardness results for 1 hour tempering at 650°C are presented. One hour represents a reasonable length of time for a plate to reside in a furnace during production. These results add further support for the idea of the existence of an optimum level of copper and heat treatment for the best gain in

hardness/strength due to the precipitation of copper. The optimum indicated by these results seems to be around 0.6%. The lower hardnesses of both the 0.8% Cu and the 1% Cu steels is difficult to explain. As will be seen in further results this general trend continues, with the steels of higher copper levels exhibiting lower hardness/ mechanical properties than steels with intermediate copper contents.

Using the above hardness results, equations describing the tempering behaviour can be generated. The technique outlined earlier in this work, originally developed by Holloman and Jaffe⁵⁷, was used to determine a set of equations to describe the effect of copper on the hardness response to heat treatment. Hardness results corresponding to the steels 3588(1.0%Cu), 3589(0.8%Cu), 3590(0.6%Cu) and 3720(0.0%Cu) were included. The details of the calculation will be described for 3588, the method being the same for the rest of the steels. The only alloy for which equations were not determined was 3677 due to a lack of appropriate data.

Figure 6.11 contains tempering data for alloy 3588. To determine C in the Holloman and Jaffe parameter values of time and temperature for a common hardness are needed. In this case 315Hv and 320Hv were selected. From this information Figures 6.12 and 6.13 were produced and regression analysis performed on these points. These regression analyses produce two values of C. The average of these was used as the value of C in the equation for the Holloman and Jaffe parameter.

Table 6.2 contains the results of the regression analyses.

Table 6.2 Results of Regression analysis to Determine C.

Alloy	Regression Lines	R ²	C
3588	-7747.42x + 9.86	0.48	11.45
	-10438.00x + 13.05	0.64	
3589	-3718.29x + 5.94	0.36	5.94
3590	-5213.81x + 7.26	0.66	7.62
3720	-5005.05x + 7.41	0.92	7.85
	-5246x + 8.29	0.95	

C is the constant in these lines ie: for 3588 $C = (9.86 + 15.05)/2 = 11.45$.

From Table 6.2, the fit (R^2 , the correlation coefficient) for the regression lines representing 3588, 3589 and 3590 is not particularly good. The reason for this can be seen in Figure 6.11 where hardnesses at 700°C are higher than those for 650 C. This was seen in all steels (3588,3589,3590) except 3720 and was probably due to the greater precipitation of copper at 700°C than 650°C. This behaviour confounds the analysis as it is then impossible to obtain a straight line on the semi-log plots of 1/Temp vs 1/time and thus the line of best fit determined via regression analysis does not describe the points well. This is seen in Figures 6.12 and 6.13. The fit for 3720 is very good as this steel displays no significant precipitation hardening. The implication is that this analysis is not well suited to precipitation hardening steels.

Setting this reservation aside and continuing the analysis for 3588, using the average value of C, then H (the Holloman and Jaffe parameter) can be determined for every value of time and temperature. The graph in Figure 6.14, an illustration of the dependence of hardness on H, can

be constructed and regression analysis performed on the data. For $H > 6000$ an equation relating H and hardness can be written. Similar equations were determined for the other steels, 3589, 3590, and 3720.

Table 6.3 shows the equations for all the steels examined here.

Table 6.3 Equations Relating H and Hardness

Alloy	Equations
3588	$H = T(11.45 + \ln(t))$ $H > 6000 : \text{Hardness} = -0.0237(H) + 537$ $H < 6000 : \text{Hardness} = 401$
3589	$H = T(5.74 + \ln(t))$ $H > 1500 : \text{Hardness} = -0.0280(H) + 432$ $H < 1500 : \text{Hardness} = 404$
3590	$H = T(7.26 + \ln(t))$ $H > 3000 : \text{Hardness} = -0.0275(H) + 467$ $H < 3000 : \text{Hardness} = 403$
3720	$H = T(7.85 + \ln(t))$ $H > 3000 : \text{Hardness} = -0.031(H) + 480$ $H < 3000 : \text{Hardness} = 394$

Where :

Hardness is Vickers hardness (Hv)

T = Furnace temperature in Kelvin

t = furnace residence time in hours

These equations allow calculation of hardness from time and temperature information.

Figure 6.15 is a combination of H vs Hardness for all four steels. Superimposed on the plot is a representation of the lines of best fit describing the tempering behavior. The most obvious detail from this graph is the difference between 3588(1%Cu) and the other steels. The only significant difference between the steels is the copper proportion but to attribute this difference to copper denies the similarity between 3720(0%Cu), 3589(0.8%Cu) and 3590(0.6%Cu). It would seem more likely that differences would exist between 3720 and the other alloys, due to the lack of copper. No apparent trend of changes in slope is obvious across the four alloys. The value of C (which influences H) for 3588 is, however, considerably different from the other 3 steels. The reason for the difference in the value of C is unknown.

Lacking independently generated data to test the formulae, selected values from the original data were used to test the formulae. Table 6.4 contains the results of this crude test.

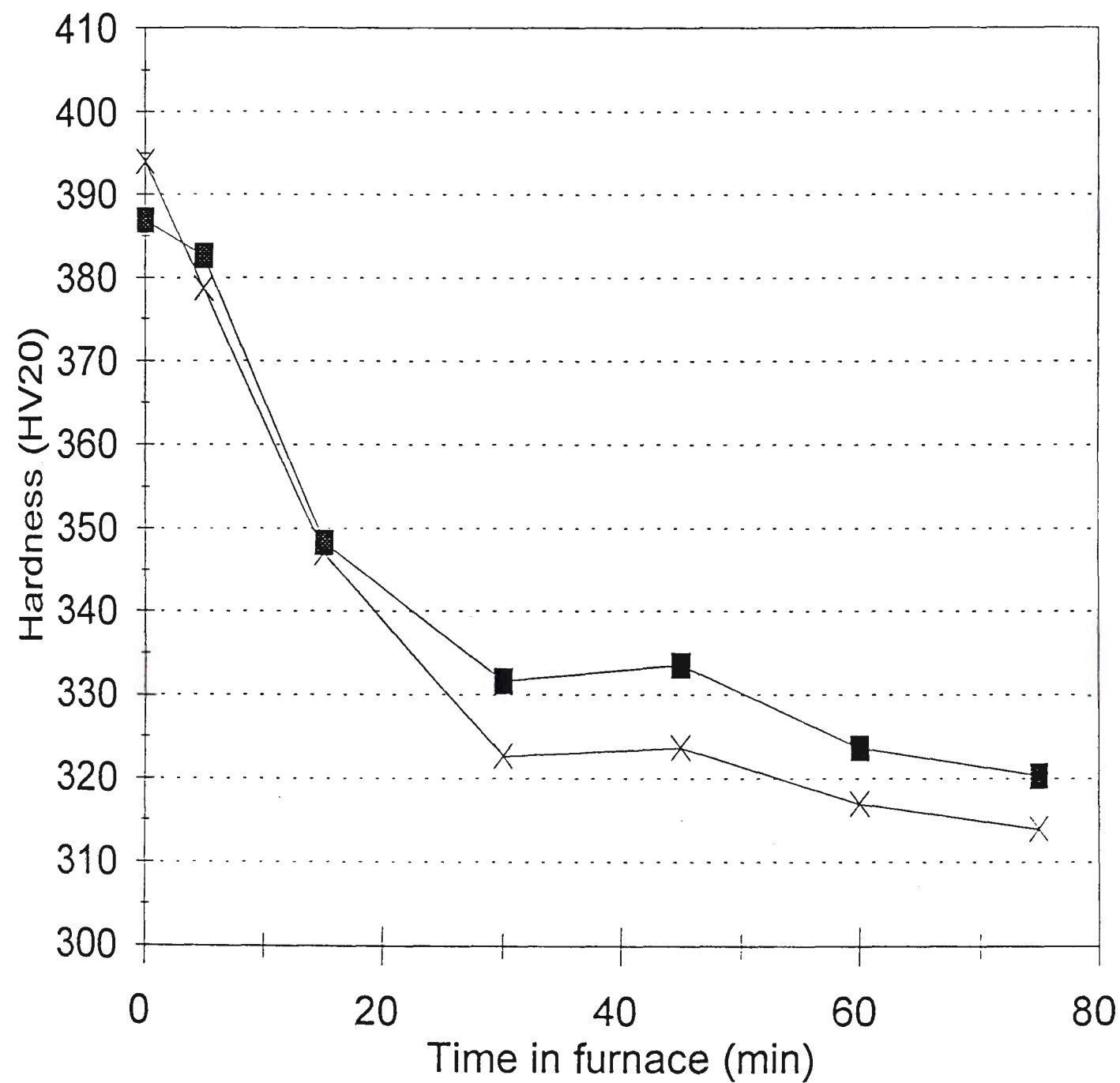
Table 6.4 Actual and Predicted Hardness values for the Copper Steels.

Alloy	Time(hrs)	Temp(K)	Hardness	Predicted Hardness
3588	32(0.533)	650(923)	285	300
	45(0.75)	550(823)	326	319
	30(0.5)	700(973)	298	288
3589	30(0.5)	550(823)	316	315
	15(0.25)	600(873)	315	326
	5(0.083)	700(973)	342	343
3590	30(0.5)	600(873)	303	309
	60(1)	650(923)	282	283
	75(1.25)	700(973)	284	267
3720	15(0.25)	450(723)	347	335
	60(1)	500(773)	297	291
	75(1.25)	600(873)	265	261

From the results in Table 6.4 the predictive capacity of the equations is surprisingly good. It should be noted that these equations are only applicable to this type of steel over a range of temperatures from 0°C to 700°C and for times up to 1.5 hours. Any variation outside these limits should be considered with caution.

Figure 6.1

Tempering Curves for Copper Steels at a temperature of 450 C



■ 3721 × 3720

Figure 6.2

Tempering Curves for Copper Steels
at a temperature of 500 C

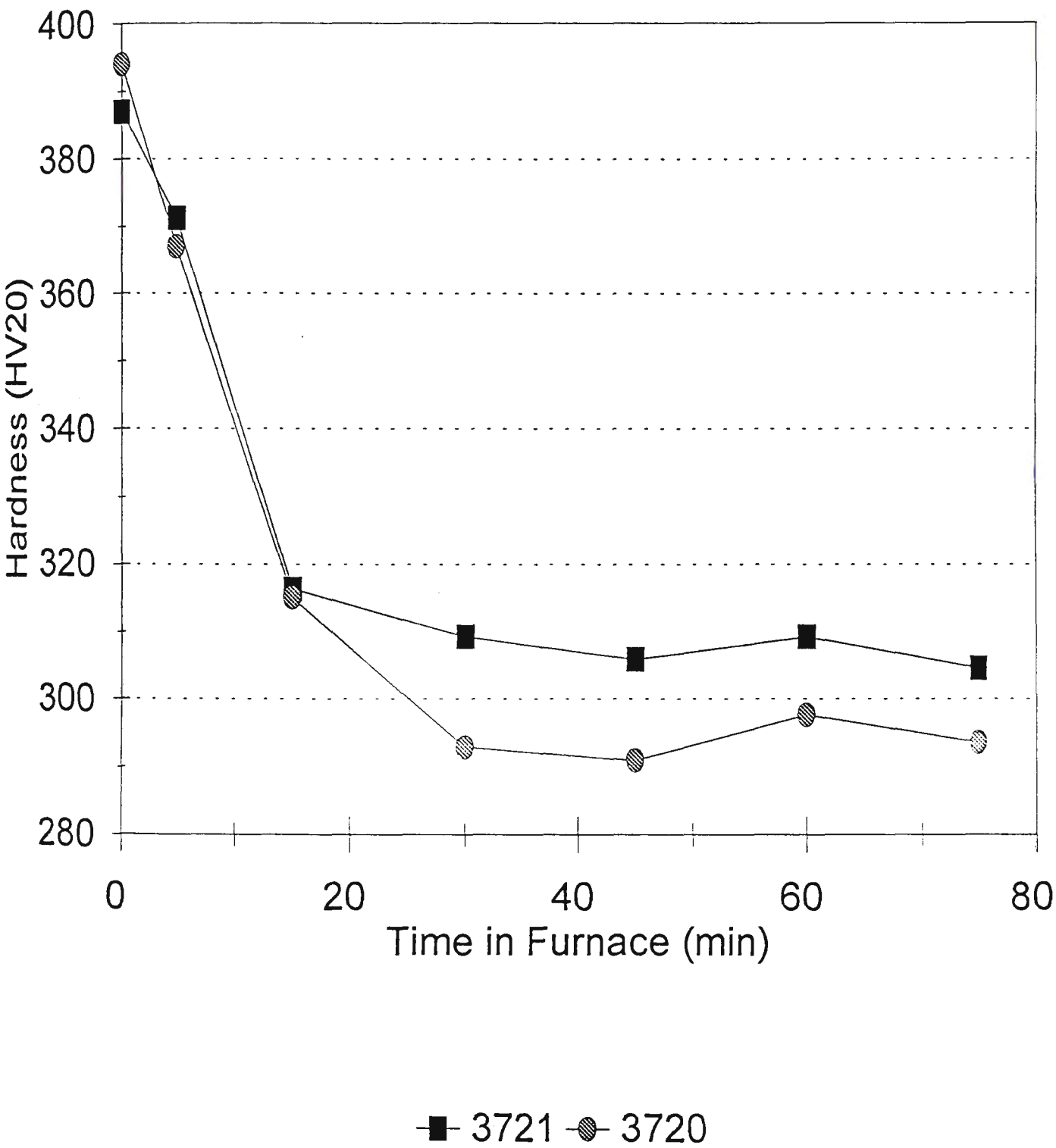


Figure 6.3

Tempering Curves for Copper Steels
at a temperature of 550 C

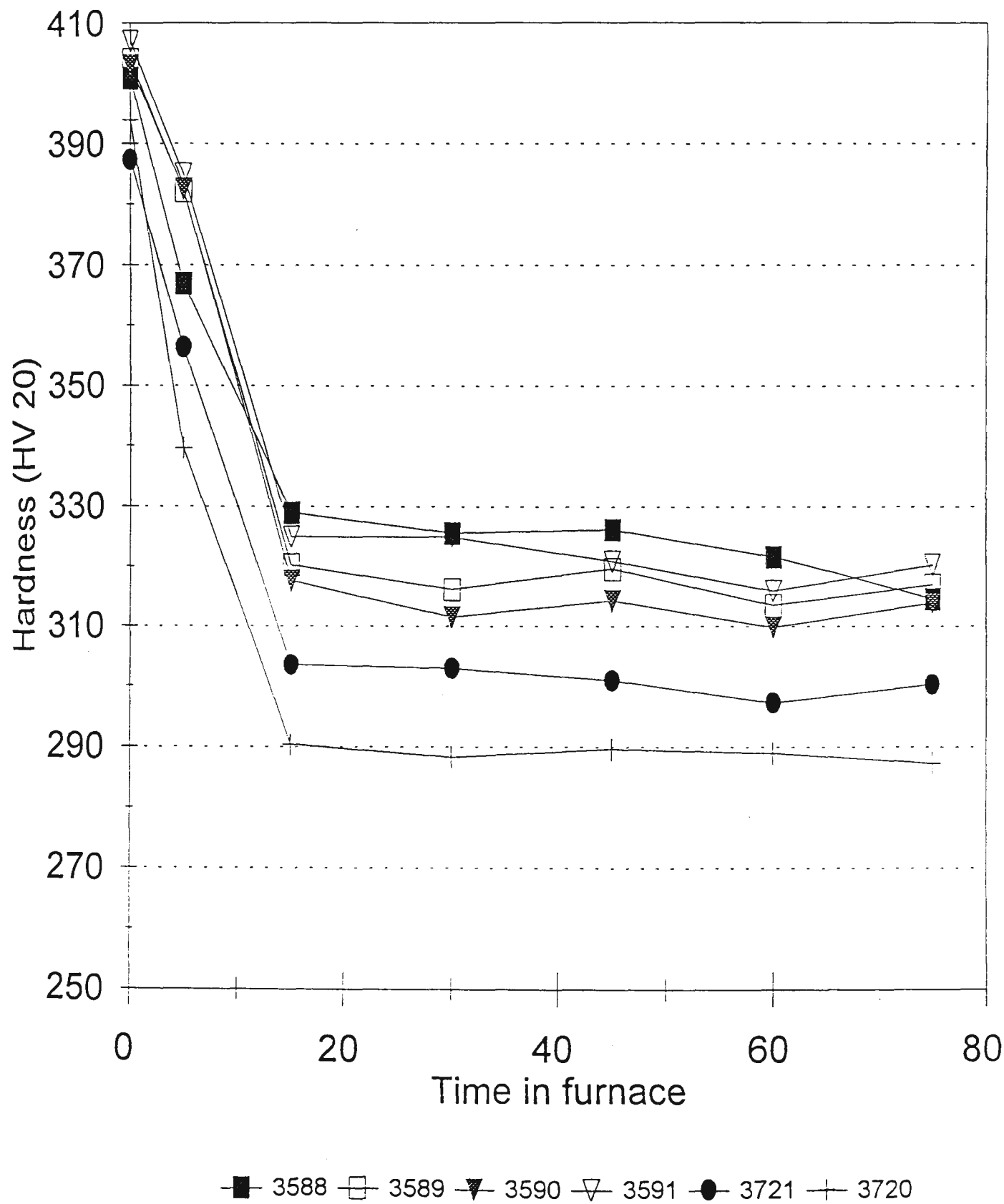


Figure 6.4

Tempering Curves for copper Steels at a temperature of 600 C

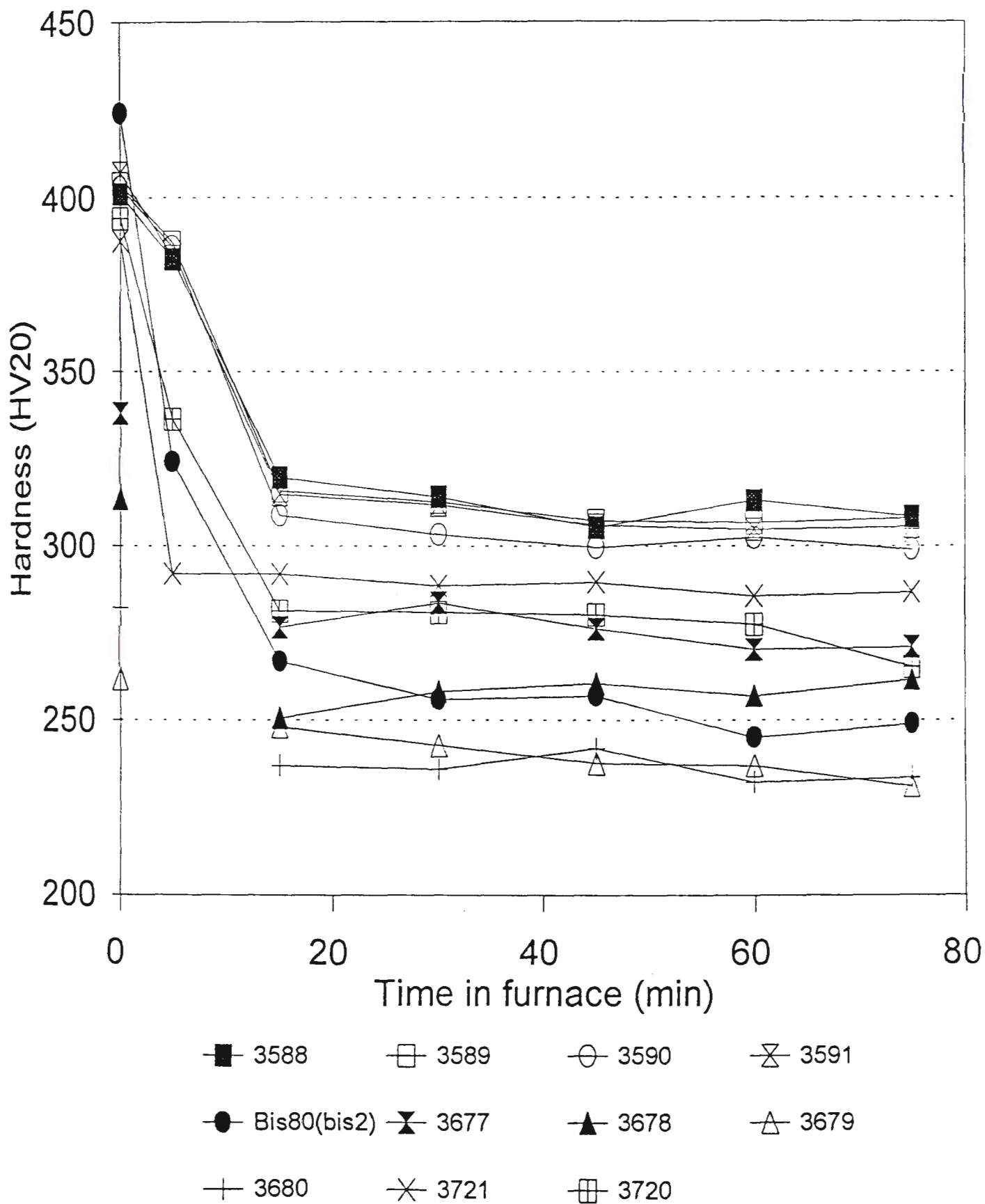
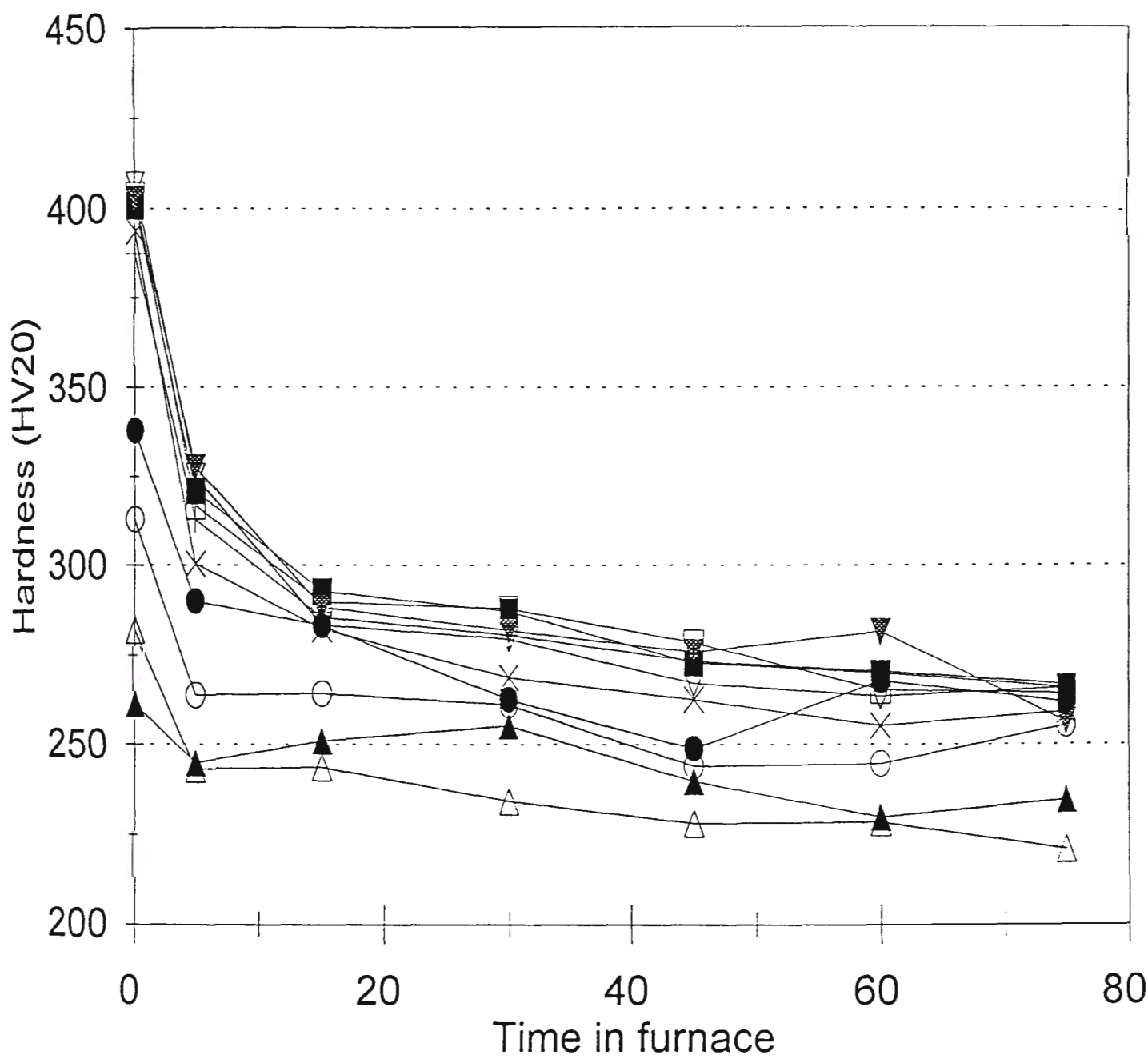


Figure 6.5

Tempering Curves for Copper Steels
at a temperature of 650 C



■ 3588 □ 3589 ▼ 3590 ▽ 3591 ● 3677
○ 3678 ▲ 3679 △ 3680 + 3721 × 3720

Figure 6.6

Tempering Curves for Copper Steels at a Temperature of 700 C

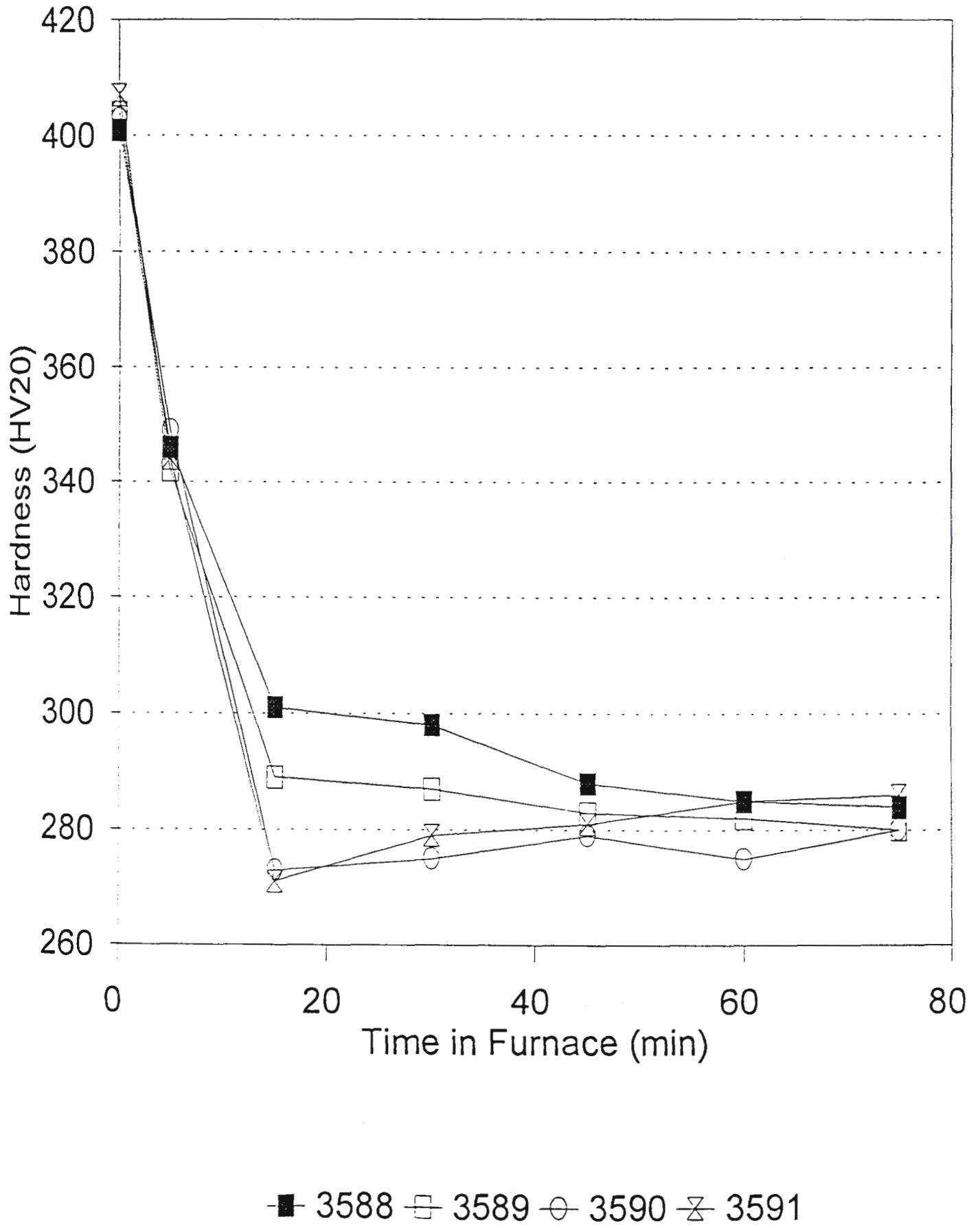
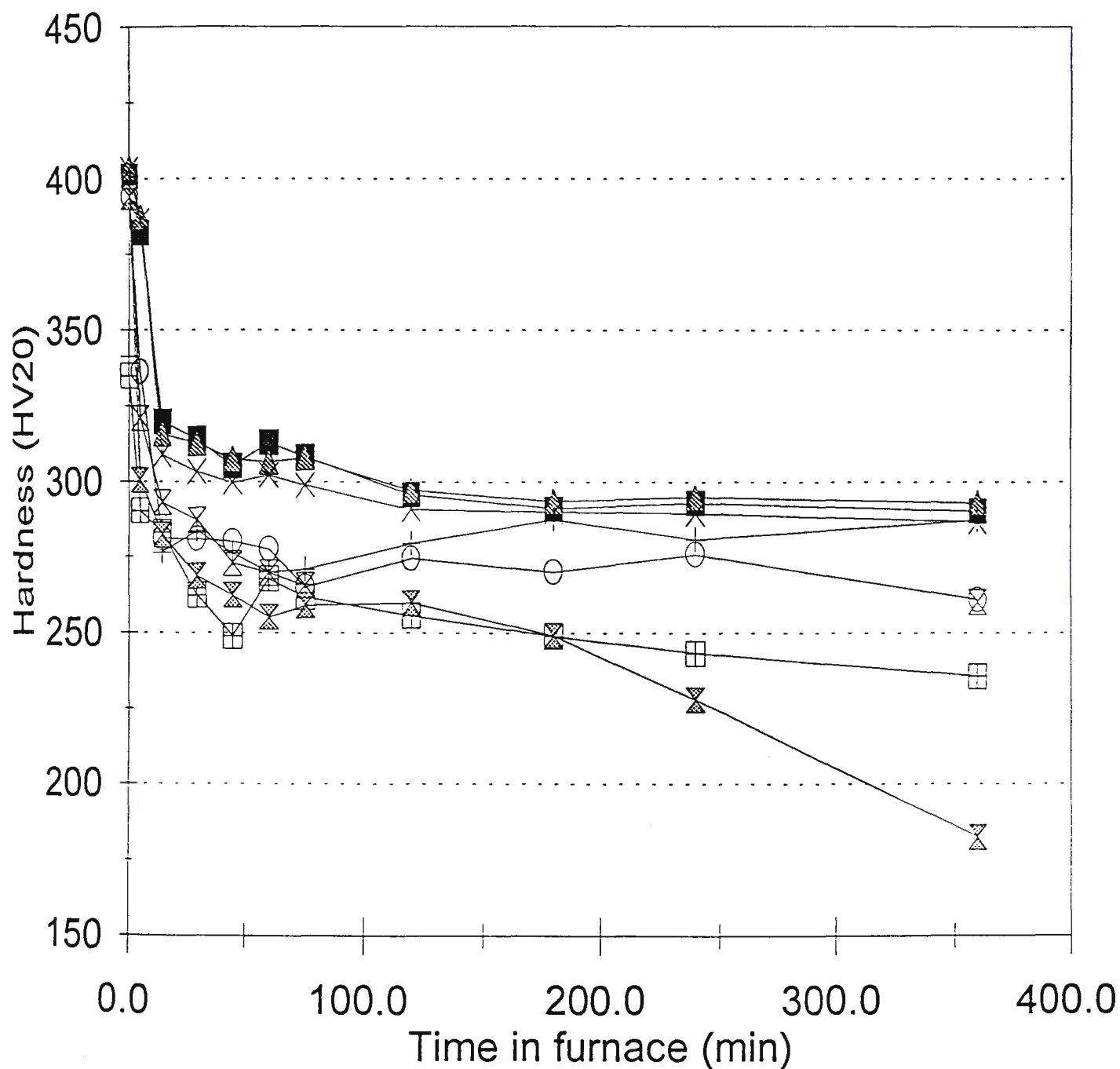


Figure 6.7

Effect of Copper on Tempering of Copper Steels at temps of 600,650 C



■ 3588- 1% Cu ▲ 3589- 0.8% Cu ✕ 3590- 0.6% Cu
 + 3677- 0.4% Cu ⊖ 3720- 0.0% Cu ⊞ 3677 650C
 ⊗ 3720 650 C ⊗ 3588 650 C

Figure 6.8

Effect of Copper on Tempering of Copper Steels at 600 C

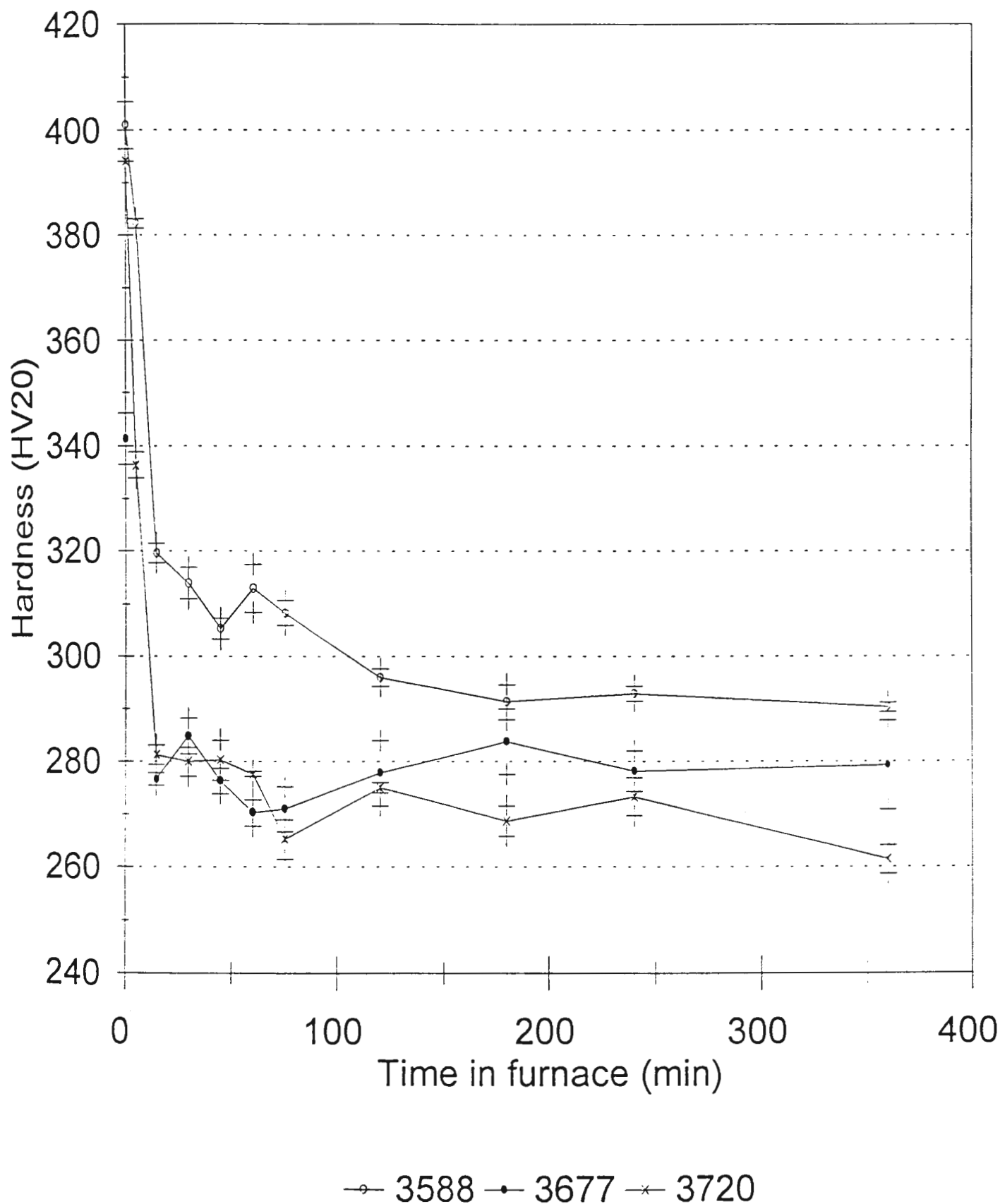


Figure 6.9

Effect of Copper on Tempering
of Copper Steels at 650 C

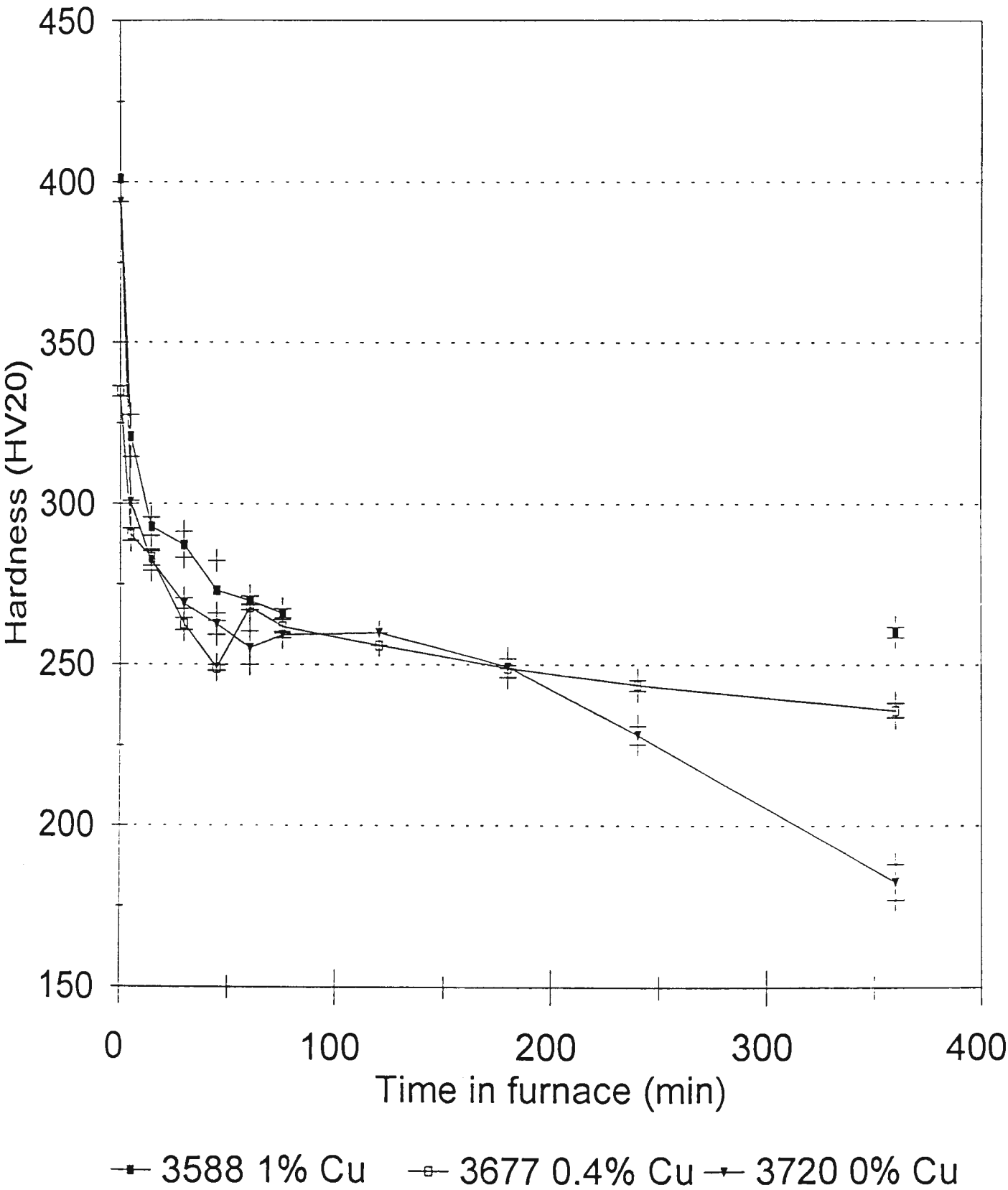


Figure 6.10

Effect of Copper on Tempered Hardness of Copper Steels, 1 Hr temper at 650 C

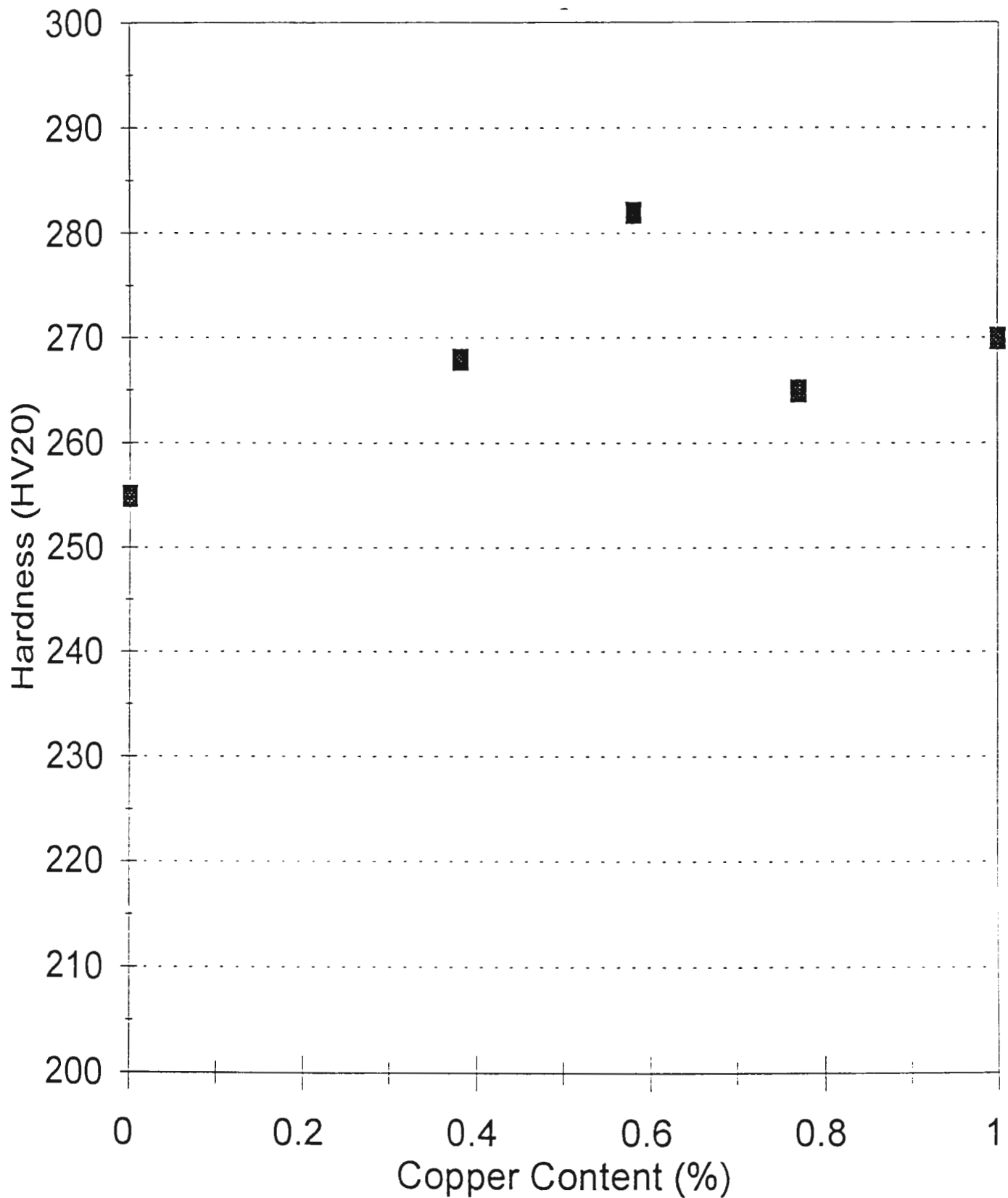


Figure 6.11

Tempering Curves for Alloy 3588 1% Copper

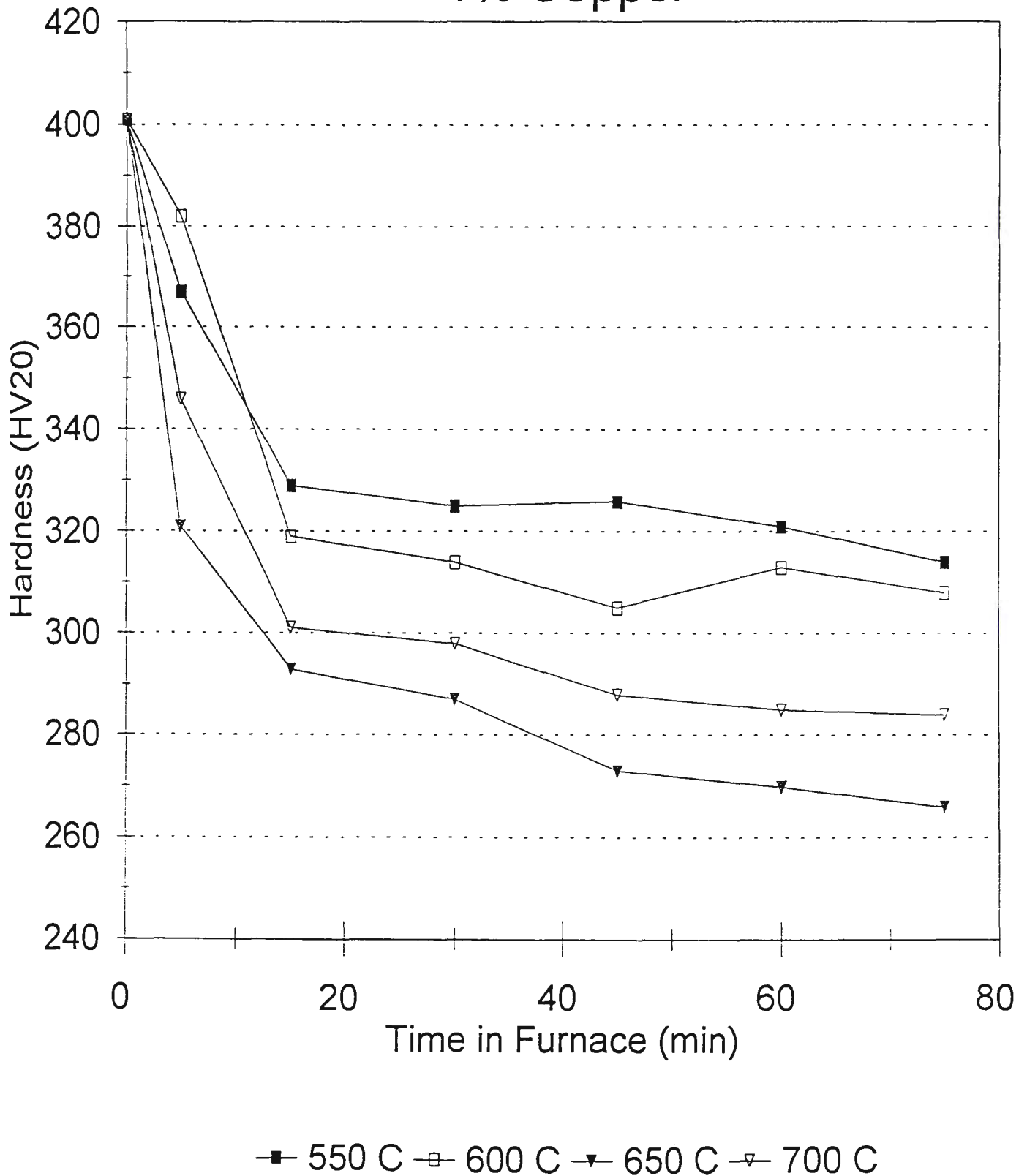


Figure 6.12

Graph of 1/temp. vs 1/ time for Alloy 3588, used in the determination of C

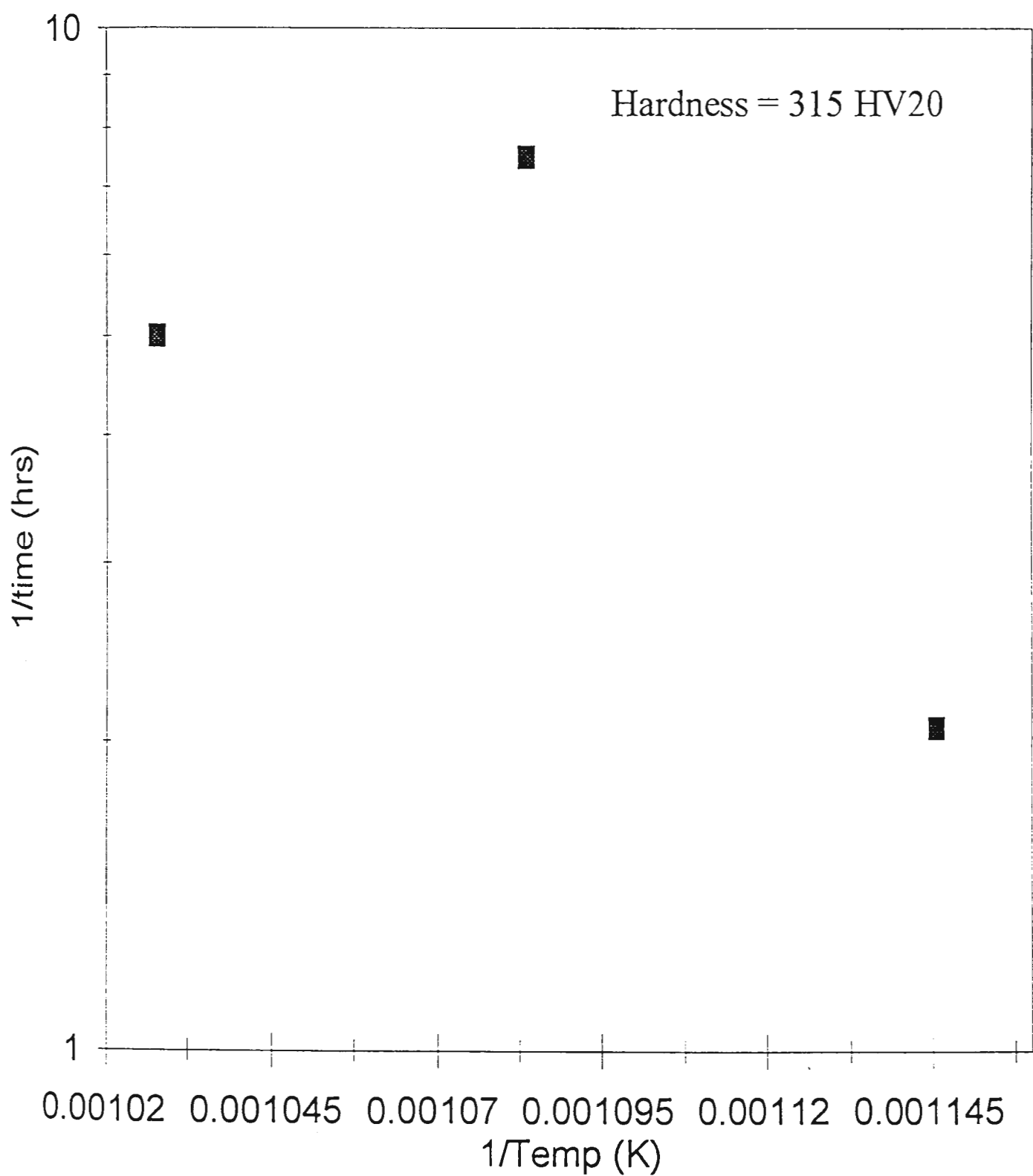


Figure 6.13

Graph of 1/time and 1/temp. for Alloy 3588, used in the determination of C

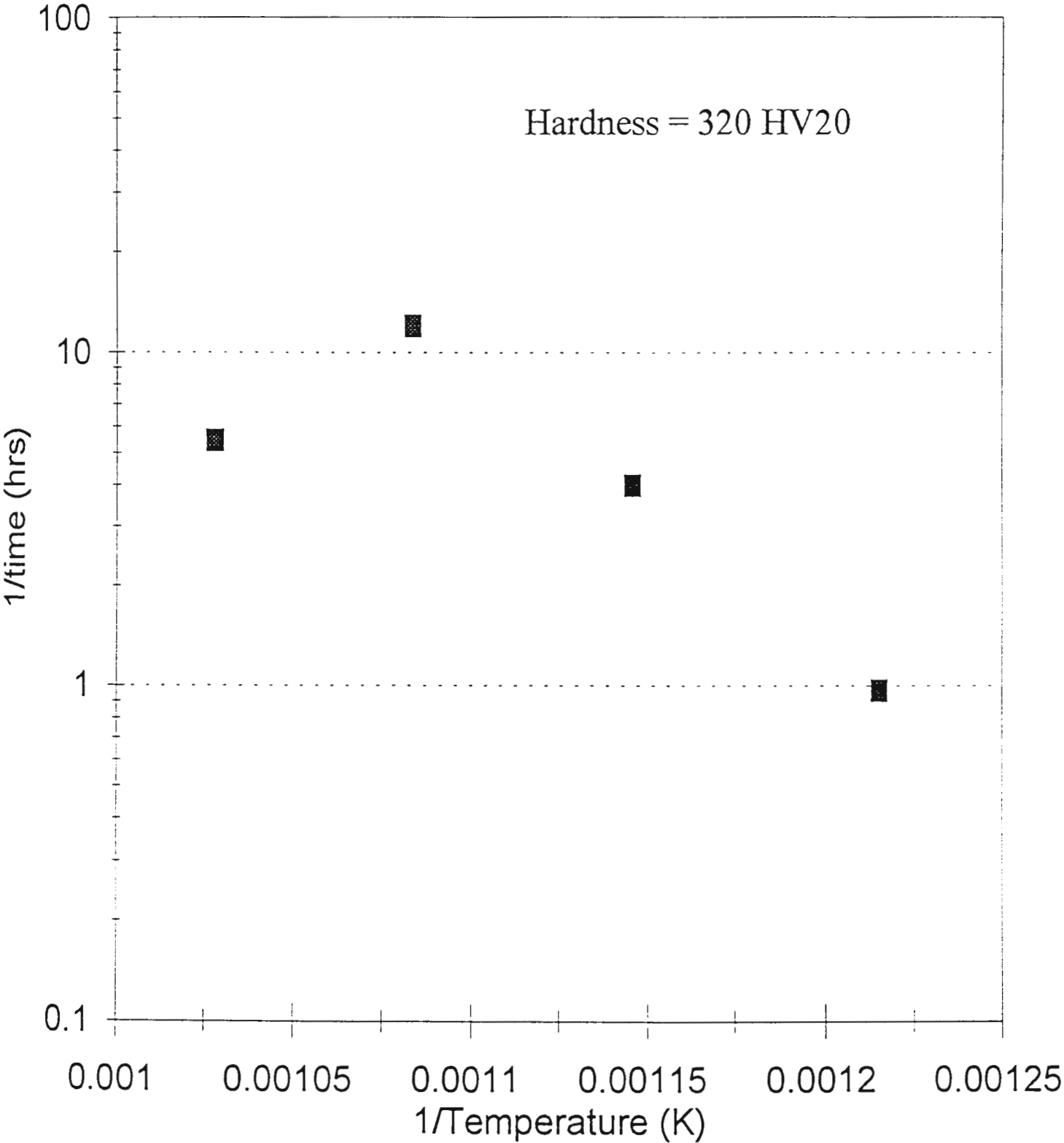


Figure 6.14

Graph of H vs Hardness for Alloy 3588
calculated with $C=11.45$

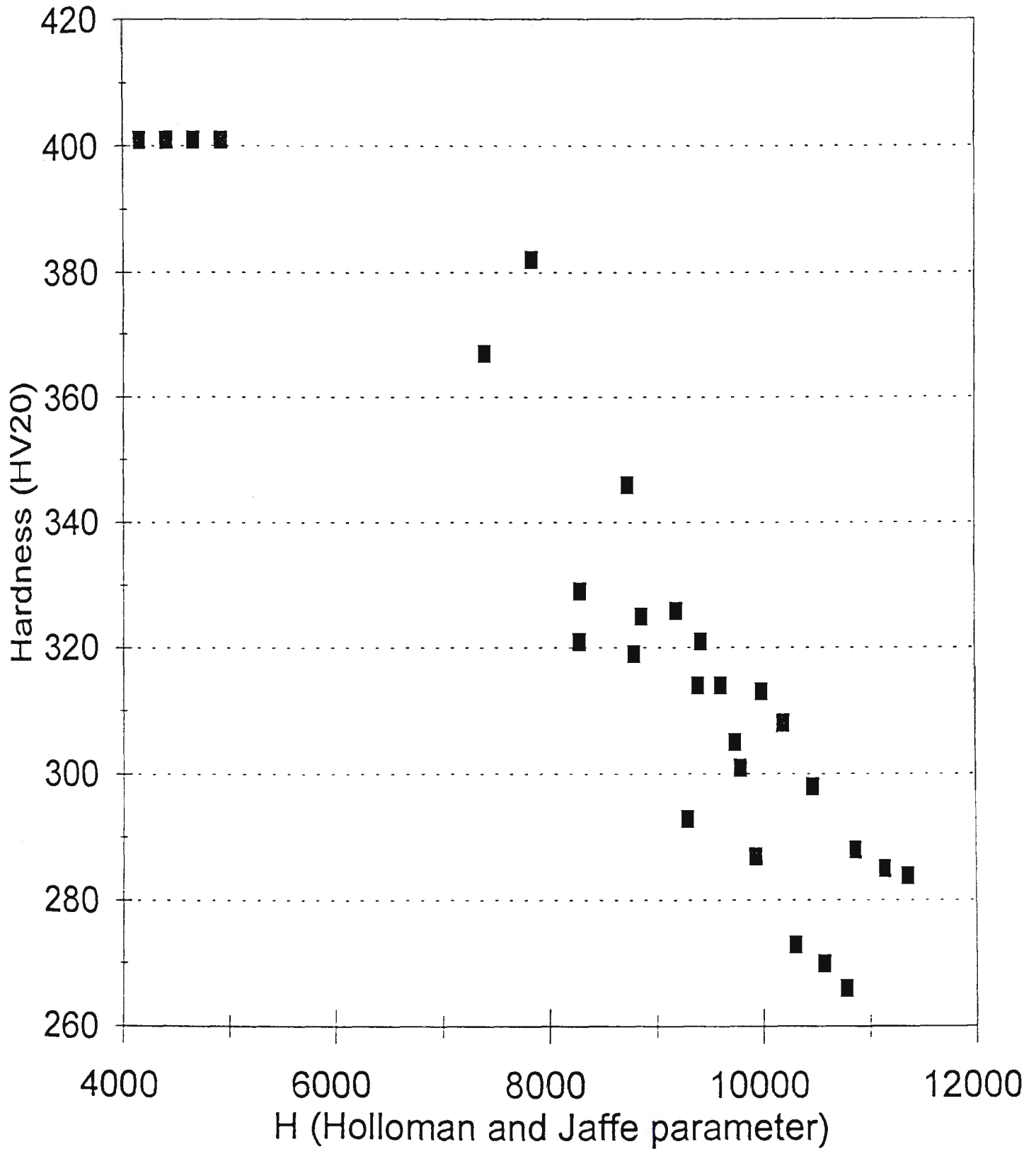
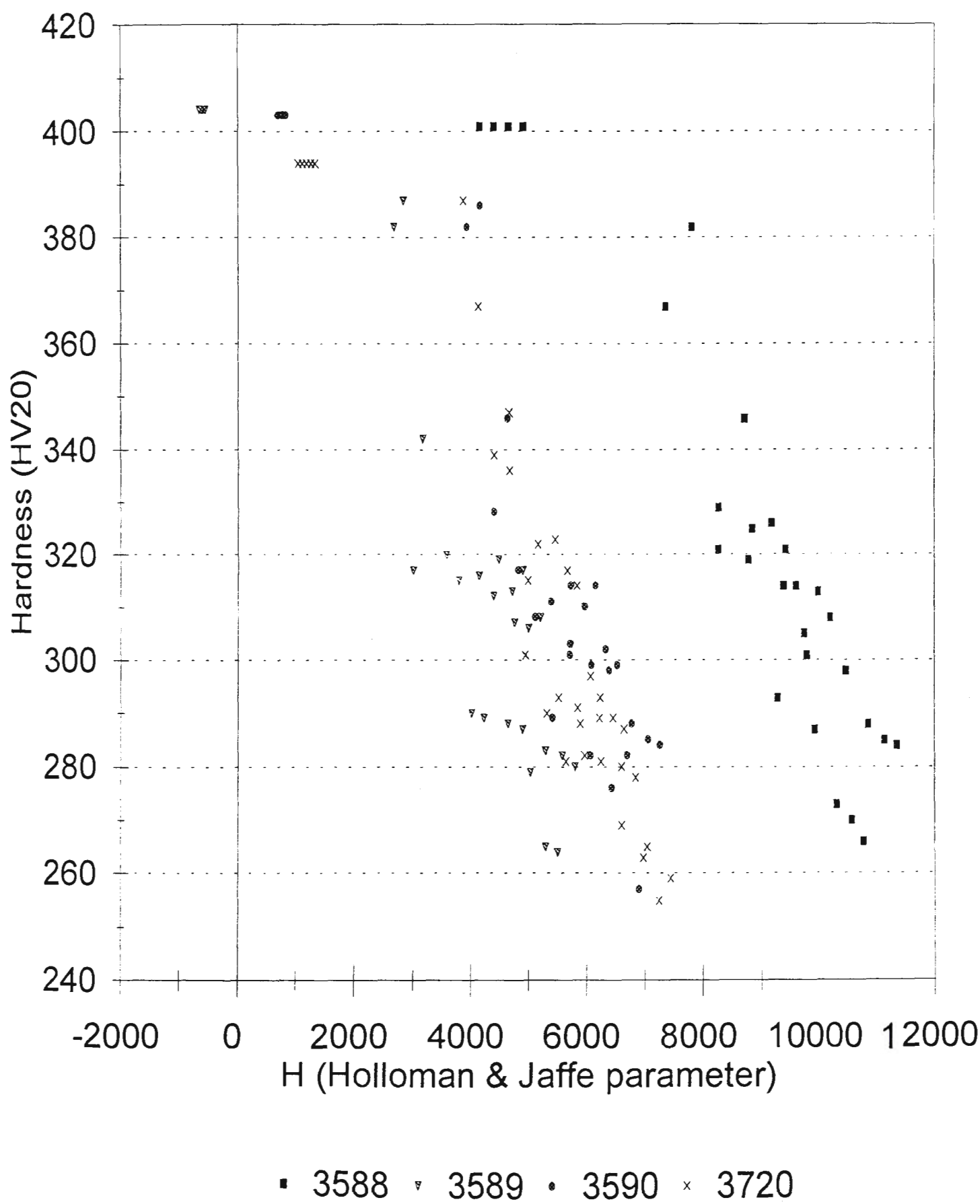


Figure 6.15

Combined Graph of H vs Hardness
For Alloys 3588, 3589, 3590, 3720



CHAPTER 7

Tensile Testing of Copper Containing Steels.

Results

As described previously in chapter 4, tensile testing was carried out in accordance with Australian Standard AS 1391-1991⁷². The test pieces used were 10mm in diameter and approximately 200mm long.

Table 7.1 contains the results of tensile tests carried out.

Table 7.1 Tensile Test Results

Series 1.

Alloy	Heat	Hardness	YS	UTS	Ext %	ROA %	Ratio
	T'ment	(Hv)			50mm		
					GL		
3588	1	401	1088*	1206*	12	57	.90
	2	391	1028	1176	14	58	.87
	3	325	953	973	16	62	.98
	4	287	783*	807*	18	70	.97
	5	270	749*	791*	24	67	.94

* - Mean of two results, the rest are single results
Hardness results are an average of three indentations.

Note

- 1 = as quenched
- 2 = 1hr 200 C
- 3 = 1hr 500 C
- 4 = 0.5 hr 650 C
- 5 = 1hr 650 C
- 6 = 1hr 450 C
- 7 = 1hr 600 C
- = not determined

Hv is Hv20

Table 7.1 continued

Alloy	Heat	Hardness	YS	UTS	Ext %	ROA %	Ratio
	T'ment	(Hv)			50mm		
				GL			
3589	1	404	961*	1172*	12	47	.82
	2	376	1008*	1191*	10	63	.85
	3	321	912	935	16	67	.98
	4	288	790*	822*	14	69	.96
	5	265	778	798	20	65	.97
3590	1	403	992*	1196*	14	55	.83
	2	399	1001	1174	12	60	.85
	3	319	898	918	16	63	.98
	4	282	776*	803*	18	69	.97
	5	282	761*	791*	18	72	.96
3591	1	407	992*	1205*	14	56	.82
	2	407	1057	1206	14	59	.88
	3	333	939	973	16	64	.97
	4	280	797*	817*	16	70	.97
	5	264	764*	791*	18	71	.97

Table 7.1 continued

Series 2

Alloy	Heat	Hardness	YS	UTS	Ext %	ROA %	Ratio
	T'ment	(Hv)			50mm		
					GL		
3677	1	338	763	966	18	-	.79
	6	-	802	880	18	71	.91
	3	-	721	797	20	-	.90
	7	270	715	782	20	-	.91
	5	268	661	738	20	-	.89
3678	1	313	645	848	-	-	.76
	6	-	702	801	-	74	.87
	3	-	659	748	22	-	.88
	7	257	644	729	22	-	.88
	5	245	622	702	22	-	.89
3679	1	262	616	802	20	-	.77
	6	-	678	770	20	77	.88
	3	-	657	724	20	-	.90
	7	237	647	717	24	-	.90
	5	230	640	685	22	-	.93

Table 7.1 continued

Alloy	Heat	Hardness	YS	UTS	Ext %	ROA %	Ratio
	T'ment	(Hv)	(MPa)	(MPa)	50mm		
					GL		
3680	1	282	627	816	20	-	.77
	6	-	677	769	18	79	.88
	3	-	621	700	20	-	.88
	7	232	629	699	20	-	.90
	5	228	592	674	22	-	.88

Table 7.1 continued

Series 3

Alloy	Heat	Hardness	YS	UTS	Ext %	ROA %	Ratio
	T'ment	(Hv)	(MPa)	(MPa)	50mm		
					GL		
3720	1	394	760*	965*	14*	57*	0.79*
	2	-	803*	981*	12*	54*	0.82*
	3	297	722*	791*	15*	68*	0.92*
	4	-	669*	728*	19*	71*	0.92*
	5	255	635*	701*	20*	73*	0.91*
	6	317	765*	839*	14*	67*	0.91*
3721	1	387	893*	1116*	5*	32*	0.80*
	2	-	973*	1118*	6*	33*	0.87*
	3	309	854*	884*	10*	46*	0.97*
	4	-	769*	799*	9*	49*	0.97*
	5	271	737*	775*	16*	62*	0.95*
	6	323	933*	962*	10*	48*	0.97*

Analysis and Discussion of Results

Figures 7.1 and 7.2 contain the yield and tensile strengths measured for all alloys in this study, also shown on these graphs are the specifications for BIS 80 ie yield strength above 690 MPa. and tensile strength between 790 and 930 MPa. Using these graphs it is easy to see which steels and heat treatment conditions pass the specification for Bisalloy 80. These graphs also show that only small variations in tempering temperature are needed to fine tune the mechanical properties of some of the steels and others will not pass the specification without the use of very low tempering temperatures.

It is evident from the above results and graphs that the following steels pass the Bis 80 specification for strength:

Table 7.2 Steels Passing the Tensile requirements of the BIS 80 Specification.

Alloy	Heat treatment condition	Comments
Series 1		
3588	0.5hr@650C	ratio 0.97
	1hr@650C	
3589	1hr@650C	ratio 0.97
3590	0.5hr@650C	ratio 0.97
	1hr@650C	ratio 0.96
3591	1hr@650C	ratio 0.97

Alloy	Heat treatment condition	Comments
Series 2		
3677	1hr@450C	
	1hr@500C	
3678	1hr@450C	
Series 3		
3721	1hr @ 500C	Elon<18%, ratio 0.97
	0.5hr@650C	Elon<18%, ratio 0.97
	1hr@650C	Elon<18%

The tensile information can also be used to determine which steels pass the military specifications MIL-S-16216(SH) and MIL-S-24645(SH). Table 7.3 contains the steels that pass the tensile requirements of MIL-S-16216(SH) (HY100).

Table 7.3 Steels Satisfying the Tensile Requirements for MIL-S-16216

Alloy	Heat Treatment Condition	Comments
<i>Series 1</i>		
3588	0.5hr@650°C, 1hr@650°C	
3589	1hr@650°C	
3590	0.5hr@650°C, 1hr@650°C	
3591	1hr@650°C	
<i>Series 2</i>		
3677	AQ, 1hr@450°C, 1hr@500°C, 1hr@600°C, 1hr@650°C	
3678	1hr@450°C	

Table 7.3 continued

Alloy	Heat Treatment Condition	Comments
<i>Series 3</i>		
3721	0.5hr@650°C,	Elon<18%
	1hr@650°C	Elon<18%

Table 7.4 shows the steels that pass the requirements for MIL-S-24645(SH) (HSLA 100).

Table 7.4 Steels Satisfying the Tensile Requirements for MIL-S-24645.

Alloy	Heat Treatment Condition	Comments
<i>Series 1</i>		
3588	0.5hr@650°C, 1hr@650°C	
3589	1hr@650°C	
3590	0.5hr@650°C, 1hr@650°C	
3591	1hr@650°C	
<i>Series 2</i>		
3677	AQ, 1hr@450°C, 1hr@500°C,	
	1hr@600°C, 1hr@650°C	
3678	1hr@450°C	
<i>Series 3</i>		
3721	1hr@500°C	Elon<18%, ROA<50%
	0.5hr@650°C,	Elon<18%, ROA<50%
	1hr@650°C	Elon<18%

The following steels satisfy the tensile requirements for all the specifications, Bis 80, MIL-S-16216 and MIL-S-24645:

Table 7.5 Steels Passing the Tensile Specifications for Bis 80, MIL-S-16216 and MIL-S-24645

Alloy	Heat treatment condition	Comments
Series 1		
3588	0.5 hr@650C	ratio 0.97
	1hr@650C	
3589	1hr@650C	ratio 0.97
3590	1hr@650C, 0.5hr@650C	ratio0.97,0.96
3591	1hr@650C	
Series 2		
3677	1hr@450C	
	1hr@500C	
3678	1hr@450C	
Series 3		
3721	1 hr @ 500C	Elon<18%, ratio0.97, ROA<50%
	0.5hr@650C	Elon<18%, ratio0.97, ROA<50%
	1 hr@650C	Elon<18%

The following steels also satisfy the BHP SPPD steelmaking compositional constraints :
3677 and 3721.

Several of the alloys studied, notably the Series 1 steels and 3721 have difficulty satisfying the ratio constraints of the Bis 80 specification. High ratios of yield to tensile strength are not uncommon for these types of steels^{31,32,33,35,36}. It is possible that this problem could be solved by using a higher austenitising temperature. Work by Wingrove and Chevis⁸⁵ on Bisalloy 80pv has shown that an increase in austenitising temperature reduces the yield to tensile strength ratio from high in the 90 percentile to, in some cases, less than 90%. Although this may reduce the impact toughness slightly, due to the mechanism reducing the ratio, these steels demonstrate more than adequate toughness and a reduction could probably be tolerated.

The Series 3 steel 3721 fails all specifications with respect to the elongation observed. This steel demonstrated odd fracture faces on the tensile samples. There appeared to be a lack of centreline ductility and a shear zone in the centre of the specimen rather than the characteristic cup and cone failure. Scanning Electron Microscope (SEM) analysis revealed high levels of segregation of silicon and manganese in the centre of these samples. This segregation probably contributed to the unusual fracture and is almost certainly related to the lack of ductility measured in this steel, consequently the elongation quoted is probably not characteristic of the alloy in production circumstances. This steel certainly stands out from all the others in all series when compared on the basis of measured elongation to fracture, particularly when tempered at temperatures above 450°C.

Figure 7.3 comprises mechanical property information showing the effect of copper on yield and tensile strength as the tempering temperature changes.

Figures 7.4 and 7.5 are composite graphs made up of information from a study by Cabello⁸⁶ of as rolled and aged copper containing steels and information from this study. Figure 7.4 is a comparison of thermomechanically controlled processed (TMCP) results from Cabello and as quenched results from the work presented here. TMCP and as quenched results are

compared because, in both cases no aging was carried out. Figure 7.5 compares results in the TMCP and aged condition with those in the quenched and tempered condition. This allows comparison of results after copper has precipitated and affected mechanical properties.

Table 7.6 contains the results of regression analyses carried out on the combined results.

Table 7.6. Regression Analysis Results

Heat	Fit	
treatment	Regression line	R ² (correlation coefficient)
state		
comparing TMCP and As Quenched results		
Yield	$y = 1.98x + 99.07$	0.952
Tensile	$y = 2.43x + 144.41$	0.967
comparing Aged 550 and Tempered 650 results		
Yield	$y = 2.93x - 68.95$	0.895
Tensile	$y = 2.53x + 105$	0.903

The high correlation coefficients indicate the consistency between the two sets of data used for each regression line.

Figure 7.6 presents the effect of variation of copper content on mechanical properties, yield and tensile strength at a tempering temperature of 650°C. Results for copper contents from 0-1% are presented and it is evident that, within the limitation of varying boron in the various steels, as the copper content rises the yield and tensile strengths increase, up to a maximum between about 0.7 and 0.9 %. The presence of about 50% bainitic ferrite in the 0.4% Cu, B free steel (3677) would only be expected to have a small effect on the subsequent precipitation

hardening by copper⁹³. The rise is gradual between 0 and 0.4% copper becoming more rapid from 0.4 to the maximum. The yield strength, particularly, increases in this region rising from about 660 to 760 MPa. This dramatic rise in yield strength is accompanied by a less dramatic rise in tensile strength and thus the ratio between the two increases. This is not desirable in structural steels but not atypical of these types of steels. Krishnadev³⁶ reports similar behaviour in copper containing, precipitation hardening steels, water quenched and aged at 550 °C. The results presented in Figure 7.6, support the previously stated observation (chapter 6) that the optimum level of copper for producing precipitation hardening in this type of steel and this process appears to be around 0.7-0.9% copper.

Figure 7.7 shows essentially no effect of copper on either elongation or reduction of area. Figure 7.8 shows previously discussed results on the effect of various copper contents on the ratio of yield to tensile strength.

Figure 7.1

Effect of Tempering Temperature on the Yield Strength of Copper Steels

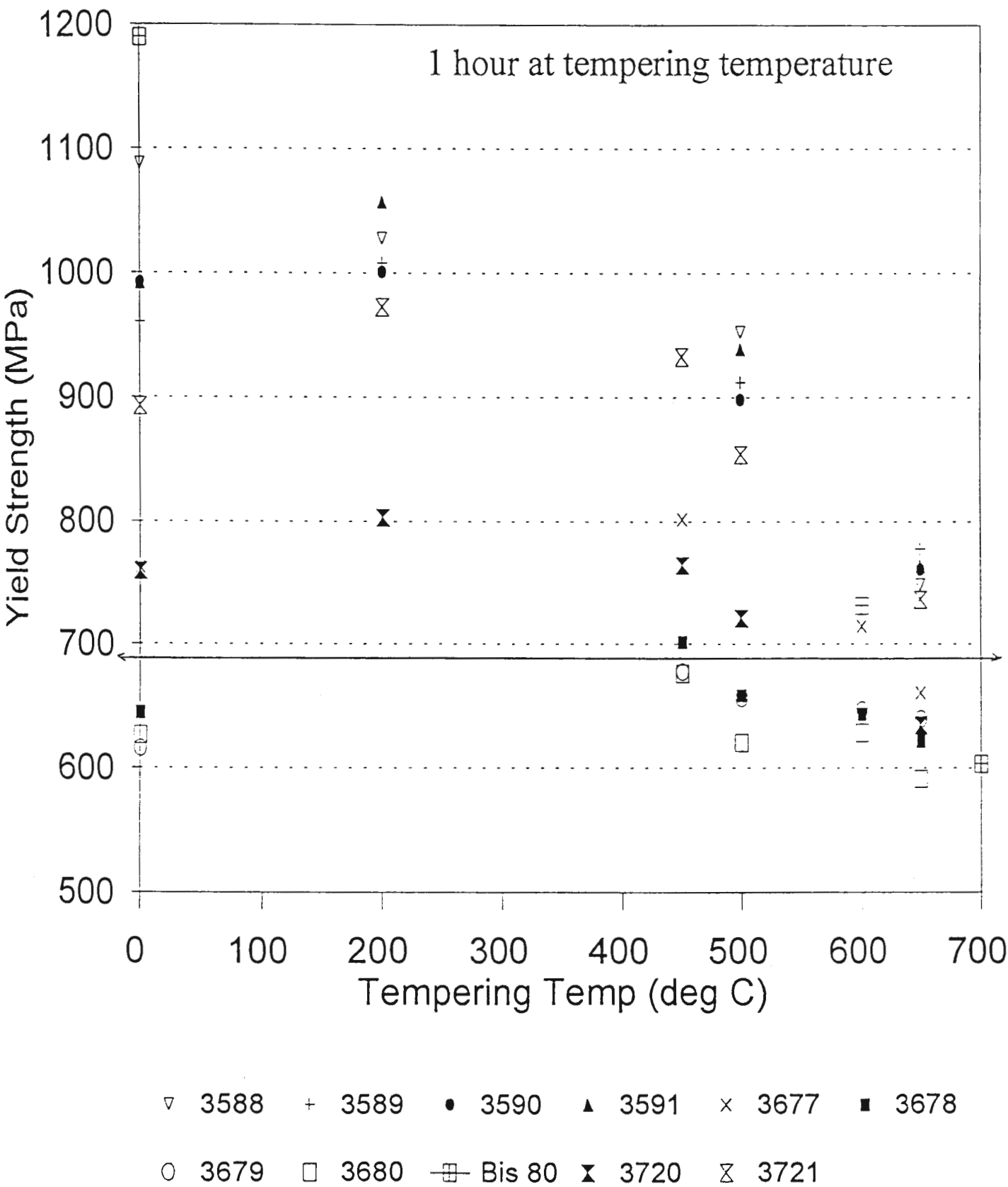


Figure 7.2

Effect of Tempering Temperature on the Tensile Strength of Copper Steels

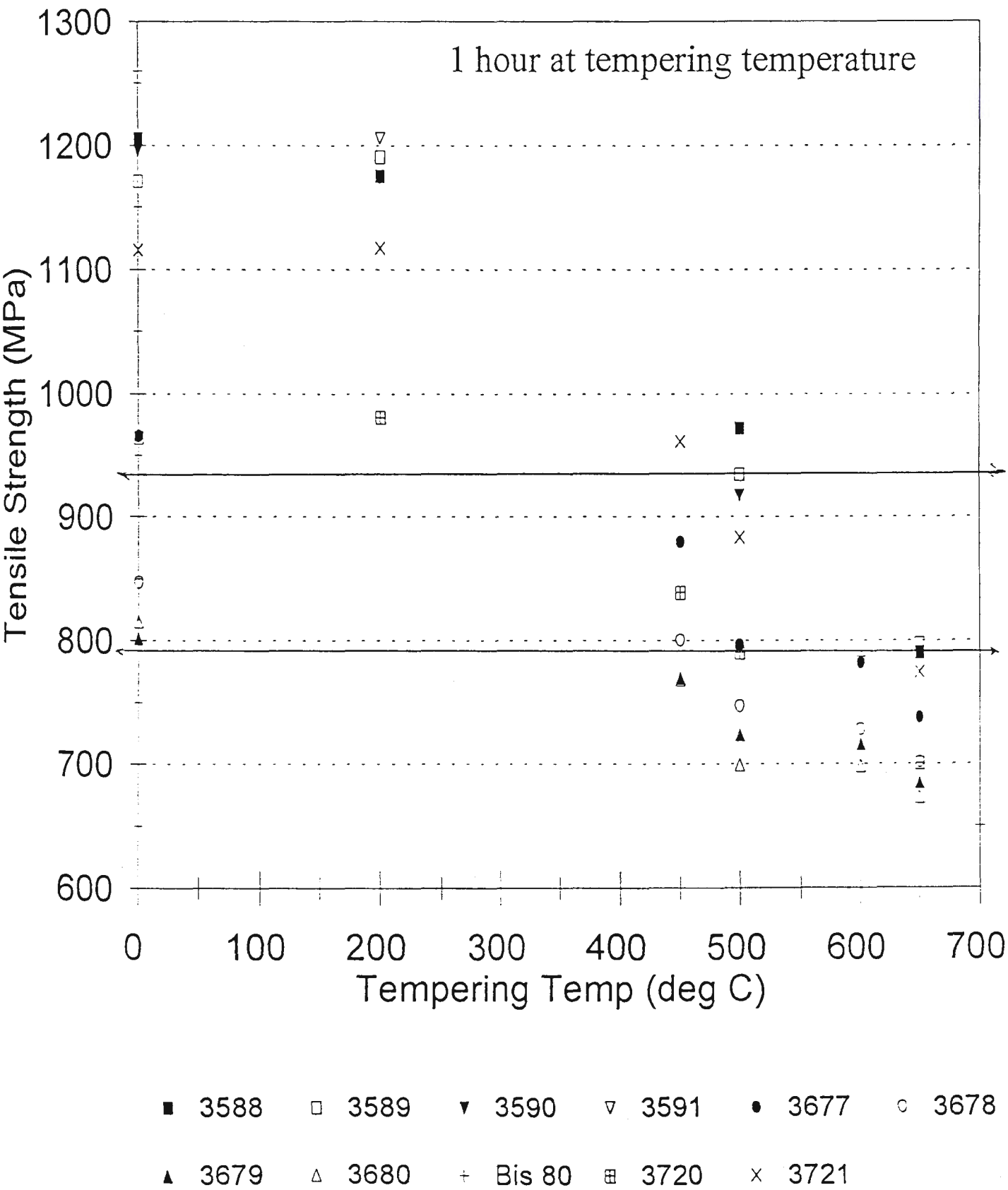
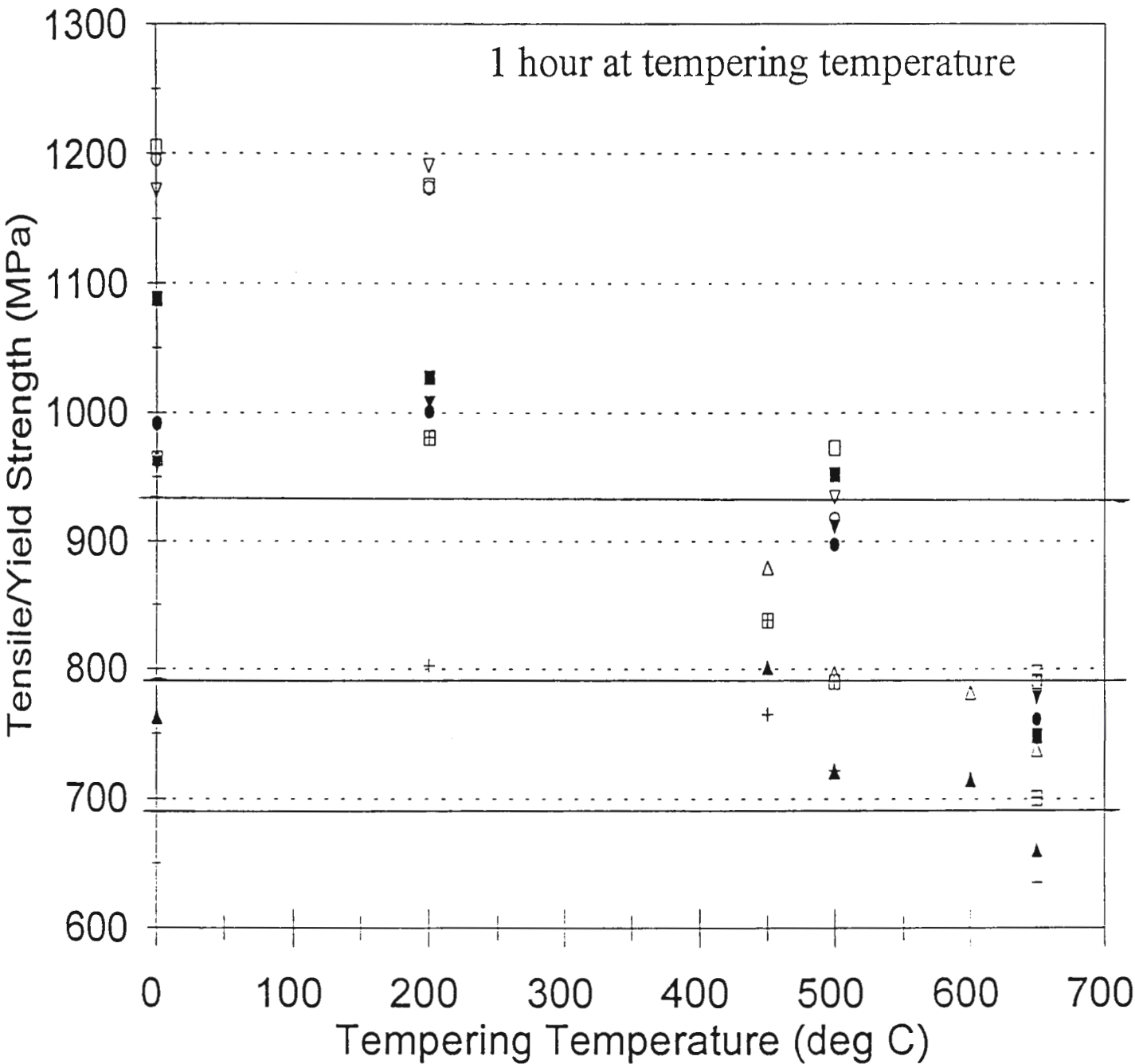


Figure 7.3

Effect of Tempering Temperature on the Tensile Properties of Copper Steels



■ 3588 1%Cu Y/S □ 3588 1%Cu T/S ▼ 3589 0.8%Cu Y/S ▽ 3589 0.8%Cu T/S ● 3590 0.5%Cu Y/S
○ 3590 0.6%Cu T/S ▲ 3677 0.4%Cu Y/S △ 3677 0.4%Cu T/S + 3720 0%Cu Y/S ▣ 3720 0%Cu T/S

Figure 7.4

**Comparison of TMCP & As-Quenched
Results for Copper Steels**

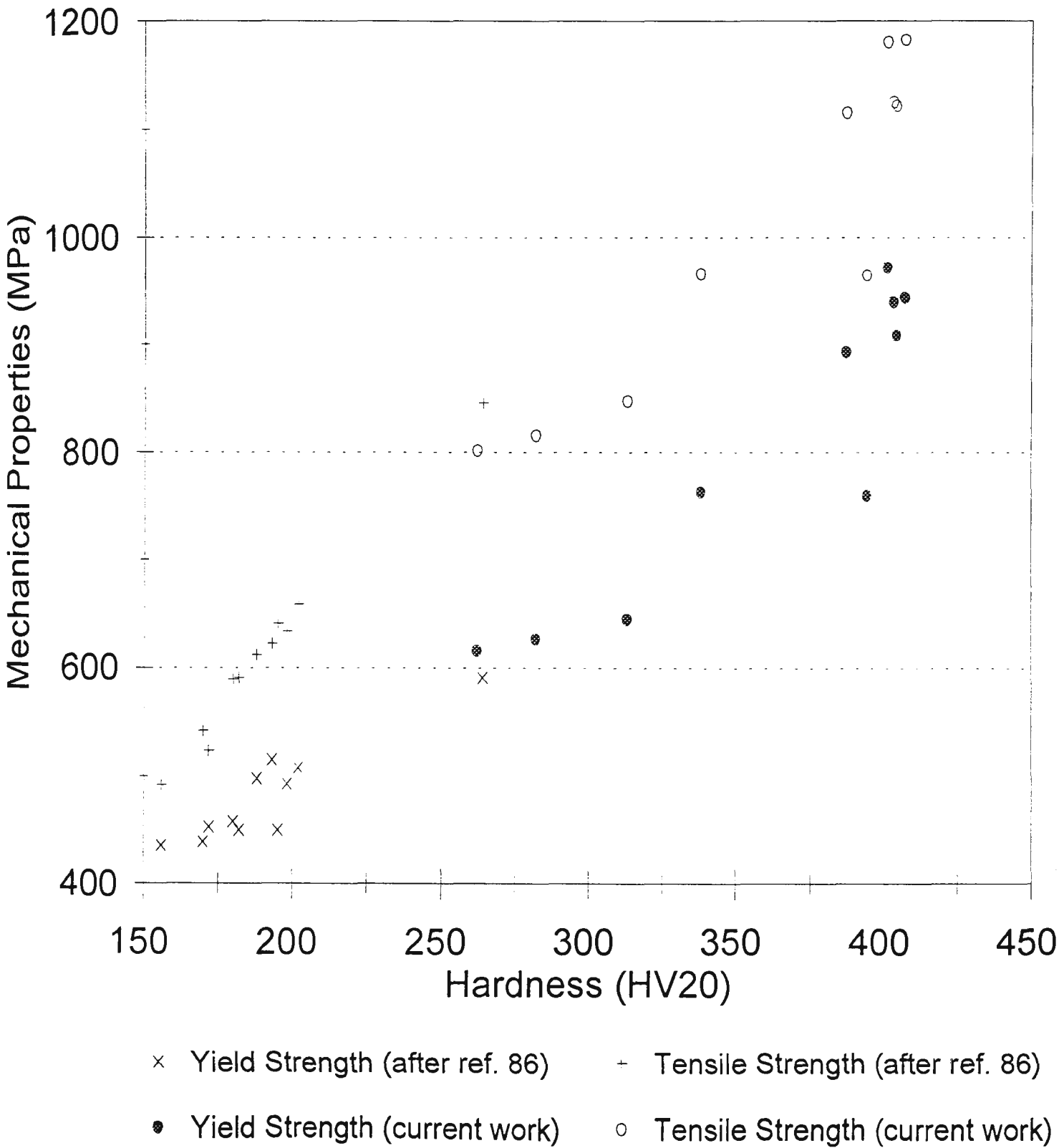
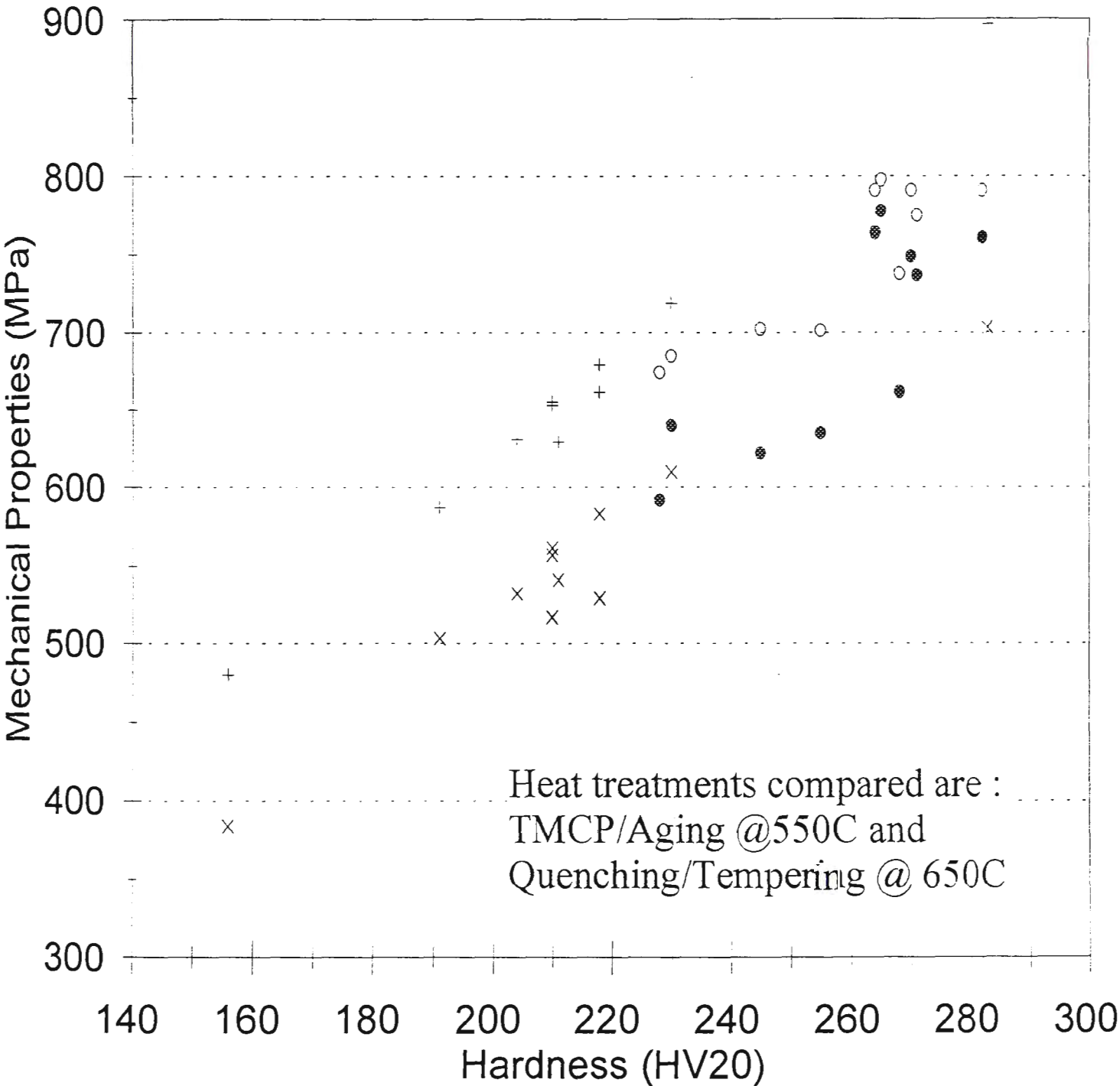


Figure 7.5

Comparison of TMCP/Aged and Q&T
Results for Copper Steels



- x Yield Strength (after ref.86)
- + Tensile Strength (after ref. 86)
- Yield Strength (current work)
- Tensile Strength (current work)

Figure 7.6

Effect of Copper on Tensile Properties of Copper Steels

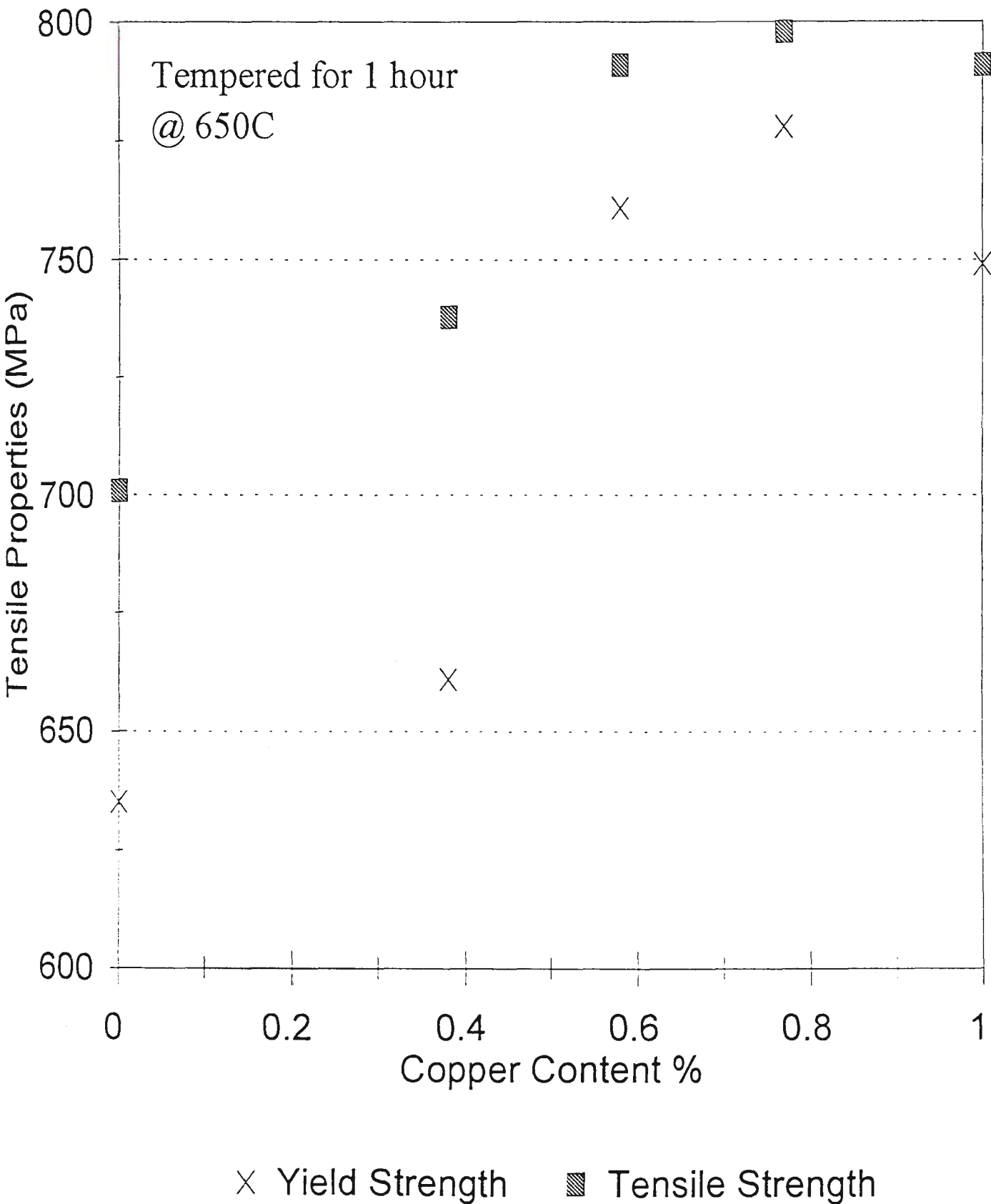


Figure 7.7

Effect of Copper on Tensile Elongation and Reduction of Area

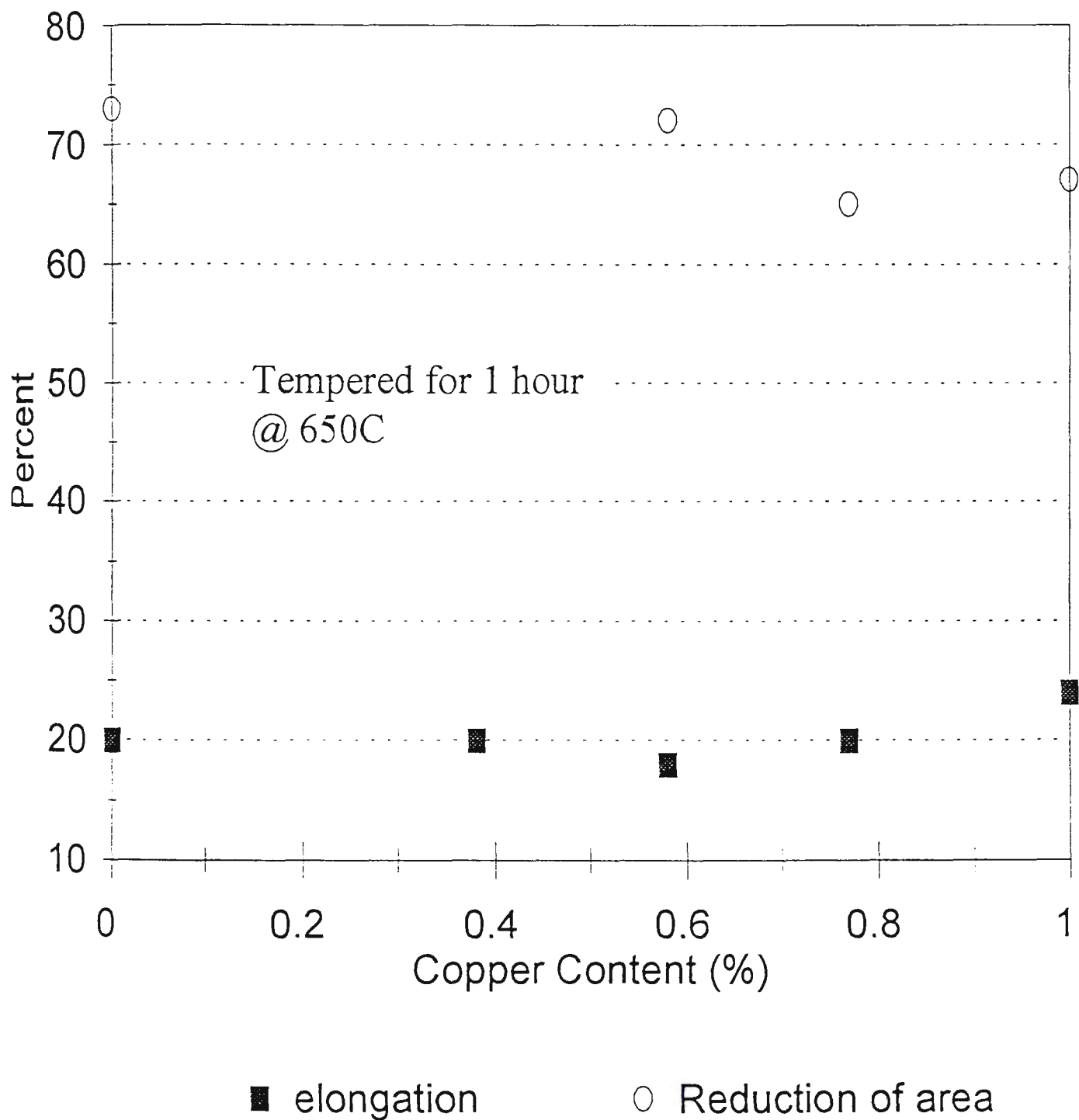
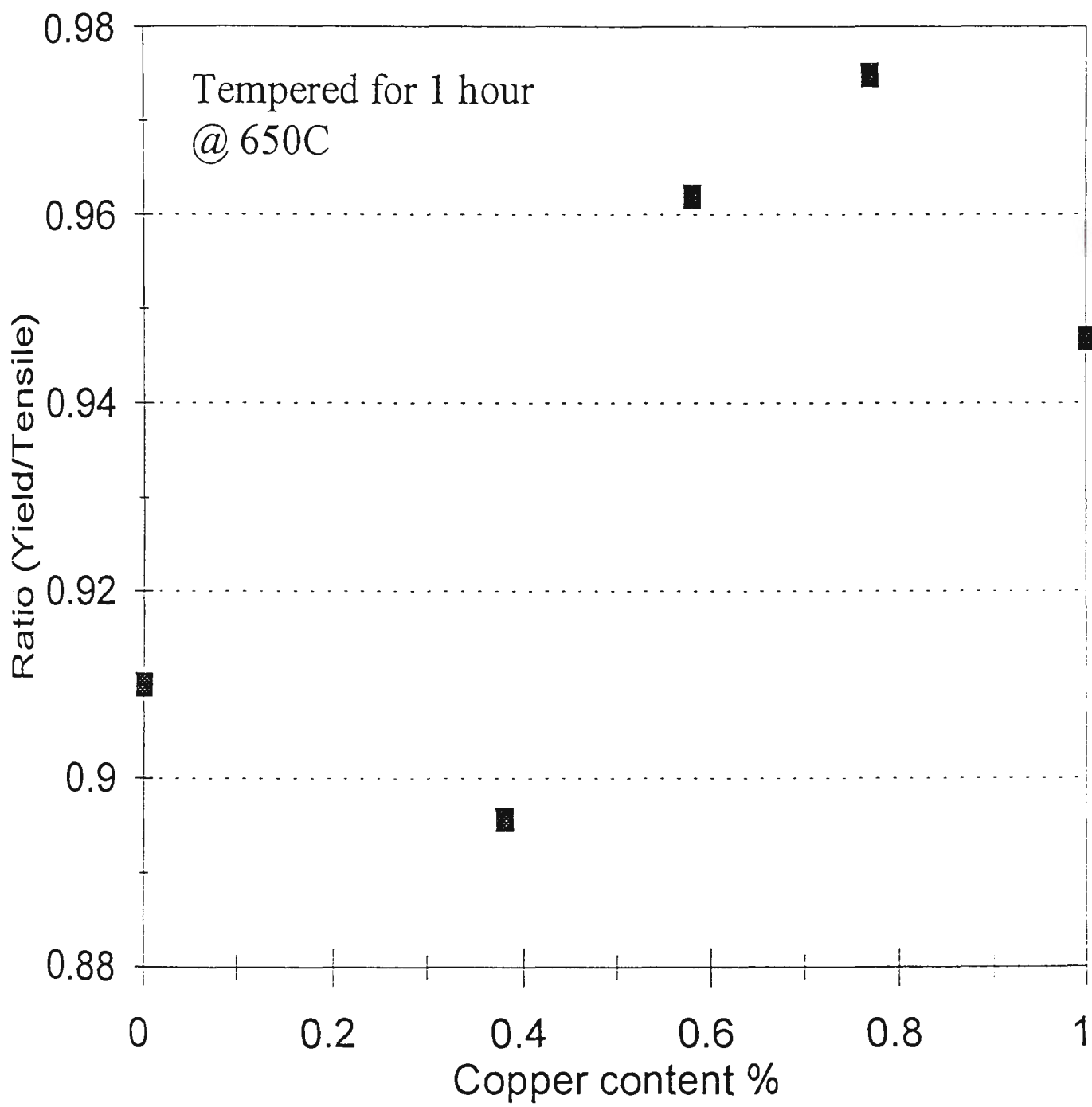


Figure 7.8

**Effect of Copper on the Ratio of Yield
to Tensile Strength**



CHAPTER 8

Charpy V Notch (CVN) Testing of Copper Containing Steels.

Results

The details of the testing carried out to produce the results presented here are described in the experimental procedures, Chapter 4. Table 8.1 contains the results of Charpy impact testing.

Table 8.1 Charpy Impact Results

Alloy	heat	Temp (°C)			
	treat't	+20	-20	-84	
Series 1					
3588	1	191	165	-	Energy(J)
		-	-	-	Fibrosity(%)
	7	209	165	-	
		-	-	-	
	5	-	-	32	
		-	-	20	

Note

- 1 = as quenched
- 2 = 1 hr 200C
- 3 = 1 hr 500C
- 4 = 0.5 hr 650 C
- 5 = 1 hr 650 C
- 6 = 1 hr 450 C
- 7= 1 hr 600 C
- = not determined

Charpy impact results quoted are an average of 3 tests as are fibrosities.

Table 8.1 Continued

Alloy	heat treat't	Temp (°C)			
		+20	-20	-84	
3589	1	193	207	-	Energy(J)
		-	-	-	Fibrosity(%)
	7	224	207	-	
		-	-	-	
	5	-	-	49	
		-	-	27	
3590	1	194	193	-	Energy(J)
		-	-	-	Fibrosity(%)
	7	214	204	-	
		-	-	-	
	5	-	-	195	
		-	-	92	
3591	1	171	116	-	Energy(J)
		-	-	-	Fibrosity(%)
	7	185	151	-	
		-	-	-	
	5	-	-	81	
		-	-	43	

Table 8.1 continued

Series 2

Alloy	heat treat't	Temp (°C)			
		+20	-20	-84	
3677	1	192	102	-	Energy(J)
		-	-	-	Fibrosity(%)
	6	260	221	38	
		100	100	40	
3678	1	246	211	-	Energy(J)
		-	-	-	Fibrosity(%)
	6	289	300+	135	
		96	100	68	
3679	1	298	270	-	Energy(J)
		-	-	-	Fibrosity(%)
	6	300+	300+	193	
		100	99	100	
3680	1	313	284	-	Energy(J)
		-	-	-	Fibrosity(%)
	6	300+	300+	276	
		98	100	99	

Table 8.1 continued

Alloy	heat	Temp (°C)			
	treat't	+20	-20	-84	
series 3					
3720	1	151	83	18	Energy(J)
		93	50	5	Fibrosity(%)
	6	198	136	12	
		100	77	5	
	5	227	202	23	
		100	85	15	
3721	1	177	125	23	Energy(J)
		100	81	5	Fibrosity(%)
	6	207	142	11	
		100	77	10	
	5	233	241	50	
		100	98	8	

The above results and graphs in Figures 8.1 to 8.4 present the results of Charpy impact testing.

Analysis and Discussion of Results

Figure 8.1 demonstrates the effect of tempering temperature on absorbed energy. The general trend in all the steels tested is that absorbed energy increases as tempering temperature increases. Figures 8.2 and 8.3 show the same data separated for clarity. It is evident that all the steels examined satisfy the Bisalloy 80 specification of 40 J at -20°C.

Figure 8.4 is an attempt to determine any effect on -20°C Charpy energy of copper content. No clear trend is evident here and it may be too simplistic a view to expect any trend due solely to variation in copper.

Figure 8.5 presents a collection of Charpy transition curves for temperatures from +20°C to -84°C. All the steels were tested in the heat treatment condition that satisfied the 690 MPa yield strength criterion. The Series 2 steels, 3679 and 3680 which failed to satisfy this yield strength criterion, were tempered at the same temperature as the other Series 2 steels. Shown on figure 8.5 is the information for the series 1, 2 and 3 steels. All the steels show a loss of impact toughness as test temperature falls. From the energy results it is not clear whether the lower shelf energy has been reached at -84°C, however Figure 8.6 indicates that two and probably three of the Series 1 steels are approaching the lower shelf of absorbed energy (fibrosity <10%) at -84°C while 3590 is still on the upper shelf. Due to a lack of data, the +20°C fibrosity for the Series 1 steels was assumed to be 90%. Judging by the absorbed energy and the fibrosities displayed by the other Series (2 and 3) at +20°C this appears a reasonable assumption. Figure 8.7 indicates that two of the Series 2 steels show 100% fibrosity and are still on the upper shelf, while 3677 and 3678 exhibit falling fibrosity at -84°C but are still not at the lower shelf of toughness. The Series 3 steels exhibit the lowest impact toughness at low temperature and appear to be at, or very near

the lower shelf at -84°C.

These impact transition curves are important in assessing which steels have satisfied the impact requirements for the BIS 80 specification and the two U.S military specifications MIL-S-16216 and MIL-S-24645.

Table 8.2 indicates the alloys that satisfy the BIS 80 specification for impact toughness.

Table 8.2 Steels passing the impact energy requirements for BIS 80 (40J at -20°C).

Steel	Heat treatment Condition
<i>Series 1</i>	
3588	All investigated
3589	All investigated
3590	All investigated
3591	All investigated
<i>Series 2</i>	
3677	All investigated
3678	All investigated
3679	All investigated
3680	All investigated
<i>Series 3</i>	
3720	All investigated
3721	All investigated

The two specifications for HY100(MIL-S-16216(SH)) and HSLA 100(MIL-S-24645(SH)) call for the following impact toughness: 81J@-84°C and 54J@-18°C for HY100, 108J@-18°C and 81J@-84°C for HSLA 100. Table 8.3 shows the steels that pass the impact toughness specification for MIL-S-16216(SH).

An assumption has been made that a steel that satisfies the specification at -20°C will satisfy the specification at -18°C. Some interpolation of values for missing results has also been conducted in order to carry out this part of the analysis.

Table 8.3. Steels passing the impact energy requirements for MIL-S-16216(SH) HY 100.

Steel	Heat treatment Condition
<i>Series 1</i>	
3590	1 hr @ 650°C
3591	1 hr @ 650°C
<i>Series 2</i>	
3678	1 hr @ 450°C
3679	1 hr @ 450°C
3680	1 hr @ 450°C

Table 8.4 contains the steels that pass the impact energy requirements for MIL-S-24645(SH)

Table 8.4. Steels passing the impact energy requirements for MIL-S-24645(SH) HSLA 100.

Steel	Heat treatment Condition
<i>Series 1</i>	
3590	1hr@650°C
3591	1hr@650°C
<i>Series 2</i>	
3678	1hr@450°C
3679	1hr@450°C
3680	1hr@450°C

Table 8.5 highlights the steels passing the impact energy requirements of all the specifications, BIS 80, HY 100 and HSLA 100

Table 8.5 Steels Passing the Impact Energy Requirements for all Specifications

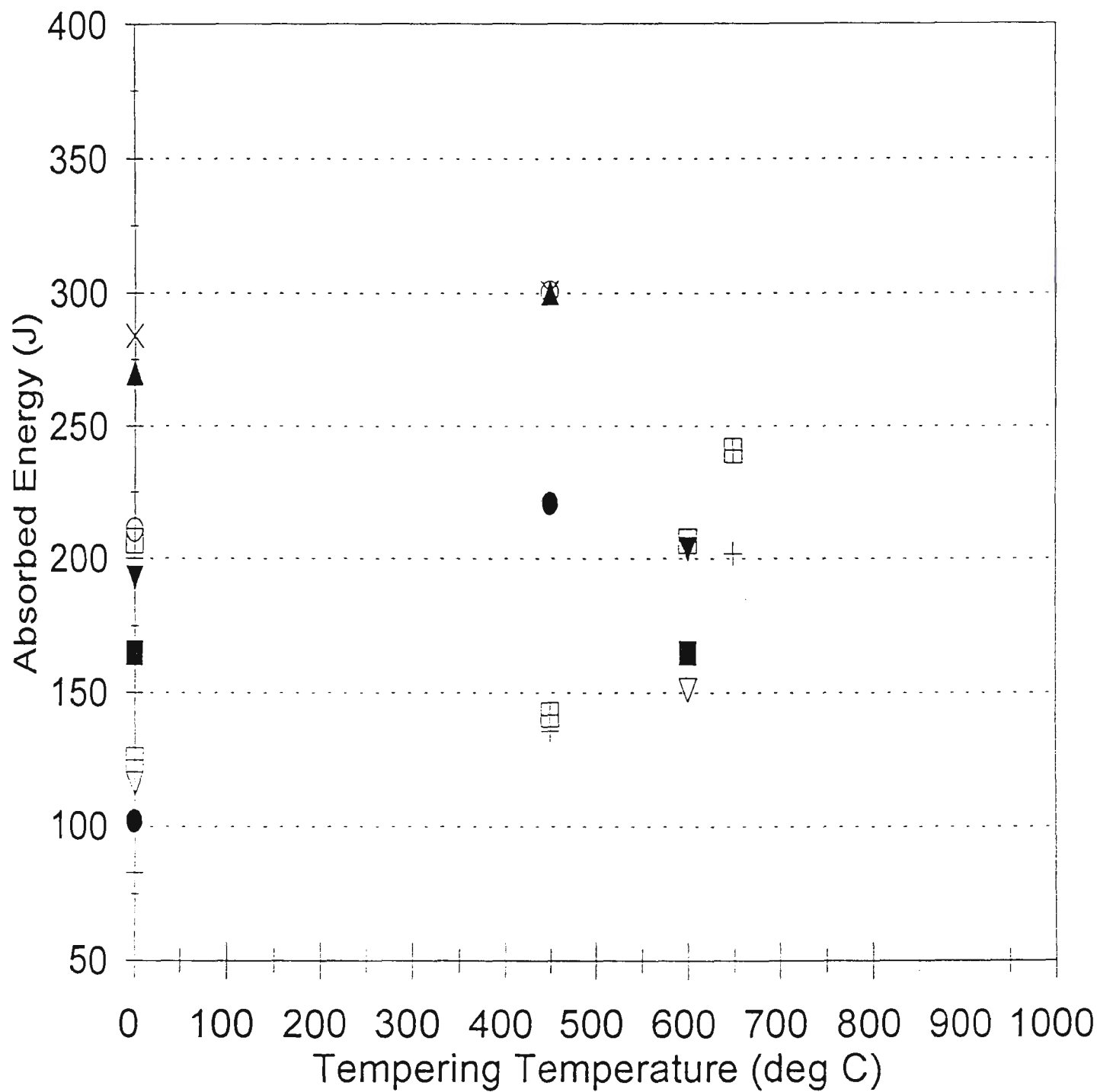
Steel	Heat treatment Condition
<i>Series 1</i>	
3590	1hr@650°C
3591	1hr@650°C
<i>Series 2</i>	
3678	1hr@450°C
3679	1hr@450°C
3680	1hr@450°C

Figure 8.8 contains the Charpy V notch toughness results for steels of various copper levels. There does not appear to be any clear and recognisable trend in the effect of copper on the impact transition behavior. One steel does, however, stand out from the others and that is 3590. This steels exhibits outstanding low temperature impact toughness and its behaviour appears somewhat anomalous when compared with the others. The reason for this behaviour is unknown and beyond the scope of this project.

Figure 8.1

Charpy Test Results for Copper Steels

Test Temperature - 20 C



■ 3588 □ 3589 ▼ 3590 ▽ 3591 ● 3677
○ 3678 ▲ 3679 × 3680 + 3720 ▣ 3721

Figure 8.2

Charpy Test Results, Series 1 Steels
Test Temperature -20 C

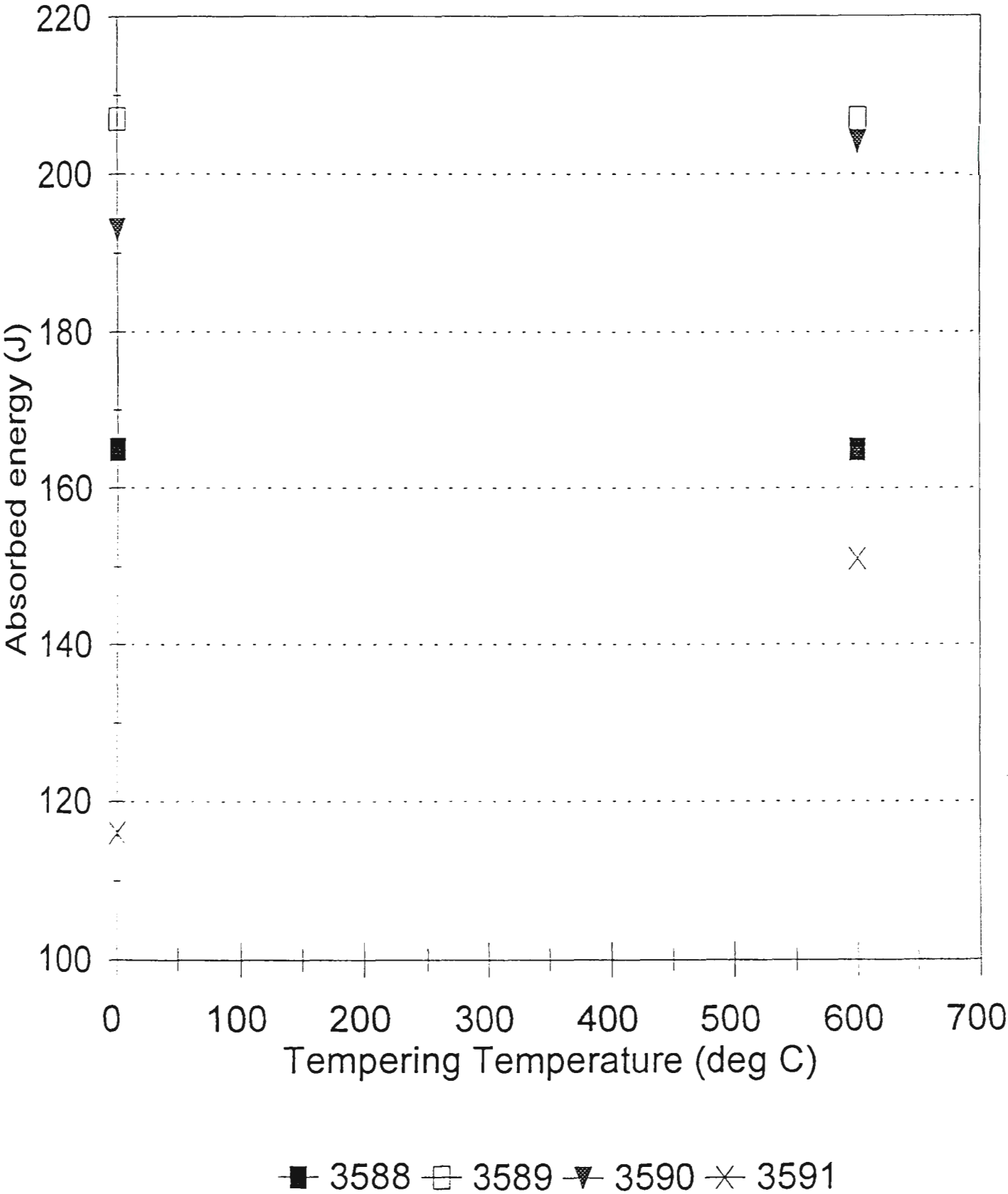
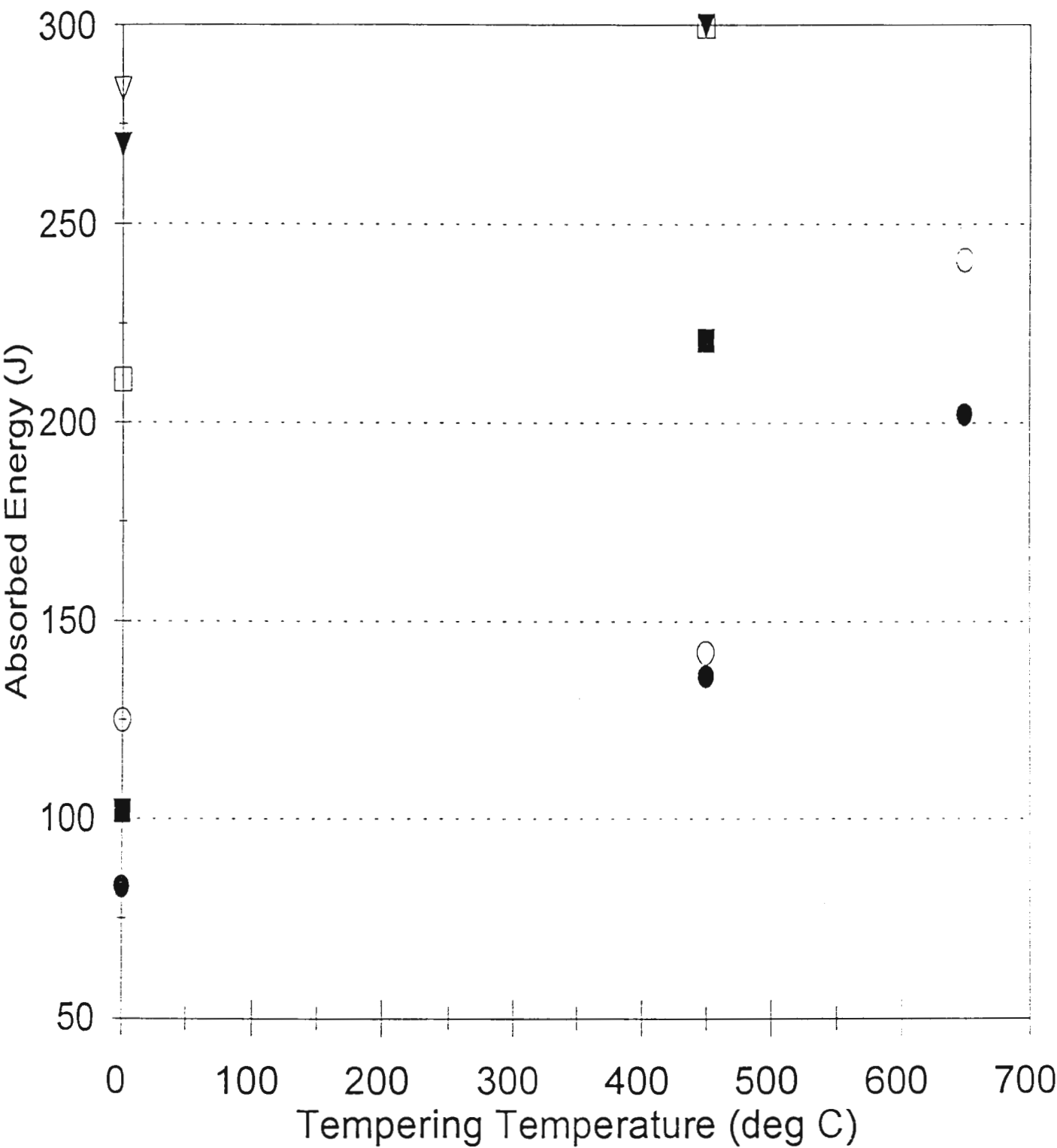


Figure 8.3

Charpy Test Results, Series 2 and 3
Steels. Test Temperature -20 C



■ 3677 □ 3678 ▼ 3679 ▽ 3680 ● 3720 ○ 3721

Figure 8.4

**Effect of copper on Charpy results for
the Steels studied. Test temp. -20 C**

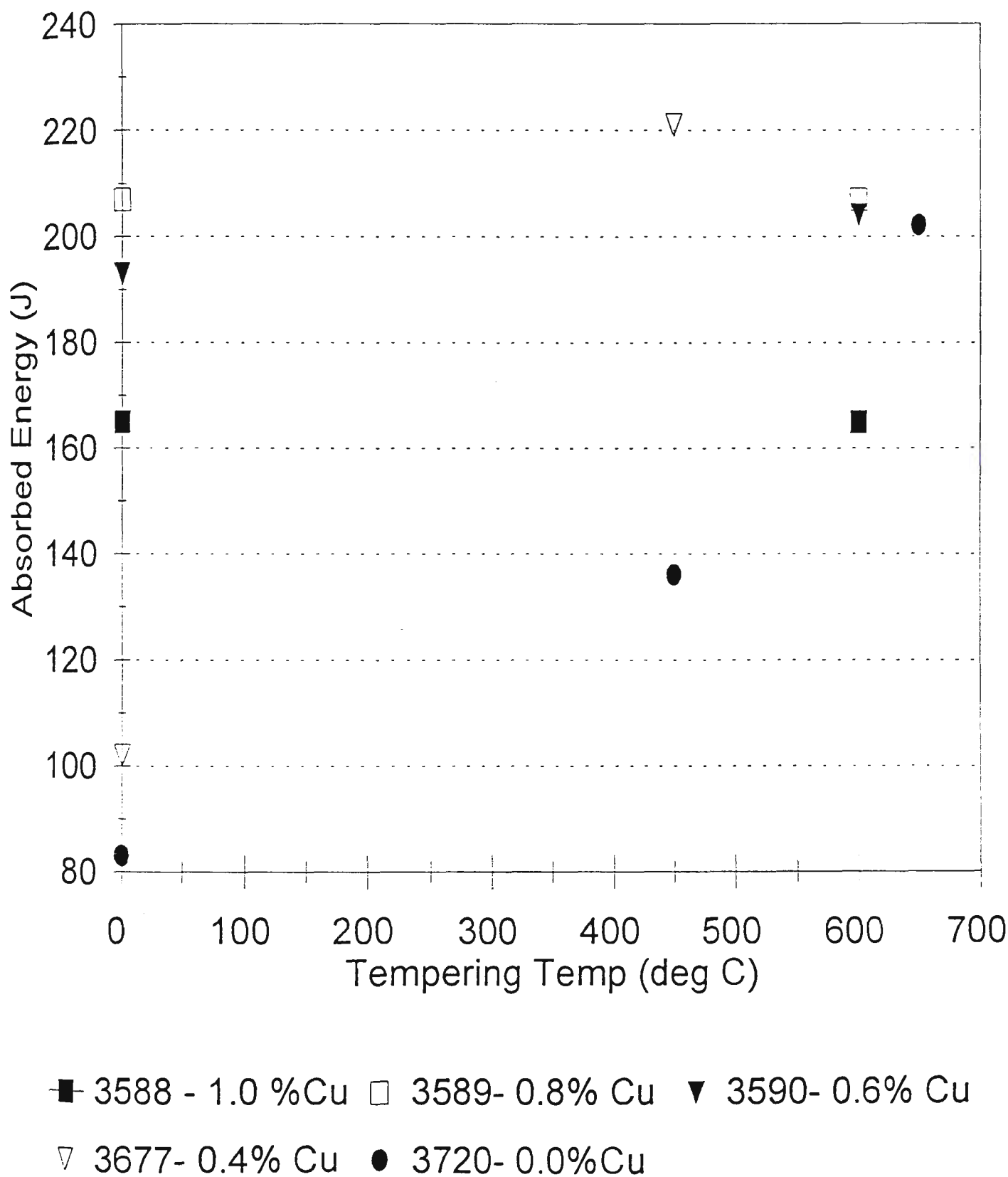
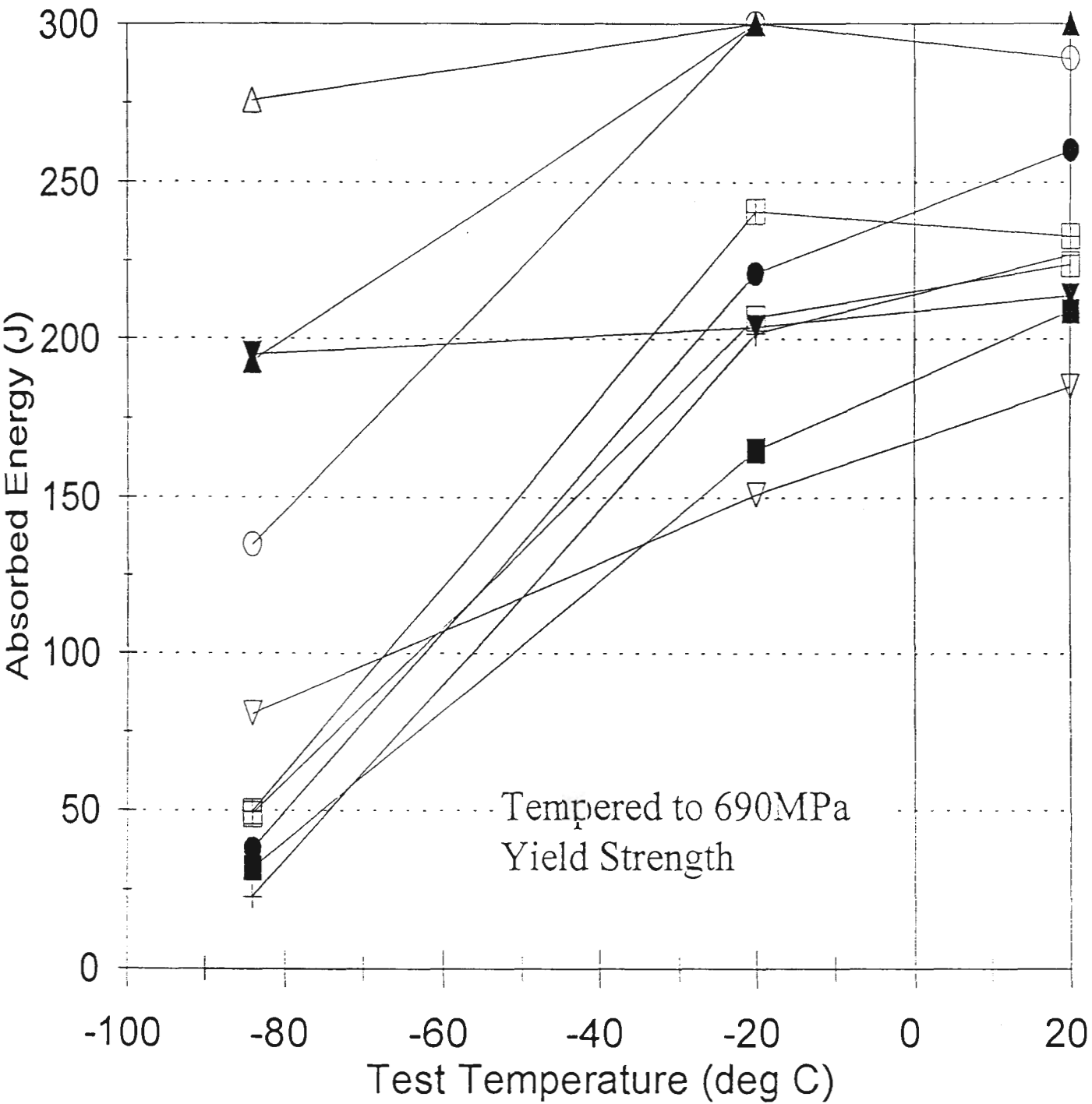


Figure 8.5

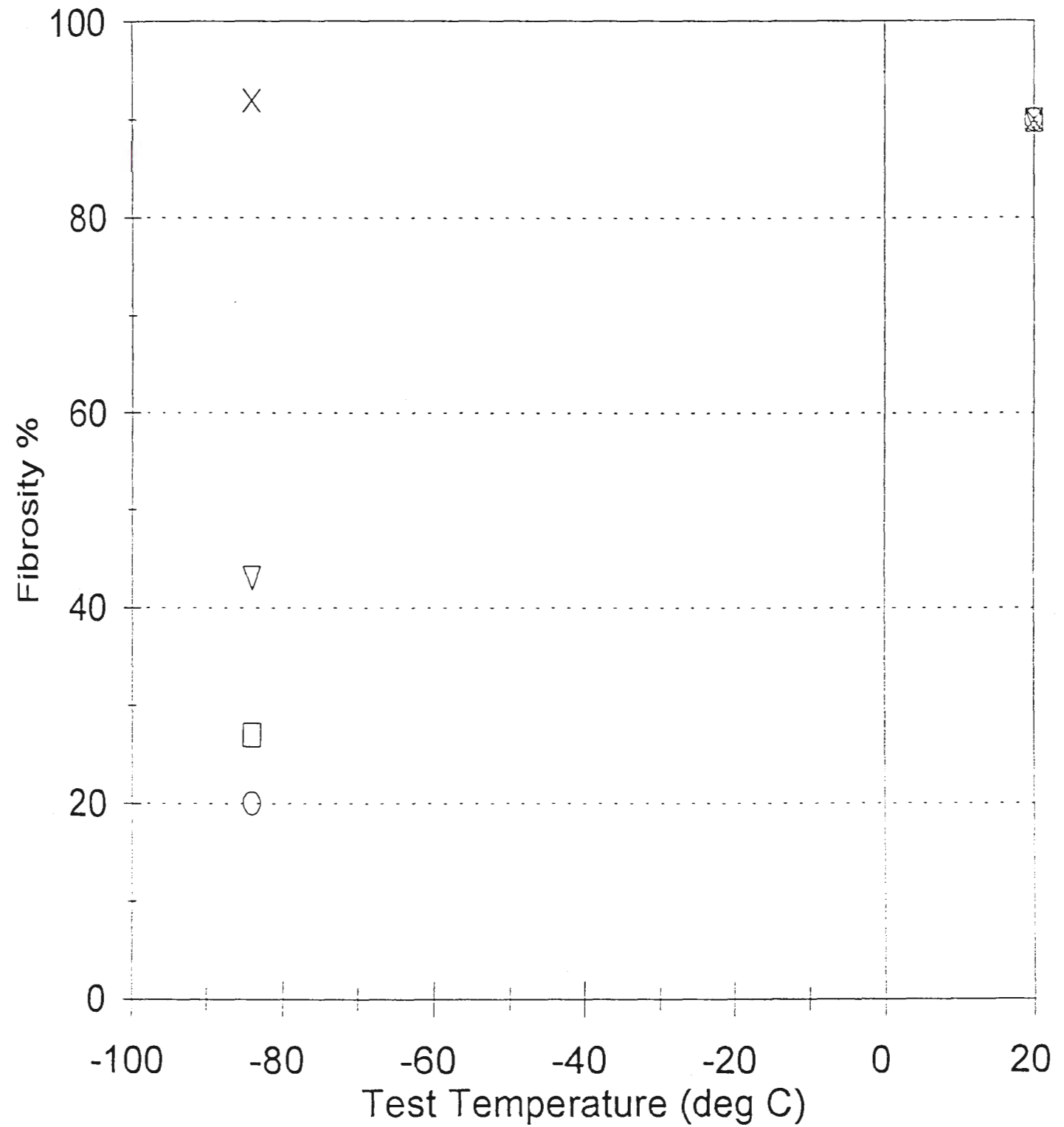
Charpy Transition Curves
Series 1, 2 & 3 Steels



- 3588 □ 3589 ▼ 3590 ▽ 3591 ● 3677
○ 3678 ▲ 3679 △ 3680 + 3720 ⊞ 3721

Figure 8.6

Fibrosity Results for Series 1 Steels
Tempered to 690 MPa yield strength

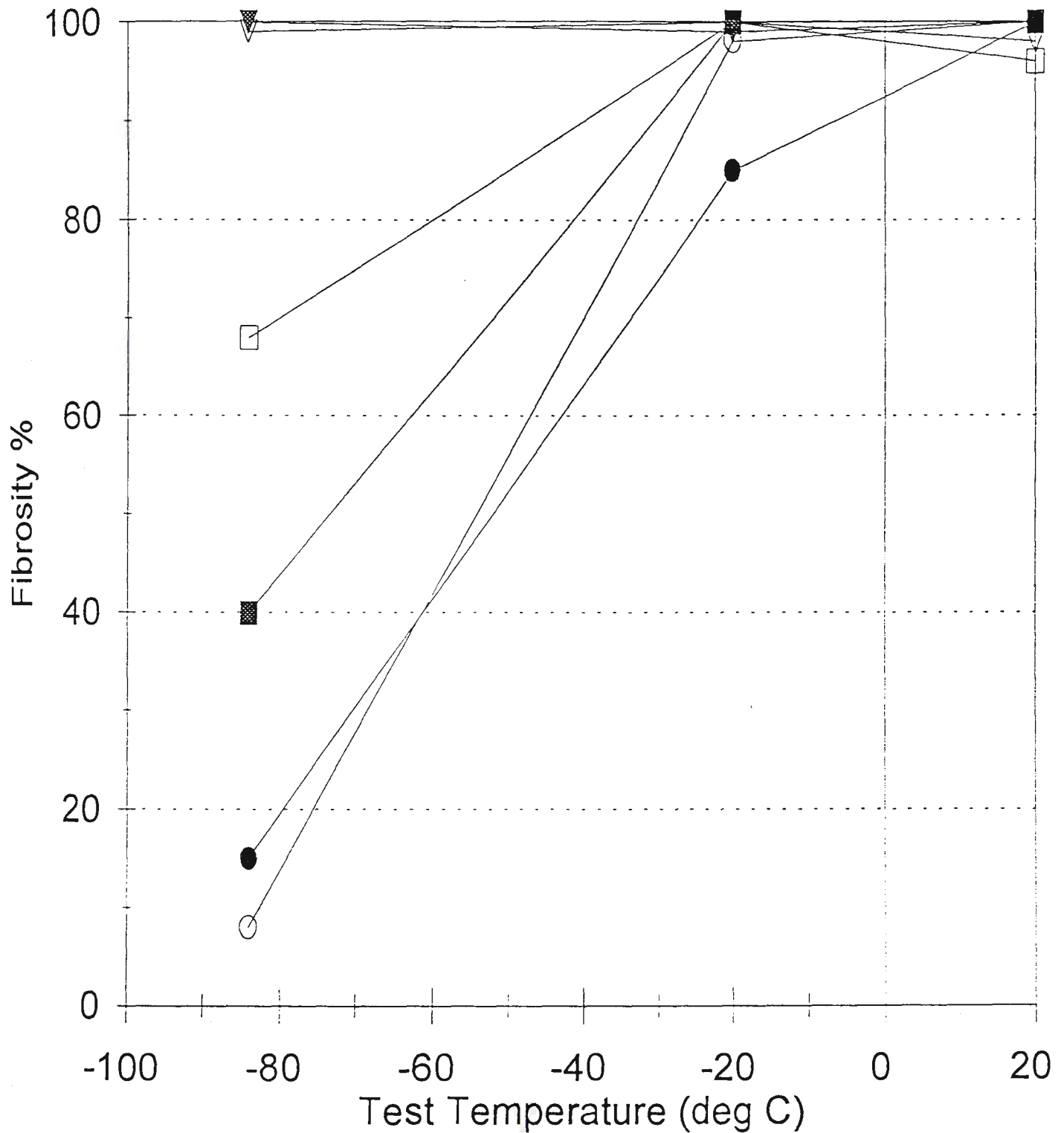


○ 3588 □ 3589 × 3590 ▽ 3591

Figure 8.7

Fibrosity Results for Series2&3 Steels

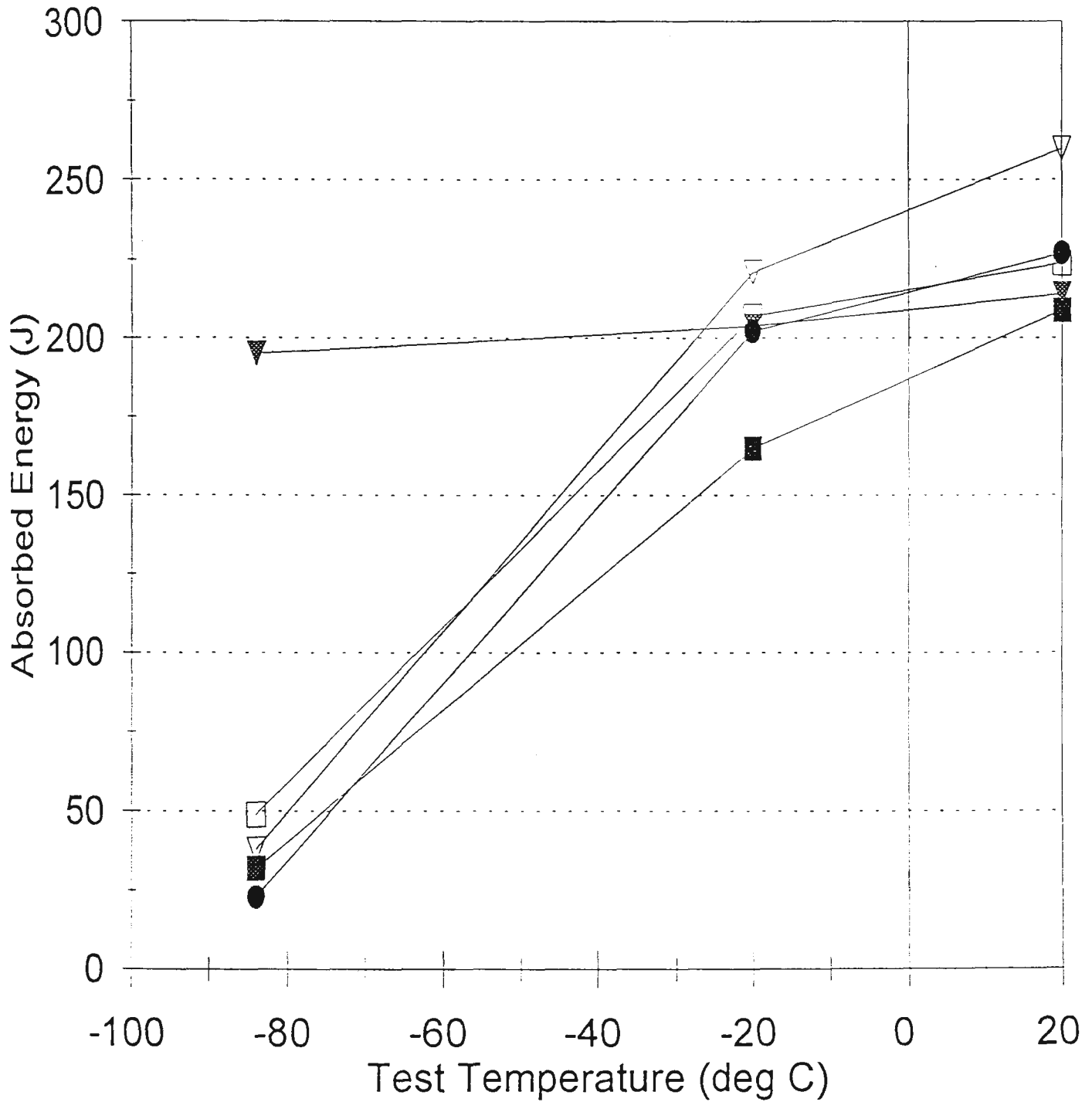
Tempered to 690 MPa yield strength



■ 3677 □ 3678 ▼ 3679 ▽ 3680 ● 3720 ○ 3721

Figure 8.8

Effect of Copper on Absorbed Energy 690 MPa Yield Strength Copper Steels



■ 3588 - 1.0% Cu □ 3589 - 0.8% Cu ▼ 3590 - 0.6% Cu
▽ 3677 - 0.4 % Cu ● 3720 - 0.0% Cu

CHAPTER 9

Prior Austenite Grain Size Measurement and Jominy Hardenability of Copper Containing Steels.

Prior Austenite Grain Size Measurement

Results

The prior austenite grain size of all the test heats was measured by the linear intercept method as detailed in Chapter 4. Various etchants and techniques described in the literature were tried with mixed success. Table 9.1 below lists the techniques tried and their level of success.

Table 9.1 Attempts to reveal Prior Austenite Grain Size

Sample	Etchant	Result/comment
heat		
treatment		
As Rec'd	100ml Sat Aq. Picric	Not etched.
	2ml Detergent	
	Room T 20 min.	
As Rec'd	100ml Sat Aq. Picric	Not etched.
	2ml Detergent	
	85°C 1 min	

Table 9.1 continued

Sample	Etchant	Result/comment
heat treatment		
As Rec'd	100ml Sat Picral 2ml detergent 20 min Room T + polish post etch	Not etched.
As Rec'd	100ml Sat Aq. Picric 2ml of detergent 6 drops conc. HCl Room T	Black film on etching. No G/B visible after polishing.
As Rec'd	100ml Sat Aq. Picric 1ml of detergent 1ml conc Hcl 2 min @ 75°C swab frequently	Black film on etching. No G/B visible after polishing.
700°C 1 hour	50ml Sat picral 0.5ml HCl 30 sec @ Room T	Reasonable def'n of G/B. Microstructure also etched.

Table 9.1 continued

Sample	Etchant	Result/comment
heat treatment		
700°C	100ml Sat Aq. Picric	Black film on
1 hour	2ml HCl	etching.
	10min @ 85°C	Surface pitted.
		Post etch polish removes black deposit and etched surface.
500°C	50ml Sat Picral	Reasonable def'n
1 hour	0.5ml HCl	of G/B.
	30 sec @ Room T	Microstructure also etched.
300&500°C	light etch 2%	Reasonable definition
1hour	Nital.	of G/B achieved
	100 ml Sat. Aq Picric	by Sly ⁸²
	1.6g CuCl ₂	and author in most
	0.5ml Teepol	alloys.
	rub with Cotton wool	
	in hot water to remove deposit on surface.	

Table 9.1 continued

Sample	Etchant	Result/comment
heat treatment		
500°C	Picral 30sec-1min @ room Temp.	Reasonable definition of G/Bs achieved in some of the alloys. Etching of structure also.
450°C	16g CrO ₃ , 80g NaOH 145mL H ₂ O heat to120-130°C preheat sample etch for 2-3 sec as discolouration starts, wash and examine. Repeat if necessary	This etch worked when all others failed.

No relationship appeared to exist between the difficulty in etching or the apparent effectiveness of etching techniques and the copper content of the alloys. In general, etching of tempered structures was easier than etching the as-quenched steels.

Table 9.2 shows the results of the calculation of grain size from photomicrographs taken of a representative area of the sample.

Table 9.2 Measured Prior Austenite Grain Size

Sample	Grain Size (microns)
3588	5.3
3589	5.3
3590	5.9
3591	4.7
3677	5.9
3678	5.6
3679	5.3
3680	5.1
3720	9.2
3721	7.3

These figures are relatively small when compared with the prior austenite grain size of Bisalloy 53 reported by Barbaro⁸⁷ as 21 microns, austenitised at 900°C, quenched and tempered. Bis 53 is a niobium free steel and the grain size would be expected to be larger than those observed in the current series of steels.

Analysis and Discussion of Results

Figure 9.1 illustrates the effect of copper content on the measured prior austenite grain size. The results in figure 9.1 indicate that grain size decreases upon addition of copper and then becomes reasonably constant as copper content increases. Abe, Kurihara, Tagawa and Tsukada³² suggest that copper plays a role in retarding recrystallisation and in inhibiting grain growth through solute drag as copper does not precipitate in austenite. Abe *et al*³² noted that significant (up to 3%) variations in the amount of copper altered the speed of recrystallisation. Easterling⁸⁸ also lists copper as an austenite stabiliser, reducing transformation temperatures and thus grain growth of transformation products. The presence of other elements also affects the grain size observed and it is probably a combination of the effects of copper, described above, and the pinning of grain boundaries by elements such as niobium and titanium (both present in the steels examined) that has produced the observed reduction in grain size. Without further detailed study quantifying the components due to particular elements is not possible.

Jominy Hardenability Tests

Results

Jominy Hardenability Tests were carried out as described in Chapter 4. Figure 9.2 contains the Jominy results for all three series and compares the response of the copper steels with that of Bis 21, a conventional medium carbon Q&T steel (see the steel alloy composition data in Chapter 3).

Analysis and Discussion of Results

These results show the marked effect of copper and also the synergistic effect of copper and boron. The Series 1 steels, 3588-3591, containing copper and boron display an almost straight

line Jominy curve, the slope of which increases with the decrease in copper content. The reason for this behaviour is probably due to the precipitation of copper as the cooling rate decreases from the quenched end. The initial hardness is chiefly due to carbon content in the martensite, but as the cooling rate decreases the extent of copper and metal carbide precipitation increases, maintaining the hardness of the bainitic or ferritic matrix.

This interpretation is supported by the behaviour of 3720. This alloy is identical in chemistry with the Series 1 steels, except that it is copper-free. Alloy 3720 exhibits a much more typical Jominy curve, similar in shape to that of Bis21. Grange, Lambert and Harrington⁸⁹ examined the effect of copper on the hardenability of a 0.45%C steel (0.45%C, 0.5%Mn 0.2%Si, 0,0.5,1,1.5%Cu) via both the Jominy end quench test and by quenching cylindrical bars of various diameters. They obtained a good correlation between the two methods and the effect of copper on hardenability. The study demonstrated that the hardness along the Jominy specimen was maintained even though the proportion of martensite fell to less than 10% approximately 6mm from the quenched end. The steels in that study contained no boron and the shape of the curves reported is very similar to that of the boron free Series 2 steels in this study.

The Series 2 steels, 3677-3680 were inadvertently supplied boron free. These steels contain various amounts of copper and carbon (see full analyses, chapter 3) but all exhibit similar responses to varying cooling rate along the Jominy sample. Hardness rapidly falls from the quenched end and although copper and carbides are expected to precipitate as the cooling rate falls, the absence of boron decreases the propensity for martensite to form at lower cooling rates and thus allows the hardness to fall rapidly. Krishnadev, Sojka, Le May, McD. Schetky and Banerji³⁴ observed what they termed a synergistic effect on mechanical properties between copper and boron in a low carbon, 2% copper steel. This effect emphasises the importance of B in enhancing the behaviour of Cu, particularly in thick plate.

Observation of the the microstructures at points along the specimen reveals that the microstructure of Bis 21, 40mm along the Jominy specimen is a mixture of martensite and bainite, whereas the microstructure of 3588 (1% Cu) is completely bainitic, an indication of the difference in hardenability despite the similarity in hardness.

Figure 9.3 provides a comparison of Jominy curves corresponding to various copper contents. Again the dramatic effect of copper is evident with the maintainance of high hardness along the Jominy bar correlating with increasing copper content. The synergism between copper and boron is also re-emphasised by the behavior of the boron free steel 3677.

Figure 9.1

Effect Of Cu % On Prior Austenite Grain Size Of Some Steels Studied

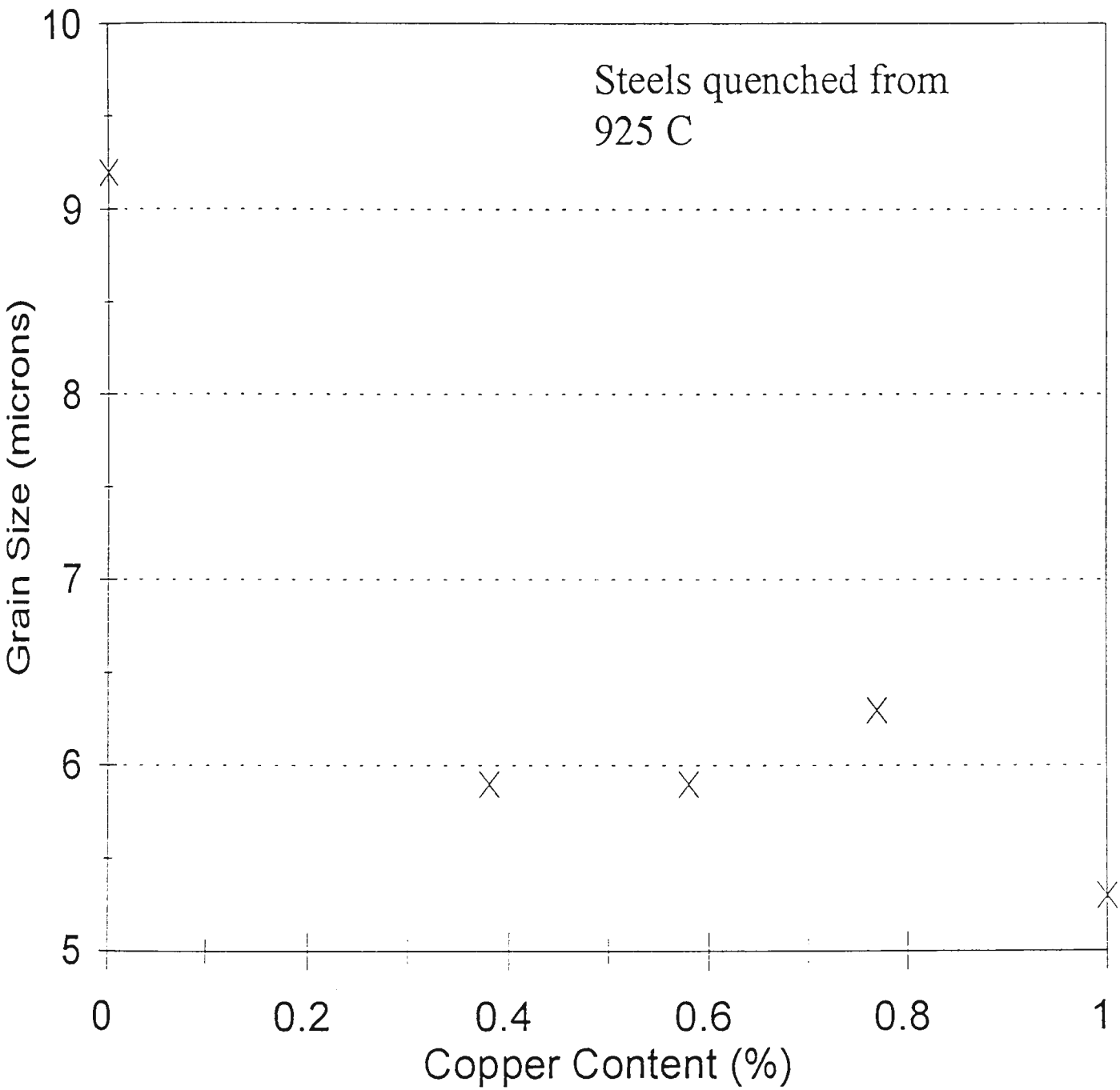
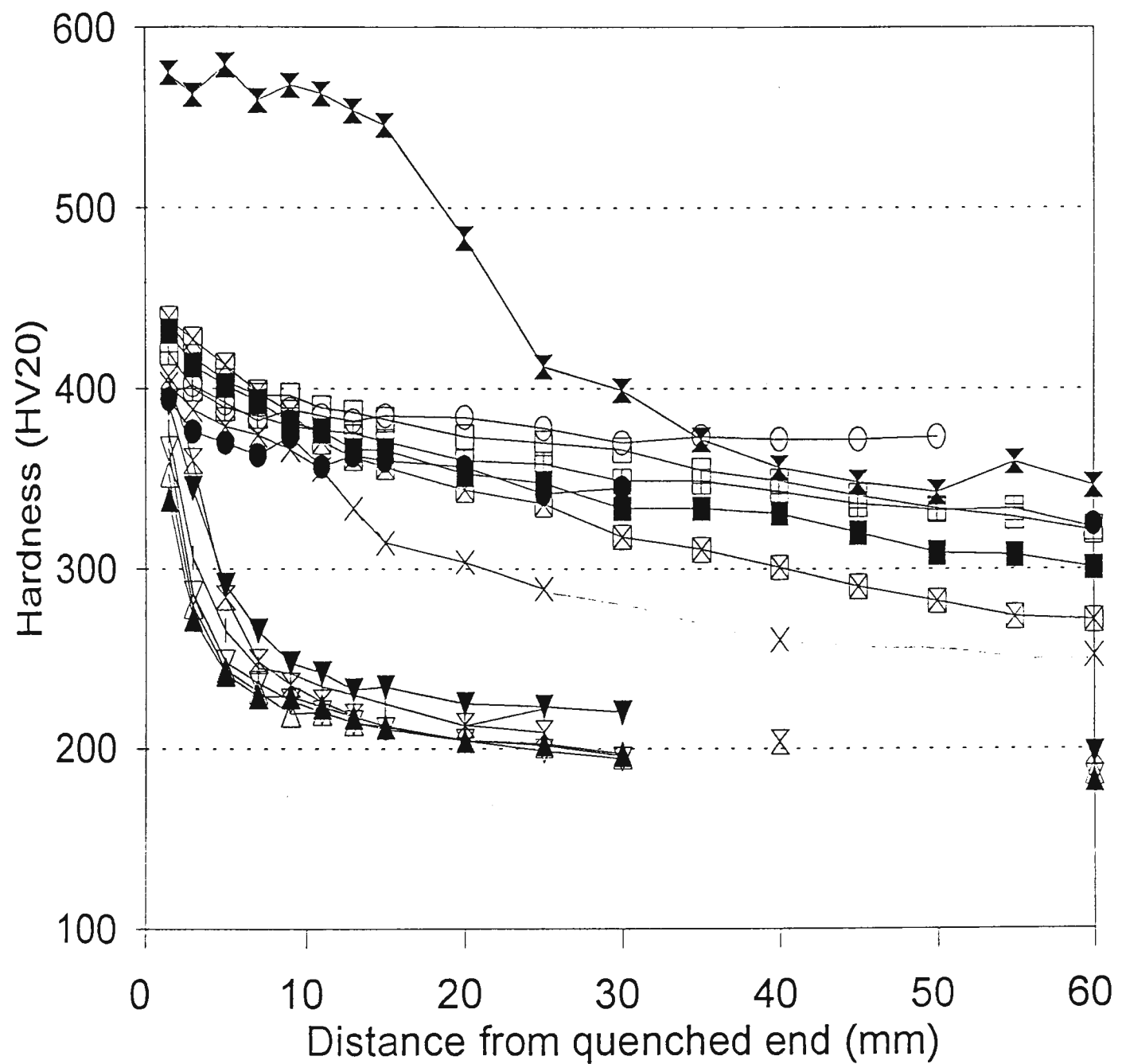


Figure 9.2

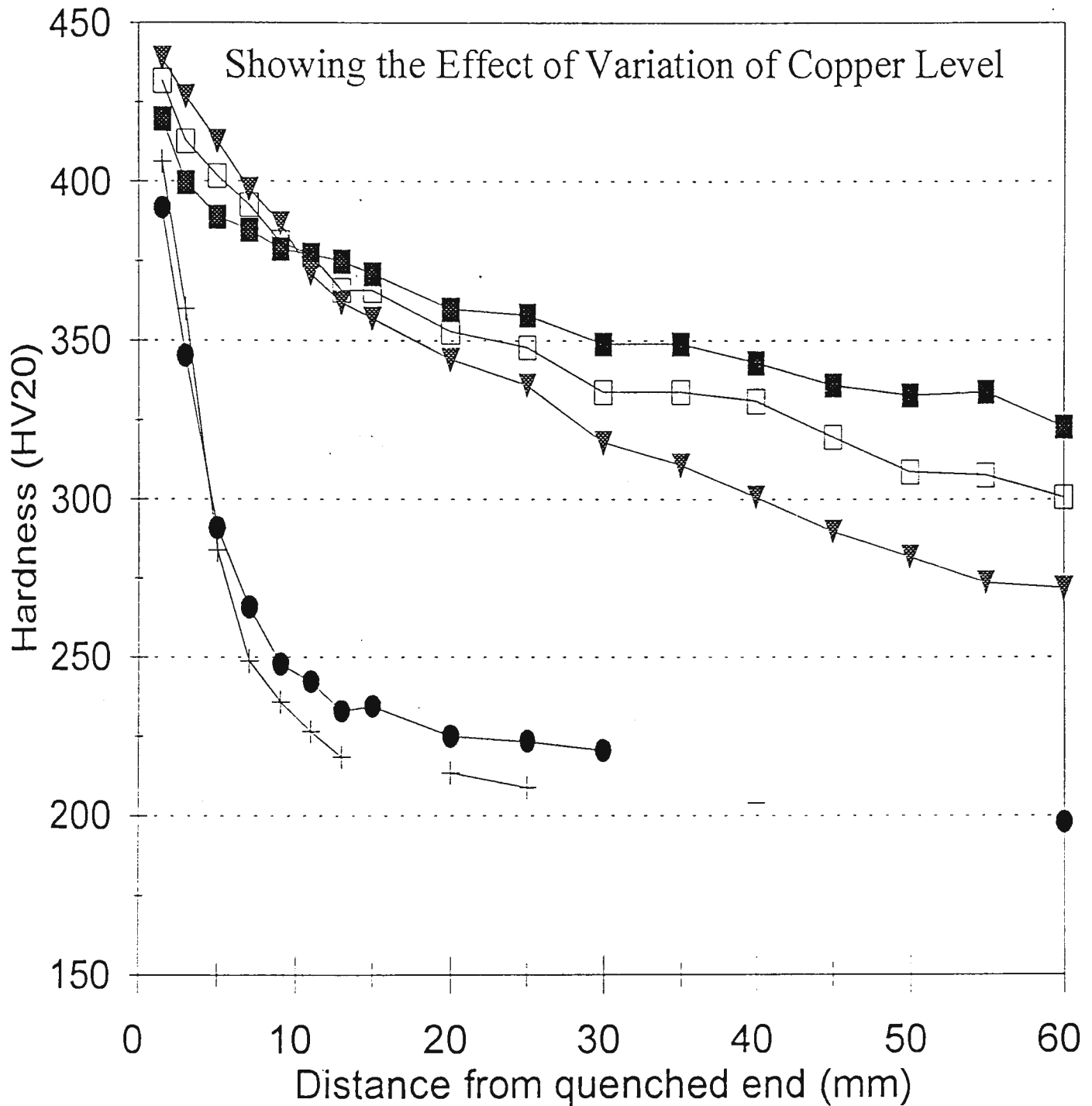
A Comparison of Jominy Curves for Copper Steels and Bis 21



- | | | | | |
|------------|------------|--------|--------|----------|
| ■ 3589 | □ 3591 | ▣ 3588 | ⊠ 3590 | ○ 3433 |
| ▼ 3677 | ▽ 3678 | ▲ 3679 | △ 3680 | ✕ bis 21 |
| + 3678 rpt | ● 3588 rpt | ⊗ 3720 | ✧ 3721 | |

Figure 9.3

A Comparison of Jominy Curves for Copper Steels



■ 3588 1.0%Cu □ 3589 0.8%Cu ▼ 3590 0.6%Cu
● 3677 0.4%Cu + 3720 0.0%Cu

CHAPTER 10

Bead-on-Plate Weld Testing of Copper Containing Steels.

Results.

In order to assess the weldability of the copper containing steels and to attempt to rank their weldability relative to some existing quenched and tempered alloys the Bead-on-Plate (BOP) test was selected. Methods used are outlined in Chapter 4 and all testing was carried out on 20mm thick plate in order to allow direct comparison between the alloys under examination.

The information that this test gives is :

1. maximum heat affected zone (HAZ) hardness.
2. the extent of hardening due to grain growth and fast cooling in the HAZ.
3. the extent of softening due to overtempering in the HAZ.

Table 10.1. contains the principal compositions of the steels used.

Table 10.1. Main alloy content of steels used in BOP test

Steel	Alloy Content (%)				
	Cu	C	Mn	Cr	Ni
Bis 21	0.01	0.26	0.52	0.92	0.026
Bis 52	0.008	0.16	1.12	0.016	0.021
Series 1 (contain B and Cu)					
3590	0.58	0.09	1.52	0.003	0.20
3591	0.76	0.09	1.49	0.6	0.20
3589	0.77	0.09	1.53	0.003	0.21
3588	1.0	0.09	1.53	0.003	0.31
Series 2 (contain Cu, B free)					
3677	0.38	0.085	1.58	0.008	0.20
3678	0.81	0.075	1.00	0.005	0.20
3679	0.81	0.044	1.48	0.007	0.20
3680	0.38	0.050	1.48	0.007	0.20
Series 3 (contain B, low Cu)					
3720	0.003	0.085	1.50	0.007	0.17
3721	0.45	0.08	1.29	0.006	0.23

Figures 10.1, 10.2 and 10.3 are graphs that show the results of BOP tests with a heat input of 1.2 kJ/mm. Figure 10.1 compares series 1 steels with Bis 52 and Bis 21. Figure 10.2 compares Series 2 steels with Bis 52 and Bis 21 and Figure 10.3 compares Series 3 steels with Bis 21 and Bis 52. The Bis 21 and Bis 52 steels were heat treated to Bis 500 and Bis 80 hardness specifications respectively.

Figures 10.4 and 10.5 contain results over a range of heat inputs. Figure 10.4 concentrates on the effect of heat input on two conventional quenched and tempered steels (Bis 21 tempered to Bis 500 and Bis 52 tempered Bis 80) and 10.5 shows the effect of the variation of heat input on the copper containing steels in this study. These copper steels were heat treated to the Bis 80 hardness specification.

Analysis and Discussion of Results

It is evident from the graphs presented that the copper containing steels exhibit a lower peak hardness than either Bis 21 or Bis 52. Also, little softening is evident in the HAZ of the Series 1 steels. A wider hardened area than Bis 80 is exhibited by the test alloys. These last two effects are probably due to the copper content of the steels. It is likely that during welding the copper in the vicinity of the weld is taken into solution and re-precipitated as the temperature falls during cooling. This will cause the relatively high hardness observed at distances greater than 1 mm from the fusion line, and the marked softened zone, observed in Bis 80 and Bis 500 to be practically non existent in the Series 1 copper steels.

The Series 2 copper containing alloys do not show the same peak hardness in the HAZ as the Series 1 steels. This is due to these steels being leaner alloys than the Series 1 steels (see compositions in Table 6.1). These steels also exhibit a softened zone in the HAZ, probably caused by a combination of the leaner composition and absence of boron.

From the results presented for alloys 3677, 3590, 3589 and 3588 which are essentially the

same except for variations in copper and boron levels (3677 is boron free), it can be seen that the width of the high hardness area in the HAZ can be related to copper content. This supports the concept that copper precipitation is maintaining the hardness with distance from the fusion boundary. The microstructure need not be martensite for the hardness in the HAZ to be maintained. Note the similarity of this effect with the hardness profile in the Jominy test.

Some alloys have elemental differences in addition to copper. One of note is 3591 (0.76% Cu), which also contains 0.6% Cr. The chromium content and its positive effect on hardenability probably causes the hardness to be maintained in the HAZ to levels similar to 3588, the 1% copper steel. It seems that the combined effect of 0.76 % Cu + 0.6 % Cr is approximately equivalent to 1.0 % Cu in its effect on the hardness of the HAZ.

Figure 10.4 shows results from hardness traverses perpendicular to the fusion line performed, as per Reference 51, on Bis 500 manufactured from Bis 21 feed plate (Bis500-21) and Bis 80 from Bis 52 (Bis80-52). There are three sets of results for each steel, corresponding to three heat inputs 0.8, 1.2 and 2.0 kilojoules/mm. As expected, the lowest heat input produced the highest peak HAZ hardness and the highest heat input produced the lowest peak HAZ hardness.

From the results pertaining to Bis 500, the 0.8 kJ/mm heat input exhibits a very narrow hardened; grain coarsened zone extending approximately 0.5mm from the fusion boundary. This narrow, high hardness GCZ is due to the high cooling rates and steep temperature gradients extending from the weld to the parent plate. The 1.2 kJ/mm heat input exhibits the widest GCZ extending about 1.5mm from the fusion line and the 2.0 kJ/mm heat input shows a GCZ of intermediate size. Pang⁹⁰ found a similar effect when examining the root pass of a 4 wire submerged arc weld. The heat inputs studied were higher but the hardness profiles had a similar shape and the profile of the highest heat input fell in-between the lower two. It is likely that this

effect is related to bead shape and cooling rate.

The HAZ hardness profiles of the Bis 80 were similar to those for Bis 500, in that the lowest heat input caused the highest peak hardness and the highest heat input the lowest hardness. The distance from the fusion line of the occurrence of the softened zone increased as heat input increased but the softened zone hardness remained fairly constant. Bis 80 does not exhibit as dramatic softening as Bis 500 due to the tempering temperature of 600°C. For softening to occur due to overtempering in the subcritical heat affected zone, the local temperature must exceed the tempering temperature. As Bis 500 is not tempered, softening occurs at relatively low HAZ temperatures but with Bis 80 the HAZ temperature must reach at least 600°C before overtempering can occur.

The graph in Figure 10.5 shows the effect of copper on the HAZ hardness at heat inputs of 1.2 and 2.5 kJ/mm. The alloys 3589(0.8%Cu), 3721(0.5%Cu) and 3720(0.0%Cu) were selected for study, lack of material precluded more detailed study involving more alloys. As expected, based on the work on Bis 80 and 500 the maximum HAZ hardness fell with increasing heat input. The degree of HAZ softening increased with heat input and is also influenced by copper content, increasing copper content decreases the degree of HAZ softening. In both the copper containing steels examined by BOP testing the fall in hardness was less than that of the copper free steel, 3720 which softened markedly at both heat inputs examined (1.2 and 2.5 kJ/mm).

Using a heat input of 1.2 kJ/mm a model developed by Yurioka, Okumura, Kasuya and Oshita⁹¹ was used to try to predict the HAZ hardness and preheat required to prevent cold cracking in the HAZ. Formulae developed by Cottrell⁵⁰ were used to predict the HAZ hardness. This was done with the aim that the steels might be compared with each other in terms of other weldability indices rather than just HAZ peak hardness and to test the predictive capability of

these models for copper precipitation hardening steels. Table 10.2 shows the results of the calculations and a comparison with the experimental values for HAZ hardness.

<div> <div>Table 10.2</div> <div>Predicted hardnesses and preheat temperatures for the steels studied</div> </div>			
Yurioka <i>et al</i> ⁹¹			
Alloy	Calc. Max HAZ hardness (Hv10)	Exp. Max. HAZ hardness (Hv10)	Predicted Preheat Temp. (°C)
Bis 52	364	401	105
Bis 21	507	525	>250
Series 1			
3588	369	386	75
3589	365	386	60
3590	359	381	<50
3591	373	391	120
Series 2			
3677	349	336	<50
3678	331	269	amb(20)
3679	322	276	amb
3680	312	273	amb
Series 3			
3720	324	365	amb
3721	338	371	amb
Misc.			
3433	366	384	140

Note:- Predicted preheat temperature is the preheat required to prevent cold cracking in the HAZ.

Cottrell ⁵⁰		
Alloy	Cal. HAZ hardness (Hv)	Exp. HAZ hardness (Hv)
Bis 52	358	401
Bis 21	493	525
Series 1		
3588	345	386
3589	344	386
3590	342	381
3591	364	391
Series 2		
3677	340	336
3678	300	269
3679	310	276

Table 10.2 continued.

3680	315	273
Series 3		
3720	332	365
3721	322	371
Misc.		
3433	360	384

As is clear from Table 10.2, the predicted HAZ hardness values calculated from the formulae devised by Yurioka *et al* are closer to the experimental values than those given by the Cottrell formulae for the Series 1 steels. The Yurioka *et al* prediction is some 37 hardness points low at worst (for Bis 52) and the closest estimate is still 17 points low. Both calculations give the correct order of increasing or decreasing hardness with alloys exhibiting a higher experimentally determined hardness maintaining their ranking if calculated values are used for comparison.

The Series 2 steels seem to have challenged the models severely. The estimates of maximum HAZ hardness are in some cases quite inaccurate. The models are unable to rank the alloys correctly with the Cottrell model estimates being more accurate.

Results for the Series 3 steels are similar to those for Series 2. The hardness predictions for the two conventional quenched and tempered steels Bis21 and Bis52 indicate that the Yurioka *et al* model is marginally more accurate than the Cottrell model but that both under estimate the maximum HAZ hardness.

Further examination of the maximum HAZ hardnesses shows that both models underestimate maximum HAZ hardness when the steels contain boron (conventional Bis 52 and 21, Series 1 and Series 3) and overestimate maximum HAZ hardness in those steels that are boron free (Series 2).

The Yurioka *et al* model allows prediction of preheat temperature needed to prevent HAZ

cold cracking and this enables the steels to be ranked according to their theoretical propensity for cold cracking in the HAZ. It is evident that the Series 2 and 3 steels would out perform the Series 1 alloys which would in turn be superior to the conventional quenched and tempered steels when gauged using this criterion. If the alloy compositions are examined then it is plain that the order of increasing cold cracking risk (decreasing weldability) is roughly the order of increasing alloy content with carbon and chromium having a high weighting and thus a strong influence on theoretical preheat temperature.

Table 10.3 demonstrates the sensitivity of the Yurioka analysis to changes in carbon content. It is a table of preheat temperatures needed to prevent cracking in the HAZ of the root pass of a single vee configured weld. The preheat for the Series 1 steels is compared with Bis 80, Bis 500 and 3433 (a high Mn-Cu steel used in preliminary investigation). The preheat temperature is calculated using the critical cooling time to 100 °C from solidification. This is the time needed to cool to 100°C to prevent HAZ cracking. The critical cooling time is calculated from alloy chemistry information, weld joint restraint and configuration and diffusible hydrogen content. Preheat is then determined such that the weld cools in a time longer than the critical time. Yurioka *et al* provide many empirically determined graphs to enable this critical cooling time to be determined and then translated into a preheat temperature.

Table 10.3 Preheat needed to prevent HAZ cold cracking.

Alloy	preheat (°C)	preheat with 0.01 % decrease in C (°C)
Bis80-52	105	85
Bis500-21	>250	>250
3588	75	55
3589	60	<50
3590	<50	<50
3591	120	100
3433	140	125

The parameters used to determine the preheats in tables 10.2 and 10.3 are:

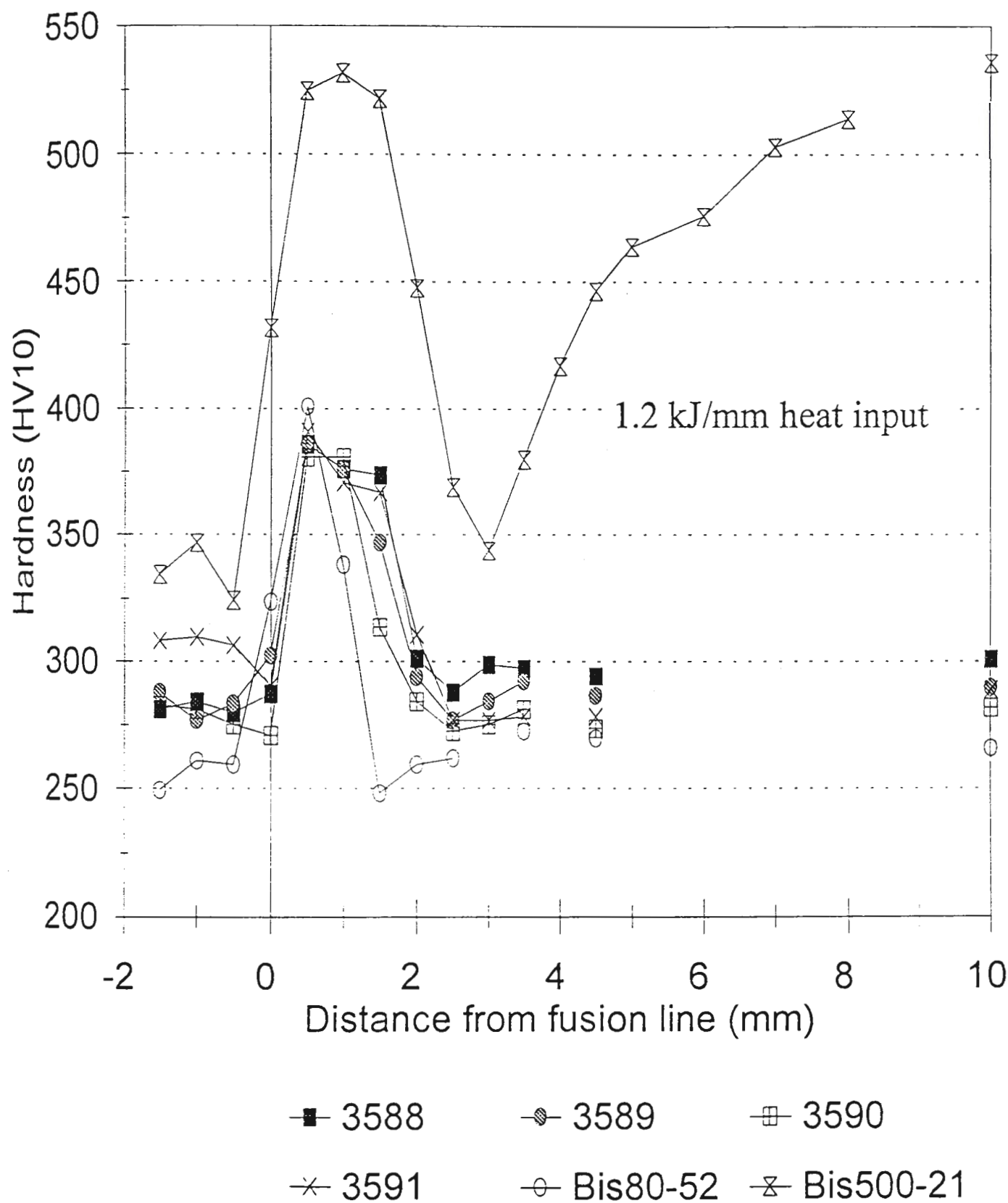
1. a plate thickness of 20 mm;
2. preheat using a hand gas burner (as opposed to an electric heater);
3. ambient temperature of 20 °C;
4. a welding heat input of 1.2 kJ/mm.

Fifty degrees celsius is the lowest practical preheat temperature used and therefore a determined preheat temperature of <50 °C is, in reality, no preheat. As can be seen, a decrease of 0.01% in carbon content causes a significant change in required preheat temperature with three of the steels requiring little or no preheat.

This method seems to give a sensitive means of comparison between the copper bearing test heats and indicates that the copper bearing steels should perform at least as well if not better than Bis 52. Bis 52 is the leanest in alloy content and most weldable of the existing Bisalloy grades. It is currently marketed as a preheat free steel in all the thicknesses in which it is offered.

Figure 10.1

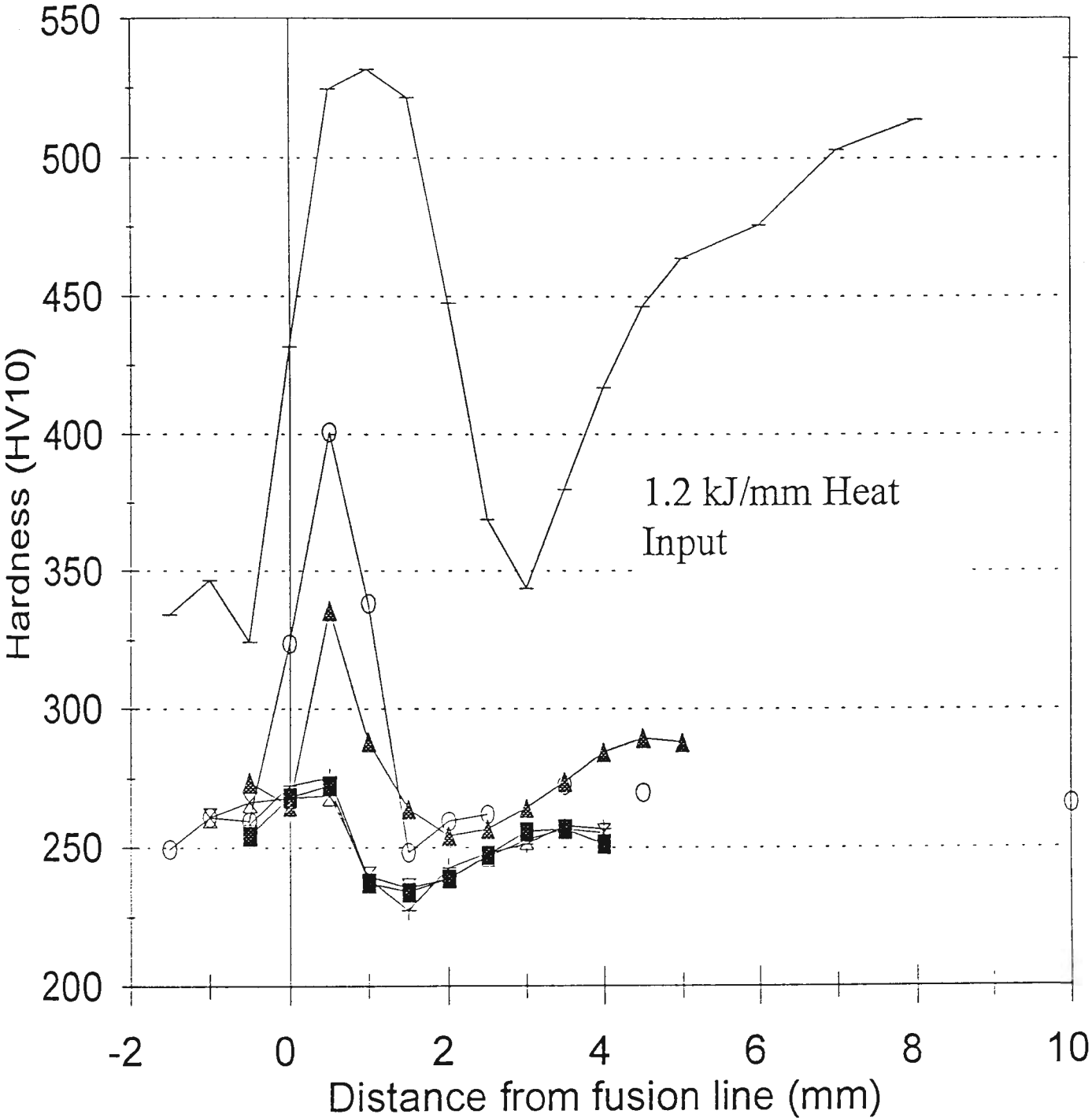
Bead on Plate Weld Test Results
Flux Cored Arc Process



Series 1 Steels Compared with Bis500/Bis80

Figure 10.2

Bead on Plate Weld Test Results
Flux Cored Arc Process

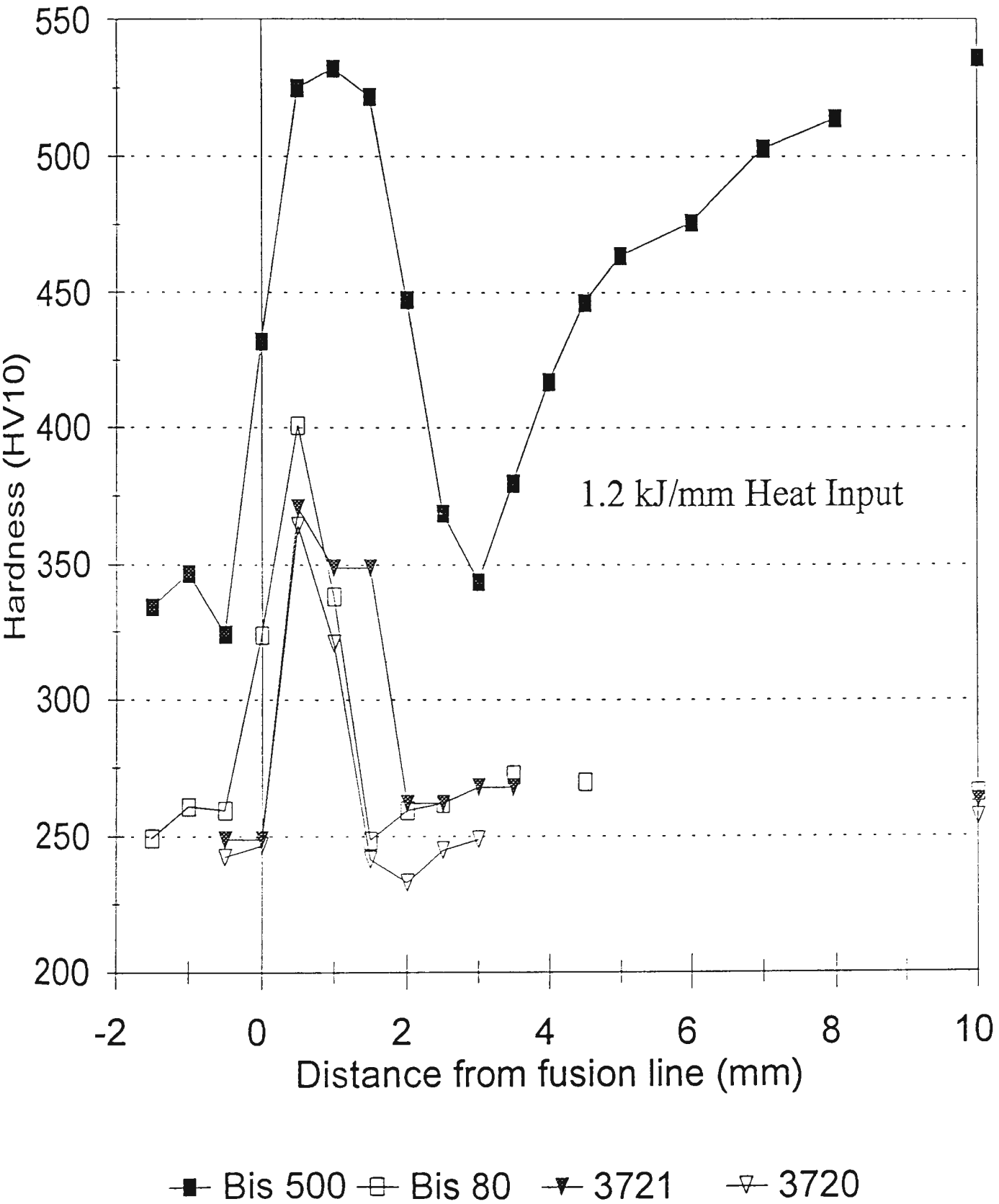


■ 3680 + 3679 ▲ 3677
⊗ 3678 ⊕ Bis80-52 — Bis500-21

Series 2 Steels compared with Bis 500/Bis80

Figure 10.3

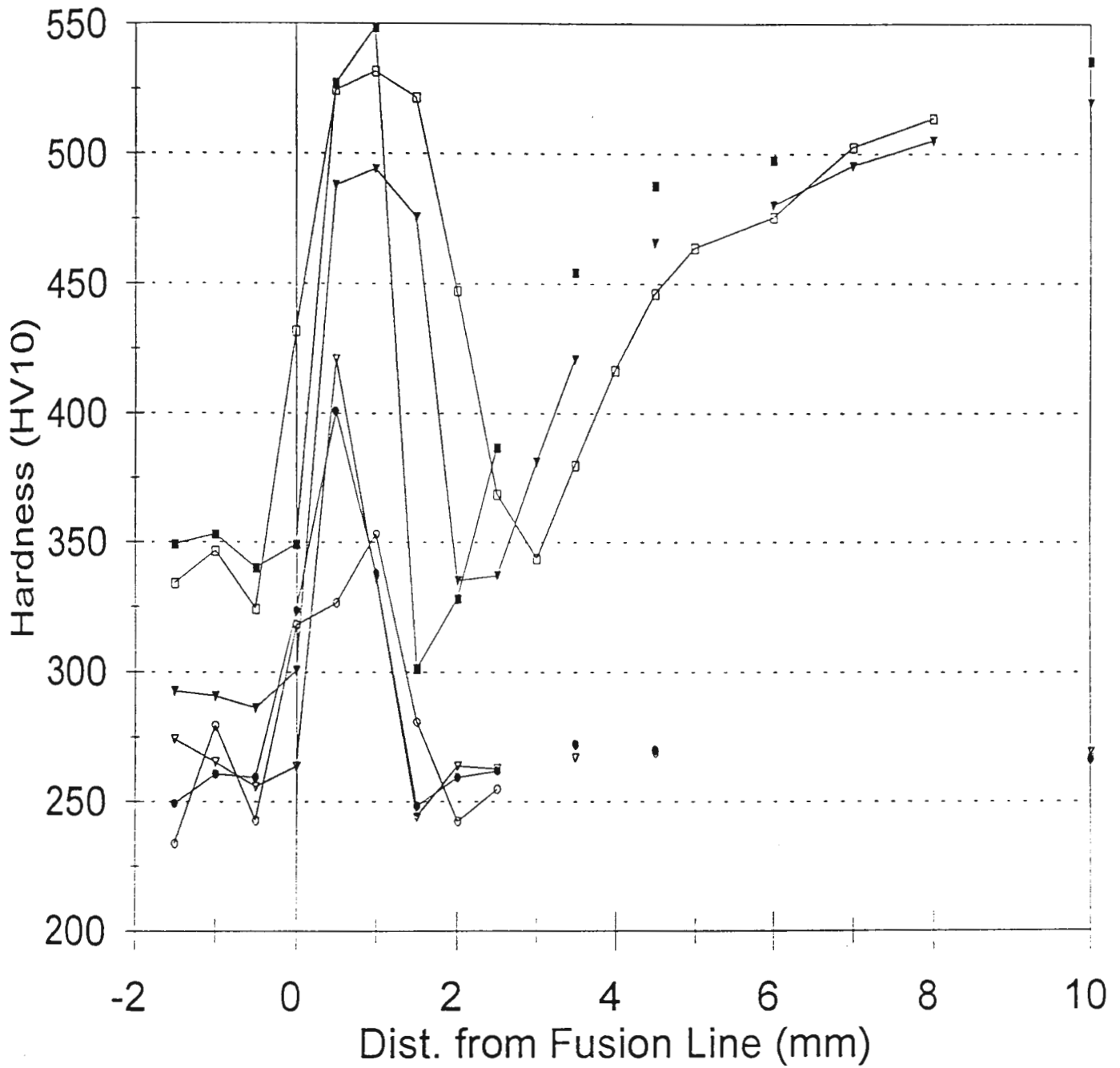
Bead on Plate Weld Test Results
Flux Cored Arc Process



Series 3 Steels Compared With Bis 500 and Bis 80

Figure 10.4

Bead on Plate Weld Test Results Flux Cored Arc Process

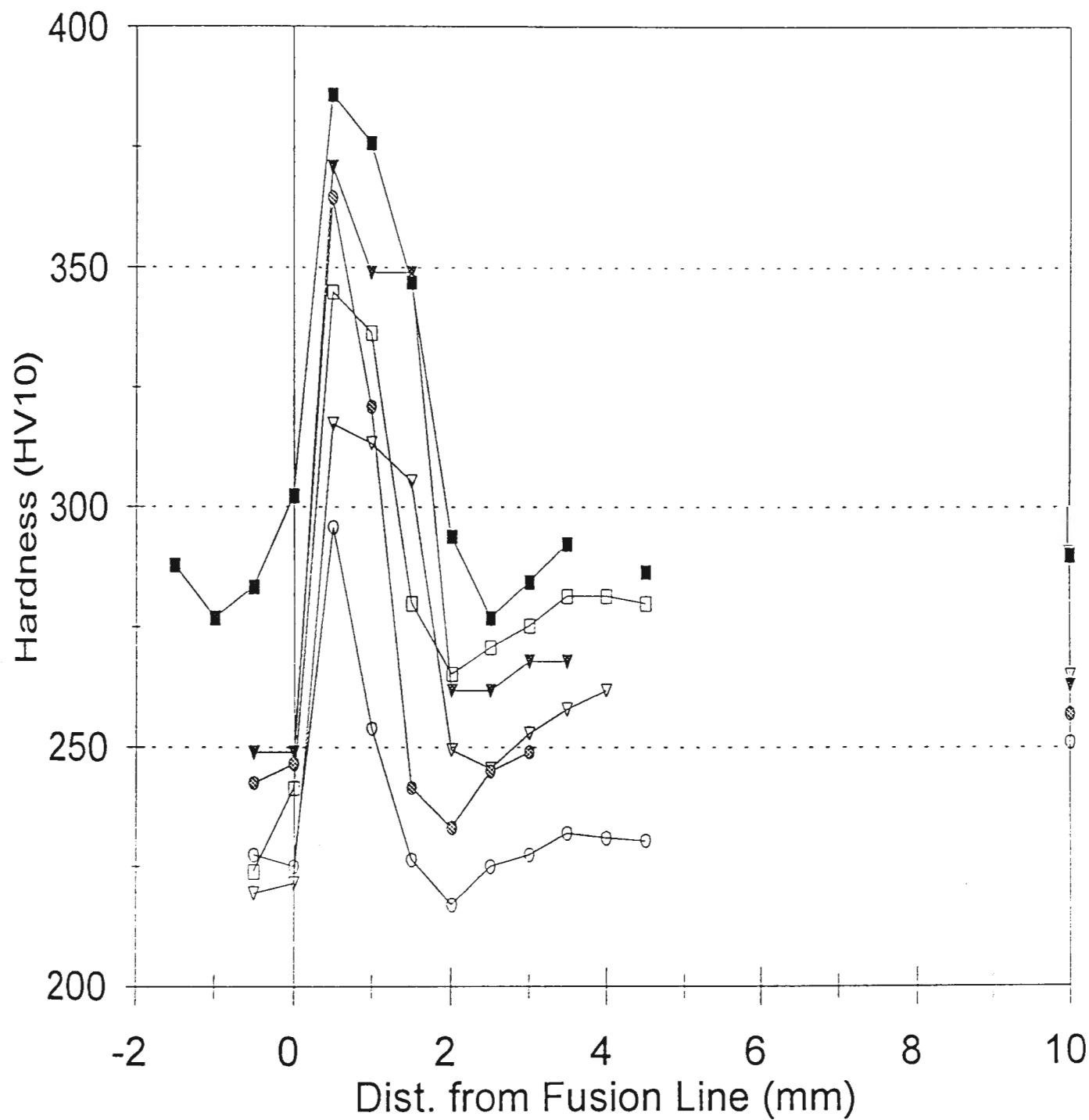


+ Bis 500 0.8 kJ/mm □ Bis 500 1.2 kJ/mm ▲ Bis 500 2.0 kJ/mm
+ Bis 80 0.8 kJ/mm ● Bis 80 1.2 kJ/mm ○ Bis 80 2.0 kJ/mm

Effect of Heat Input on Bis 500 and Bis 80

Figure 10.5

Bead on Plate Weld Test Results
Flux Cored Arc Process



■ 3589 1.2 kJ/mm □ 3589 2.5 kJ/mm ▼ 3721 1.2 kJ/mm
▽ 3721 2.5 kJ/mm ⊗ 3720 1.2 kJ/mm ⊙ 3720 2.5 kJ/mm

Effect of Heat Input on Copper Steels

CHAPTER 11

Microstructural Analysis of Copper Containing Steels.

Results

Measurement of Cooling Rate of Quenched Samples.

The cooling rate of samples used for examination of heat treatment response was the same as that used for the hardness surveys as samples of the same size were quenched in the same manner as the hardness samples. See Chapter 4 for details.

Microstructures Observed.

Etching methods used in this section are recorded in Chapter 4.

Figures 11.1 to 11.20 are micrographs of the steels examined in this study, for both the as quenched, and tempered condition. The tempering temperature was 650°C and the samples were held at temperature for 1 hour.

Representative micrographs of various microstructures are presented by Samuels⁹² in his book Optical Microscopy of Carbon Steels. This work was used extensively as a reference in this part of the current study.

Microstructures of Series 1 Steels.

The as quenched microstructure of the Series 1 steels consists, mainly, of lath martensite. Allowing for differences in cooling rate and some dissimilarities in alloy composition this is similar to results reported previously,^{31,39,41} and especially those reported by Thompson and co-workers⁴⁰.

In agreement with results reported by Krishnadev and Le may³¹, the tempered structure of these steels still shows traces of the lath structure of the fine bainite and martensite.

Microstructures of Series 2 Steels

The as quenched microstructure of the Series 2 steels consists of lath martensitic grains surrounded by grain boundary allotriomorphic ferrite and coarse bainitic ferrite. This structure reflects the lack of hardenability of these steels due primarily to the absence of boron but also the lower levels of alloying elements. These steels were intentionally leaner than the series 1 steels in an effort to determine the lower compositional limits.

The tempered samples show the vestiges of the lath structure of the martensite.

Microstructures of the Series 3 Steels

The microstructures exhibited by the as-quenched Series 3 steels show lath martensite possibly with some fine bainitic ferrite.

Upon tempering, the lath structure is partially destroyed but is still evident after 1 hour at 650°C.

Analysis and Discussion of Results

Table 11.1 Microstructure and Mechanical Property Relationships

Smpl Id.	Microstructure	Mechanical Properties			
		Ys (MPa)	Ts (MPa)	HV20	CVN(J)(-20C)
As quenched					
Series 1					
3588	LM & BF	1088	1206	401	165
3589	"	961	1172	404	207
3590	"	992	1196	403	193
3591	"	992	1205	407	116
Series 2					
3677	LM & GBF & BF	763	966	338	102
3678	"	645	848	313	211
3679	"	616	802	262	270
3680	"	627	816	282	284
Series 3					
3720	LM & BF	760	965	394	83
3721	"	893	1116	387	125

where LM is lath martensite

GBF is grain boundary ferrite or allotriomorphic ferrite

BF is bainitic ferrite

Table 11.1 continued

Smpl Id.	Microstructure	Mechanical Properties			
		Ys (MPa)	Ts (MPa)	HV20	CVN(J)(-84C)
Tempered @ 650C 1hr					
Series 1					
3588	Tempered structure	749	791	270	32
3589	"	778	798	265	49
3590	"	761	791	282	195
3591	"	764	791	264	81
Series 2					
3677	"	661	738	268	-
3678	"	622	702	245	-
3679	"	640	685	230	-
3680	"	592	674	228	-
Series 3					
3720	"	635	701	255	23
3721	"	737	775	271	50



Fig. 11. 1. 3588 As quenched

Nital 1285X

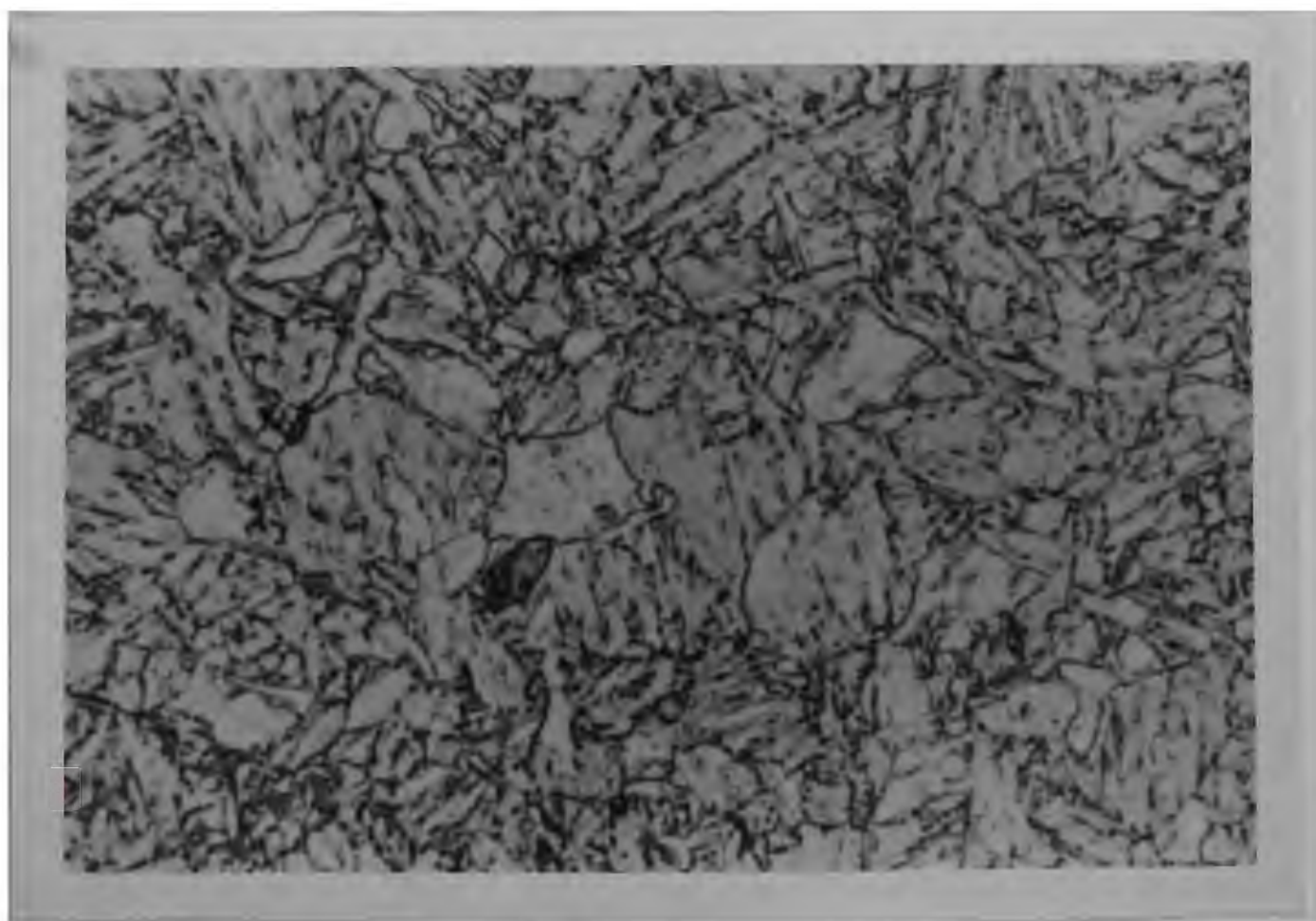


Fig. 11.2. 3588 1 hr 650

Nital 1285X



Fig. 11. 3. 3589 As quenched

Nital 1285X



Fig. 11.4. 3589 1 hr 650

Nital 1285X



Fig. 11. 5. 3590 As quenched

Nital 1285X



Fig. 11.6. 3590 1 hr 650

Nital 1285X



Fig. 11. 7. 3591 As quenched **Nital 1285X**



Fig. 11.8. 3591 1 hr 650 **Nital 1285X**



Fig. 11. 9. 3677 As quenched

Nital 1285X



Fig. 11.10. 3677 1 hr 650

Nital 1285X



Fig. 11. 11. 3678 As quenched

Nital 1285X



Fig. 11.12. 3678 1 hr 650

Nital 1285X

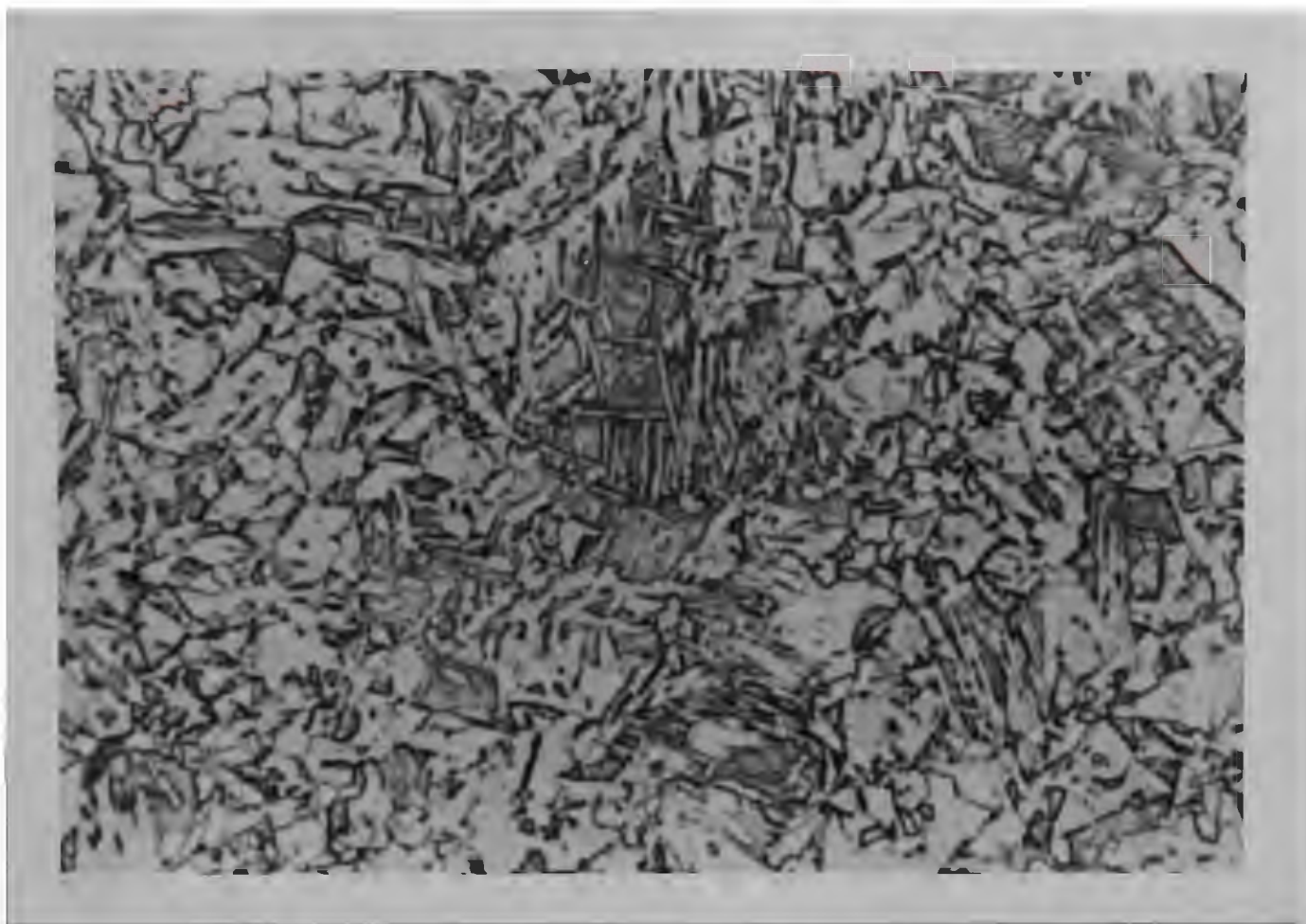


Fig. 11.13. 3679 As quenched

Nital 1285X



Fig. 11.14. 3679 1 hr 650

Nital 1285X



Fig. 11. 15. 3680 As quenched

Nital 1285X

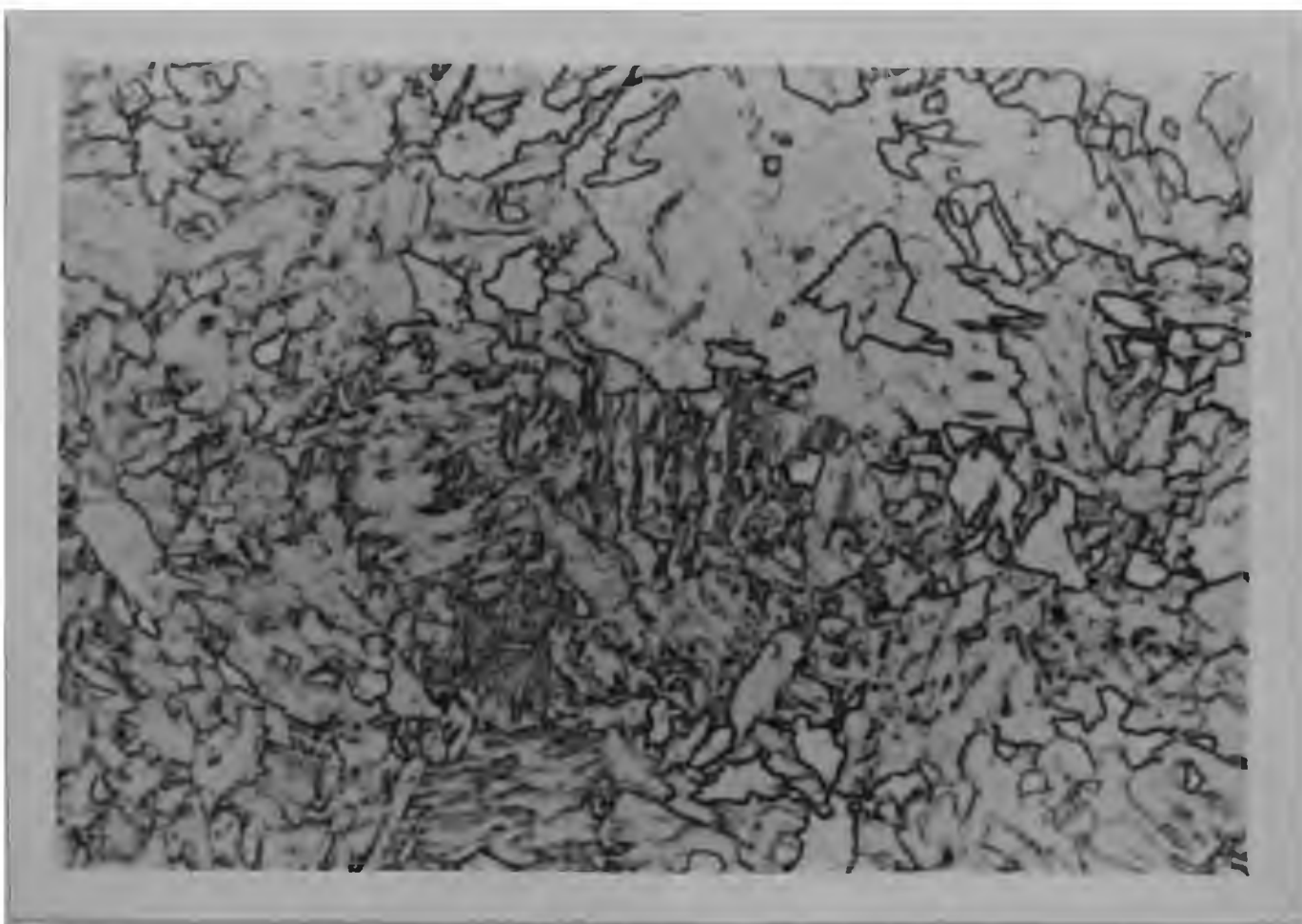


Fig. 11.16 3680 1 hr 650

Nital 1285X



Fig. 11. 17. 3720 As quenched

Nital 1285X



Fig. 11.18. 3720 1 hr 650

Nital 1285X



Fig. 11. 19. 3721 As quenched **Nital 1285X**



Fig. 11.20. 3721 1 hr 650 **Nital 1285X**

CHAPTER 12

General Discussion.

Equations describing the tempering behaviour of low carbon steel alloys, both with and without copper, were determined. These are given in Table 12.1 below.

Table 12.1 Tempering Equations

Alloy	%C	%Cu	Equations
Bis 2	0.18	0.0	$H = T(16.53 + \ln(t))$ $H > 9000$: Hardness = $-0.041(H) + 831$ $H < 9000$: Hardness = 430
3720	0.08	0.0	$H = T(7.85 + \ln(t))$ $H > 3000$: Hardness = $-0.031(H) + 480$ $H < 3000$: Hardness = 394
3590	0.08	0.6	$H = T(7.26 + \ln(t))$ $H > 3000$: Hardness = $-0.0275(H) + 467$ $H < 3000$: Hardness = 403
3589	0.08	0.8	$H = T(5.74 + \ln(t))$ $H > 1500$: Hardness = $-0.0280(H) + 432$ $H < 1500$: Hardness = 404
3588	0.08	1.0	$H = T(11.45 + \ln(t))$ $H > 6000$: Hardness = $-0.0237(H) + 537$ $H < 6000$: Hardness = 401

Where:

H is the Holloman and Jaffe parameter,

Hardness is Vickers hardness (HV),

T = furnace temperature in Kelvin,

t = furnace residence time in hours.

Testing these equations, where possible with independent information, shows them to be acceptably accurate within their limitations: temperatures between 0 and 650°C and times from 0 to approximately 1.5 hours.

Examination of heat treatment response shows that the Series 1 and 3 steels reach hardness levels consistent with required strength after ageing times of 30 minutes or more at 650°C. The Series 2 steels do not meet this hardness at 650°C and only two of the Series 2 steels satisfy this requirement at 600°C. Steels with higher copper contents display an increase in hardness at 700°C over 650°C, probably due to the increased level of copper allowing faster precipitation and an increase in precipitate density at the higher temperature.

Extended tempering of steels of similar alloy composition, aside from copper proportion, resulted in little difference in properties in steels above 0.8% copper. Alloys containing 0.4% and 0.0% copper were inseparable at short ageing times but, as furnace times increased the hardness of the 0.4% copper steel increased to approach that of the 0.8% copper containing alloy. Although this convergence of hardness levels appears to be real, the time required, even at high tempering temperatures, is not economical. Some authors^{38,26} have implied that copper precipitation only occurs at proportions greater than 0.5-0.6%. The present results clearly show that precipitation is occurring in these steels at a nominal copper level of 0.4% (0.38% actual). The exact composition at which precipitation becomes significant probably depends upon the presence of precipitation enhancing elements (such as B and Mo) and microstructural/heat

treatment considerations.

Hardness results for 1 hour at 650°C imply the existence of an optimum level of copper for this process and alloy type. The optimum copper content appears to be about 0.6%

The results of tensile tests show that most of the steels can be heat treated to pass the Bis 80 tensile specification with the exception of two Series 2 steels, 3679 and 3680 and one Series 3 steel, 3720. The steels which meet the Bis 80 tensile requirements also pass the tensile requirements for the military specifications MIL-S-16216(SH) and MIL-S-24645(SH).

All the Series 1, 2 and 3 steels studied satisfied the fracture toughness specifications for Bis 80. The fracture toughness requirements for the two military standards challenged the alloys more severely with the Series 1 steels 3590, 3591 and the Series 2 steels 3678, 3679 and 3680 passing all three specifications.

The series 3 alloy 3721 was designed on the basis of the earlier series with the expectation that it would meet the specified properties with reduced copper and manganese levels to reduce alloy cost. However, anomalously low values of ductility and toughness were recorded due to segregation of alloying elements. It is probable that in a normal production heat these properties would be considerably improved.

Combining both the tensile and Charpy fracture toughness results, it is plain that the following steels can be heat treated to meet the tensile and fracture toughness requirements of all specifications: Series 1 steels, 3590 and 3591 and the Series 2 steel, 3678.

The tensile results support the observation noted with the hardness results, that there is an optimum copper content for precipitation hardening of this type of steel. The hardness results indicated that this occurred at approximately 0.6% copper. The tensile results indicated that the optimum was 0.7%-0.9%. Increases above this level appear to produce no further benefit in these alloys when quenched and tempered. Combination of the tensile results with results determined

by Cabello⁸⁶ on similar hot rolled steels show good agreement when regression analysis is carried out, which confirms that copper is contributing to the observed strength, either in solid solution in the as rolled and as quenched conditions; and as precipitates after aging of both rolled and quenched steels.

Although the effect of copper on prior austenite grain size and by inference, grain growth rate appears to be quite marked, increasing the copper proportion from low (0.4%) to high levels (1%) has a negligible effect on grain size. The small austenite grain size (typically < 10 microns) will affect the hardenability of copper containing alloys and should be borne in mind when heat treating copper containing steels.

Consideration of the Jominy end quench hardenability tests indicate that these steels have outstanding hardenability. The measured Jominy distances would imply deep hardening character but examination of the microstructure 40mm along the Jominy bar contradicts this observation, indicating that hardness is being maintained by copper precipitation rather than by proportion of martensite. The Jominy tests also confirmed the importance of boron in enhancing the precipitation of copper.

Bead on plate (BOP) testing confirmed the validity of the current steel design approach in increasing weldability, as measured by maximum heat affected zone (HAZ) hardness. All of the three series of copper containing steels exhibited lower HAZ hardness than Bis 52, the leanest steel currently used in Bis 80. An additional advantage is the lack of HAZ softening exhibited by those steels containing boron and copper. Even up to heat inputs of 2.5 kJ/mm (a heat input normally expected to produce significant HAZ softening) HAZ softening is limited in the copper steels examined. The consequence of this effect is that welds can be performed on material heat treated to 690 MPa yield strength and designers can be assured that the material still maintains a high strength in the HAZ.

The BOP results were also used to test the predictive capability of models by Yurioka *et al*⁹¹ and Cottrell⁵⁰. Prediction of maximum HAZ hardness was tested and it was shown that, in general, for the Series 1 steels, the Yurioka *et al* analysis was more accurate, but for the Series 2 and 3 steels the Cottrell analysis was more accurate. Both the analyses are, however, only able to give coarse estimates of HAZ hardness.

The Yurioka *et al* model also allows estimates of preheat temperature to prevent HAZ cold cracking. This appeared to be a sensitive way of ranking the steels, although no data were generated to test the predictions.

Microstructural analysis indicates that there is little difference between the Series 1 and Series 3 steels, being composed, in the as quenched condition of lath martensite and bainitic ferrite. The Series 2 steels are very different. The microstructures of the Series 2 steels indicates low hardenability, with islands of lath martensite and bainitic ferrite surrounded by grain boundary ferrite. This microstructure is probably due to the lack of boron and is very tough, with high impact toughness observed in several Series 2 steels down to -84°C. The high toughness is probably a result of the presence of the grain boundary ferrite providing a site for blunting of the crack tip and absorbing energy.

CHAPTER 13

Conclusions.

1. The following steels can be heat treated to satisfy the Bis 80 specification and the two military specifications MIL-S-16216(SH) and MIL-S-24645(SH); Series 1 steels, 3590 and 3591; and the Series 2 steel, 3678
2. Although steel 3721 failed the elongation and reduction of area requirements, and only passed the Charpy impact energy requirements for Bis 80, the recorded results are considered to be anomalous and due to abnormal segregation. In the absence of segregation, 3721 would be expected to satisfy all specifications.
3. Precipitation hardening was observed in steels with relatively low copper content, 0.38% although hardening occurred too slowly to be useful in increasing the strength of steel plate in a production environment. This steel was boron free and the presence of boron may enhance precipitation hardening.
4. Weldability, when measured by the maximum heat affected hardness, can be improved, over existing quenched and tempered alloys, using this steel design approach.
5. The addition of modest levels of copper (0.5-0.6%) can have an additional benefit of reducing HAZ softening even in welds of relatively high heat input.

6. The strong synergy between copper and boron, observed in the hardness measured along a Jominy test piece, was confirmed by the present study.

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