CRYSTALLOGRAPHIC RELATIONSHIPS IN COPPER-ALUMINIUM-NICKEL SHAPE MEMORY ALLOYS

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SUMMARY

This thesis concerns an investigation of the elements of the shape strains accompanying the strain induced formation of $\gamma_1'$ martensite, and the formation of the $\beta_1$ phase from the $\gamma_1'$ after additional, but recoverable, strain. The characteristics of that strain were deduced from examination of the relationships between the two experimental shape strain matrices.

Part A of this thesis consists of detailed review of shape memory effect, general martensite transformation, martensitic transformation in Cu-based alloys, application of shape memory alloys and the phenomenological theory.

The experimental work is presented in Part B and comprised of the determinations of elements of the shape strain accompanying the strain induced formation of $\gamma_1'$ martensite during forward transformation, and the determination of elements of shape strain accompanying the formation of $\beta_1$ from strained $\gamma_1'$ martensite after additional, but recoverable, strain during reverse transformation.

The elements of the shape strains accompanying forward transformation and the elements of the shape strain accompanying the reverse transformation from strained $\gamma_1'$ martensite were similar to the elements of the shape strain accompanying the forward transformation and reverse transformation from unstrained $\gamma_1'$ martensite reported previously.

It is shown that the shape strain accompanying strain of the $\gamma_1'$ martensite does not have the characteristics of invariant plane strain but is possibly an invariant line strain. This result suggests that the additional strain in the martensite could occur by a combination of shears possibly by growth of two favourably oriented twins, or growth of one twin and stacking faulting, or growth of one twin and some other shear.

To make further progress it will be necessary to re-examine the nature of the strained $\gamma_1'$ martensite.
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DEFINITION OF TERMS

Various terms which are related to the present work are defined as follows:

**Reference surface**: a surface prepared using standard metallographic procedures for quantitative metallographic measurements

**Side surface**: a surface prepared at ~ 90° to the reference surface using metallographic procedures

**Trace**: line of intersection of an internal plane with either the reference surface or a side surface

**Variant**: two or more microstructural features of the same identity which are crystallographically equivalent

**Habit plane**: the plane of contact between the parent plate and the martensite plate

**Lattice orientation**: spatial disposition of the space lattice associated with the structure of a single crystal

**Forward transformation**: the transformation of the parent phase to the product phase

**Reverse transformation**: the transformation of the product phase to the parent phase

**$M_s$**: temperature at which martensite begins to form on cooling in absence of stress

**$M_f$**: temperature at which martensite formation is complete on cooling

**$M_d$**: highest temperature at which martensite begins to form upon deformation

**$A_s$**: temperature at which martensite begins to revert back to the parent phase upon heating

**$A_f$**: temperature at which the transformation of martensite to parent phase is completed upon heating
PART A: LITERATURE REVIEW
1.0 INTRODUCTION

The shape memory effect, and related phenomena, have been extensively studied for over two decades. Shape memory alloys (SMA) are a unique family of metals with the capacity to return to an original shape during heating or during release of stress. The shape memory effect and related characteristics such as pseudoelasticity and two way shape memory are known to occur in many alloy systems including Cu-Zn, Cu-Zn-Al, Cu-Zn-Ga, Cu-Zn-Sn, Cu-Zn-Si, Cu-Al-Ni, Cu-Au-Zn, Cu-Sn, Cu-Al, Au-Cd, Ni-Ti, Ni-Ti-X, Ni-Al, Fe-Pt, Fe-Mn-C [1,2] and Mn-C [2]. Shape memory effects have been shown to be associated with martensitic transformation [1,3] and in relevant alloys, both parent and martensite phases are ordered and the martensitic transformation is crystallographically reversible and thermoelastic.

The name "martensite" [4] was originally given to the constituent found in rapidly cooled steels, but subsequently the meaning was expanded to describe similar phases in other alloy systems. In copper-based alloys, the martensitic transformation occurs in the ordered bcc, β-phase matrix and, consequent upon the diffusionless character of the transformation, the martensite inherits any long range order existing in the β. Therefore, in any study of martensite in these alloys, the order-disorder reaction needs to be considered [5]. Specifically, in some Cu-Al-Ni alloys [6] the ordered bcc β₁ phase is retained during quenching and transformed to plates of the γ₁' martensite during subsequent cooling below Mₘ temperature. Deformation of the β₁ phase at ambient temperature also results in formation of γ₁' martensite, which is stable on removal of stress. The strain may then be recovered completely during reverse transformation by reheating between the Aₜ and Aₕ temperatures.
In general, the shape memory effect [7] is associated with thermoelastic martensitic transformation and involves three stages. The first is a self accommodating martensitic transformation to plate groups, each group ideally consists of four martensite variants which combine to produce essentially a zero net macroscopic shape change. Secondly, deformation of the martensite (below $M_f$) results in motion of coherent (or at least semi-coherent) interfaces in the martensite, the end result of which maybe a single crystal region of martensite which is most favourably orientated with respect to the applied stress. Lastly, reverse transformation of the deformed martensite to the parent phase occurs during heating to the $A_f$ temperature. The single crystal martensite phase transforms back into the original crystal parent phase, and the exact original shape is regained.

The capacity of the martensitic phase to transform back to the parent phase strongly suggests that the shape memory effect originates in the behaviour of the material upon martensitic transformation, deformation of the martensite and reverse transformation to the matrix phase [8]. Therefore, to understand the mechanism of the shape memory effect, the transformations and deformation characteristics must be clarified for alloy systems which show the effect.

Martensitic transformation [6] is a process of diffusionless movement of atoms activated by decrease in temperature or, in some alloys, by strain. Strain is accommodated by the formation of martensite and pseudoelastic behaviour occurs if the strain is recovered by reversal of the transformation during removal of stress. If the martensite is stable on removal of stress, the strain may be recovered by reverse transformation during subsequent heating.

The crystal structure of martensite depends on the basic transition associated with the lattice strain. It is clear that the typical martensite behaviour relates to the crystallography of the change in structure. Growth of a martensite crystal is accompanied
by a change of shape revealed on the flat polished surface by the tilting of the transformed region and it has been demonstrated \[4\] that the change of shape is macroscopically homogeneous. The geometry of tilting implies that the movement of atoms in the transformed region is regular and coordinated.

Coordinated atom movements are also compatible with the crystallographic nature of the habit plane and the existence of a correspondence in position of atoms in the parent phase and martensite structure, resulting in a definite orientation relationship between parent and martensite phases. A lattice correspondence implies that a labelled plane (or line) of atoms in the parent phase becomes a labelled plane (or line) of atoms in the martensite phase. Therefore the two lattices are related by a homogeneous strain and it is clear \[9\] that there must be a semi-coherent plane between the parent and martensite phase. These prominent features \[4\] of a martensitic transformation are geometric in nature and result from the coordinated atom movements. The existence of a correspondence and its practical manifestation in a shape change are unifying features of martensitic transformations with different kinetic and geometric properties and gives the basic concepts of the crystallographic theory of martensitic transformation.

The crystallographic theory was developed and established independently by Bowles and Mackenzie \[10,11\] and Wechsler, Lieberman and Read \[12\]. The theories are phenomenological and are based on the assumption that the change of shape can be described, at least approximately by an invariant plane strain (shape strain) in which the interface (habit plane) is invariant, so there should be zero average distortion at the interface. Since the shape strain does not in general describe the total atom movements, some additional distortion (complementary strain) is required. This complementary strain must be inhomogeneous on a macroscopic scale since it cannot be accompanied by any further change in shape and it is presumed that within a sufficiently small volume this strain can be described by a simple shear. If the elements of this shear are specified then, for an assumed correspondence between lattice vectors in the parent and martensite
structures, all crystallographic features of the transformation such as the habit plane, the orientation relationship and the shape strain, can be determined by the lattice parameters of the parent and martensite phase. The phenomenological theory has been used to examine the crystallographic features of several martensitic transformations.

Finally, the phenomenological theory is a tool which may be used to examine the crystallographic features of martensitic transformation which is central to the phenomenon of strain and strain recovery of alloys exhibiting shape memory behaviour. The objective of the work described in this thesis was to investigate crystallographic features of martensitic transformation in a Cu-15\%Al-3\%Ni alloy. The investigations comprised of determination of the elements of the shape strain accompanying the strain induced formation of $\gamma_1'$ martensite and the formation of the $\beta_1$ phase from the $\gamma_1'$ after additional but recoverable strain. Some characteristics of that strain were deduced from examination of relationships between the two experimental shape strain matrices.
2.0 SHAPE MEMORY EFFECT

Shape memory effect is a phenomenon exhibited in a group of alloys whereby non-elastic strain produced by deformation at an appropriate temperature is recovered during heating to a slightly higher temperature as illustrated in Figure 2.1 [2]. The shape recovery occurs as the deformed martensite transforms back to parent phase during heating.

Shape memory effects is known since the 1930's [2] but it is only within the last 30 years that substantial progress has been made in understanding the phenomenon and applying it in useful devices. Due to the relevance of the effect, martensitic transformation has assumed an upsurge [13] of interest through work on shape memory phenomena. The shape memory effect [14] has been popularised by the discovery in approximately equiatomic Ni-Ti at the US Naval Ordnance Laboratory (hence the name NITINOL alloys).

It is well established that the shape memory effect can occur in many alloys [1], notably Cu-Zn, Cu-Zn-Al, Cu-Zn-Ga, Cu-Zn-Sn, Cu-Zn-Si, Cu-Al-Ni, Cu-Au-Zn, Cu-Sn, Au-Cd, Ni-Ti, Ni-Ti-X, Ni-Al and Fe-Pt.

In 1971, Wayman and Shimizu [15] working together in a cooperative research program surveyed the then state of progress on the study of shape memory alloys. From the survey it became apparent that shape memory martensites were ordered, thermoelastic and internally twinned.
The shape memory effect has great potential for utilisation in a range of devices for industrial, medical and energy conversion applications. For industrial purposes [16] these include braid termination, shaft mounted components, radial assemblies, hermetic sealing, electrical connectors, hose clamps, tubing, pipes, thermostatics, automatic windows for green houses, recorder pen drives and collapsible antennae [1].

Figure 2.1: Diagrammatic representation of the shape memory effect showing elastic and non-elastic strain produced by loading, recovery of elastic strain during unloading and plastic strain during heating between the $A_s$ and $A_f$ temperatures [2].
Energy conversion-based applications was established since 1957 when the late Professor Read and colleagues [17] constructed a cyclic weight lifting device from an Au-47.5 at.% Cd alloy. For energy conversion, interest in shape memory alloys was aroused because of the recovery stresses which are generated during transformation of martensite phase to parent phase upon heating and which can convert heat energy directly into mechanical energy [18]. For medical-based purposes [1], applications include an artificial heart, blood clot filters, aneurism clamps and teeth straightening braces.

2.1 Shape Memory Behaviour

A common feature of all shape memory alloys is the occurrence of martensitic transformation. The martensitic transformation is usually thermoelastic in that forward and reverse motion of the interface (habit plane) occurs under a small mechanical or thermal driving force with a small temperature hysteresis [19]. Martensitic transformation proceeds when the alloy is cooled between the $M_s$ and $M_f$ temperatures or when the alloy is stressed between the $M_d$ and $M_s$ temperatures. Reverse transformation occurs during heating between the $A_s$ and $A_f$ temperatures or during reversal of stress.

Wayman and Shimizu [15] used the term of martensite memory or "marmem" to describe the general behaviour of the shape memory effect. Marmem and shape memory behaviour are equivalent terms for the shape memory effect and several related effects such as "two way shape memory", "rubberlike behaviour" and "pseudoelasticity".

The classical example of a marmem alloy is Ni-Ti; NITINOL [15] for which the shape memory effect can occur over a range of temperature that is sensitive to composition and addition of ternary alloying elements. A number of aspects, such as physical, mechanical, chemical properties, the phase diagram and the parent and the product crystal structures have been investigated for the alloys.
Delange and Zijderveld [20] reported that for the Ni-Ti alloys, the actual memory effect took place during heating as a statistical process of unit cells transforming to their original dimensions. Experimentally, this view is supported by the reproducibility of the texture effect during a cycle of deformation-heating-deformation.

Shape memory alloys such as Au-Cd [21] and In-Tl [22,23] are also described as having "rubberlike behaviour" in the martensite state. The "rubberlike behaviour" occurs in the martensitic condition by shape recovery when applied stress is removed. The shape memory effect and rubberlike behaviour phenomena are apparently different in character for the rubberlike behaviour occurs during unstressing of martensite, while the shape memory effect requires a temperature increase and reverse transformation.

The rubberlike phenomenon involves a reversible and elastic detwinning process and for Au-Cd alloys the rubberlike effect is sensitive to the time elapse after transformation has occurred. Immediately after transformation, marmem behaviour is typical, but after a certain period of time stabilisation occurs and the behaviour becomes rubberlike. Therefore, shape memory effect is closely related to the rubberlike behaviour, eventhough the two processes differ in character.

Another phenomenon related to the marmem effect is superelastic behaviour [24,25,26] or pseudoelasticity, which occurs in Cu-Al-Ni alloys and Cu-Zn-X alloys. These two alloys have two kinds of "rubberlike" behaviour. First, when the alloy is deformed below $M_s$, the behaviour is mechanistically analogous to the rubberlike behaviour which occurs in Au-Cd and In-Tl alloys. Secondly, when the alloy is deformed above the $M_s$ temperature, the stress induced martensite is associated with superelastic behaviour by which shape recovery occurs as the stress induced martensite disappear upon removal of the applied stress. The Cu-Al-Ni [27] and Cu-Zn-X alloys [28] also have shape memory capability when deformed in the martensitic condition.
below $M_f$. Thus, as with rubberlike behaviour, the shape memory effect appears to be correlated with the superelastic effect.

Nagasawa [29,30] and Kawachi [30] claimed that the shape memory effect also

(c) an ordered arrangement of atoms in the structure, and

(d) bcc and hcp structures for the parent and martensite phases respectively.

It was concluded that the origin of shape memory effects concerned the mobile character of the martensite/parent interface (thermoelastic behaviour) and the existence of internal twin boundaries.
2.2 Thermoelastic Behaviour In Martensitic Transformation

It is well-known that the thermoelastic behaviour is related to the shape memory effect and is a common characteristic of marmem alloys. The character of thermoelastic transformation requires a revision in the thermodynamic approach [31] because the reverse transformation is assisted by elastic energy stored from the forward transformation.

Kurdjumov [32] defined the concept of "thermoelastic" behaviour under the conditions that the elastic strain energy per unit volume of martensite can increase during growth, and that such growth can stop at a balance of chemical and non-chemical force.

Olson and Cohen [33] reported that the only necessary and sufficient condition for thermoelastic behaviour for martensitic transformation is the relative absence of means for all accommodation processes exceeding those required to establish the invariant plane condition specified by the phenomenological theories.

Wayman and Shimizu [15] argued that an alloy which forms martensite in non-thermoelastic manner then deformed, cannot revert perfectly to the original parent phase during reverse transformation. In a typical martensitic transformation, plates exists in different variant forms, and each plate has a different variant of the parent-martensite lattice orientation relationship. Thus, martensite plates with various habit planes and orientations are formed in a particular crystal of the parent phase. In principle, the same phenomenon should be expected for reverse transformation, and plate shape regions of parent phase with various orientations should be formed within an original martensite crystal. For instance, fcc austenite plates have been observed to form martensitically within an original bcc martensite crystal by reverse transformation in Fe-32.5% Ni [34]. These austenite plates formed by a shear mechanism on several habit planes. Thus, for this alloy at least, a particular crystal of martensite reverted to austenite "grains" with
different orientations and complete recovery could not occur because a single austenite orientation was not generated during the reverse transformation. This behaviour is in marked contrast to that exhibited by thermoelastic martensite reversed by "shrinkage" process to a single orientation of austenite with the initial orientation. Therefore, the consequence is that only those alloys in which martensite forms thermoelastically should exhibit shape memory behaviour.

Johnson and Dragsdorf [35], and Nelson and Altstetter [36] also found polycrystals to form from a single crystal as a result of reverse martensitic transformation in Fe-Ni alloys.

Dunne and Wayman [37] argued that ordering enhances thermoelastic behaviour because it increases the stress required to deform the matrix (and martensite) in an irreversible manner. On the other hand, "order hardening" of interphase boundaries is especially significant when martensitic transformation occurs between two ordered phases. For this case, the habit plane must satisfy the ordering requirements of both phases.

Shimizu and Wayman [27] also confirmed Cu-Al-Ni alloys as being thermoelastic and having shape memory capability. They found that the shape memory effect can occur both in completely transformed and in partially transformed material. In completely transformed material, plastic deformation is effected by the growth or creation of favourably orientated twins and the shrinkage of unfavourably orientated twins. For the partially transformed material, new martensite is induced by stress in the \( \beta_1 \) phase regions in addition to plastic deformation of existing martensite in the transformed region. Clearly, slip cannot contribute to the deformation process, because dislocation motion is not reversible and so the shape memory effect cannot occur. During heating, the martensites and internal twins transform back into \( \beta_1 \). This behaviour is related to thermoelastic transformation.
2.3 Shape Recovery

The process by which strain recovery takes place during reverse transformation depends on whether or not untransformed parent phase is present in the structure after stressing. If parent phase is present, the thermoelastic behaviour of the martensite ensures that the deformed martensite transforms back to parent phase by reverse interface motion during the release of stress or during heating. In the absence of parent phase, reverse transformation can occur only by nucleation and growth of the parent phase.

Wayman [1] claimed that the ordered structure of the parent phase, and lower crystal symmetry of the martensite, ensures that reversion to the parent phase follows a unique path to the original parent phase. This reversible transformation is related to the complete shape recovery.

Delange and Zijderverld [20] proposed that shape recovery is achieved by the reverse transformation during heating of deformation induced martensite. This theory was formulated during work on Ni-Ti alloys and explained the shape memory effect by assuming that recoverable plastic deformation is effected by the transformation of untransformed parent phase into martensite. This model can explain only the reverse transformation for partially transformed specimens and cannot explain shape recovery in specimens that have undergone full martensitic transformations.

Wayman and Shimizu [15,38] argued that the deformation process is reversible, and a material having shape memory capability should not contain mobile dislocations. They concluded that for those alloys having shape memory effect, the lattice invariant deformation must be internal twinning.
Otsuka and Shimizu [8,39] observed that the recoverable deformation occurs by a de-twinning mechanism as well as by the formation of reversible mechanical twins. They concluded that the origin of the shape memory effect lies in the thermoelastic behaviour of the habit plane between the parent and martensite phases and the internal twin boundaries which formed either on transformation or by further deformation following transformation.

Notwithstanding these proposals, full shape recovery requires that, the shape strain for the reverse transformation must be the same magnitude but opposite in direction to the shape strain for the forward transformation. This argument is explored further in Section 3.1.1.
3.0 THE MARTENSITIC TRANSFORMATION

In general, any phase transformation requires a change in either or both of crystal structure and composition. In the solid state, atomic re-arrangements take place during processes which are not phase reactions, for example, during the recrystallization of a deformed metal, or during subsequent grain growth. Such reactions are distinguished by their driving forces; the atoms take up new relative positions under the influence of strain energy, surface energy or external stress, and not because the free energy of one arrangement is inherently lower than that of the other.

The word "transformation" should then be used in a general sense to mean any extensive rearrangement of atomic structure. The definition of transformation is intended to exclude mechanical deformation by slip, which only changes the atomic arrangement by translation of one part of the structure over the remainder. However, deformation twinning may be included in the definition of transformation because of the highly ordered nature of the rearrangement, and its close relation to one type of phase transformation.

There are two types of rearrangement of the atomic configuration. Firstly, rearrangements of the atomic configuration may take place in an orderly, disciplined manner. Complete regimentation is found only in martensitic transformation in which none of the atoms change places with neighbours. This reaction has been called a military transformation [9]. An orderly rearrangement of the atoms predominantly occurs at low temperatures, so that the lower the transformation temperature is in relation to the melting point, the greater is the probability that the transformation is predominantly of the
military type. The theoretical concept which is related to the military transformation is the existence of a lattice correspondence [9].

Secondly, rearrangement may take place randomly with movements being independent of each other. This change is sometimes called a civilian transformation [9]. For a civilian [9] transformation, there can be no theoretical concept of a lattice correspondence.

Most transformations are heterogenous and may be classified into two groups which were originally distinguished from each other by a different dependence on temperature and time [40] of the reaction velocity and the amount of transformation.

The first group of heterogeneous transformations occurs by the cooperative movement of many atoms rather than by the movement of individual atoms. Most of the atoms have the same members of nearest neighbours (but in different arrangement) in the two phases and as a result, the net movements are such that, in small enough regions, a set of unit cells of the original phase is homogeneously deformed into a corresponding set of cells of the new phase. Consequently, a change of shape of the transforming region takes place and may be observed by the disturbances produced on an originally flat, polished surface. Generally, for this transformation, the amount of transformation is characteristic of temperature and does not increase with time at constant temperature. This reaction is known as diffusionless or perhaps shear transformation but, in recent years, it has become common practice to refer to this type of transformation as martensitic transformation.

In typical heterogeneous transformations of the second group, the new phase grows at the expense of the old by the relatively slow migration of the interphase boundary, and growth results from atom by atom transfers across the boundary. The atoms move independently at a rate which is determined by the temperature dependent diffusivity ;D:
\[ D = D_0 e^{-Q/RT} \]  (3.0)

The most convenient experimental feature to distinguish a reaction as martensitic seems to be the characteristic change of shape revealed on a flat surface by tilting of the transformed regions. This change of shape means that a volume of martensite, forming within the parent phase, will produce strain energy opposing the transformation in that parent phase. If atomic interchange were possible during transformation, much of this strain energy would be avoided. The change of shape is apparently tolerated only because there exists an easy growth mechanism, not requiring atomic diffusion, and which leads to the rapid production of new phase, and the net lowering of free energy [4].

Although the formation of surface relief serves to distinguish a class of phase transformation, it is desirable to attempt a more formal definition in terms of atomic properties. Such a definition must necessarily be more tentative, for although relative orientations of the two structures can be known, the actual atomic movements can only be inferred.

Martensitic reactions are possible only in the solid state, which do not involve diffusion, and the composition of the product is the same as the composition of the parent phase [4,40]. However, there are some other transformations, such as the formation of bainite in steel, in which a composition change is accompanied by a change of shape in the transformed region [4].

All martensitic transformations produce the same kind of distortion on an originally flat surface. The surface in the transformed region remains planar, but is tilted about the line of intersection with the habit plane (the trace of the habit plane). Fiducial lines on the surface before transformation remain straight in the transformed region, but their directions are changed; the whole of such a line remains continuous. Bowles and Mackenzie [10] pointed out that, from these observations, it may be deduced that the total
shape deformation is a close approximation to a homogeneous strain in which the habit plane remains invariant, that is all directions in this plane are unrotated and unchanged in length. In mechanical twinning, the shape deformation is a simple shear, but the more general invariant plane strain is a combination of a simple shear and uniaxial expansion or contraction normal to the habit plane.

Bowles and Mackenzie[10] assumed that directions in the habit plane are not rotated at all, but that length may change by small amount. Therefore, it was concluded that the whole of the shape deformation may be described as an invariant plane strain together possibly with a small uniform dilatation. In an invariant plane strain, each point moves in the same direction through a distance proportional to its distance from a reference plane. The strain is thus specified by the habit plane, the direction and the magnitude of atom movements and the magnitude for the dilatation.

The main characteristics of martensitic reactions [40] are summarised as follows:

(a) **Dependence on time** [40]

The amount of transformation is practically independent of time. At a constant temperature, the parent phase transforms rapidly, after which there is usually no other additional change. This is a primary characteristic of martensitic transformations, but in some reactions there is also a small amount of isothermal transformation to the martensite phase. In few cases, the change is completely isothermal. The isothermal characteristics are the result of thermally assisted nucleation processes.

(b) **Dependence on temperature** [40]

The amount of transformation is a characteristic of temperature, provided other variables such as grain size are constant. The velocity of transformation is probably independent of temperature and is normally very high. Transformation
on cooling begins spontaneously at a particular temperature, $M_s$, and as the
temperature decreases, more original phase is transformed to product phase,
until the temperature $M_f$ is reached, at which the change is complete. At any
temperature, a number of single crystals of new phase form rapidly within an
original grain. Upon cooling these crystals usually do not grow but new
crystals are formed. However, a single crystal of the original phase can
continuously transform into a single crystal of martensite phase.

(c) **Reversibility of the transformation** [40]

Martensitic reactions are usually reversible in the sense that on heating, a
martensitic phase will revert to the original phase. The reverse transformation
commences at a particular temperature, $A_s$, and is completed at the high
temperature, $A_f$. In shape memory alloys, reverse transformation results in a
single crystal of the same size, shape and orientation as the original crystal. This
reversibility is associated with a temperature hyteresis and in repeated
transformations, the plates (single crystals) which form on successive coolings
are identical having the same size and shape. The plates also appear in the same
sequence and in the same regions of the original crystal. This characteristic
probably applies in principle to most martensitic rections. Clearly there are
exceptions to this behaviour, where reversibility does not occur due to
interfering secondary effects. For example, in Fe-C alloys, the martensite phase
is thermodynamically unstable and will decompose into stable phases by
tempering before reverse transformation can begin.

(d) **Effect of applied stress** [40]

Plastic deformation is more important in martensitic reactions than in diffusional
processes. Application of stress at any temperature in the transformation range
($M_s$ to $M_f$) usually increases the amount of transformation and reaction can be
completed by this means. For single crystal parent phase, the direction of the applied stress may inhibit or promote the transformation. Deformation above $M_s$ may also result in the formation of the product phase, even though the temperature is too high for "thermal" transformation. The highest temperature at which martensite may be formed under stress is $M_d$. In general, the reverse reaction can be aided in the same way, and a suitable stress will induce transformation below the temperature at which it begins spontaneously during heating.

(e) **Composition, atomic volume and shape of the new phase** [40]

In a martensitic reaction, each original crystal transforms to new product phase having the same chemical composition. Volume changes are often small and in some cases are zero to within the limits of experimental measurement. Martensite crystals are usually lenticular plates, which thin towards the extremeties. The plates are orientated with respect to the lattice of the original structure, and the plane of that structure on which they are formed is called the habit plane. It has also been possible, in some transformations, to transform a single crystal of the original phase into a martensite single crystal by migration of an interface through the original crystal. This interface is coincident with the habit plane.
(f) **Orientation relationships** [40]

In a martensitic reaction, there is always a definite relation between the orientation of the lattice of the original structure and the lattice of the new phase. As with the habit planes, it is usually possible to find all crystallographically equivalent variants of the relation under suitable conditions. A single martensite plate may be a single crystal or may contain two or more twin orientations. In the latter case, the orientations of the twins relative to the matrix are not necessarily equivalent.

(vii) **Stabilisation** [40]

If the specimen is cooled to a temperature in the transformation range, held for a period of time, and then cooled again, transformation does not necessarily begin immediately upon resumption of cooling. At all subsequent temperatures the amount of transformation may be less than that produced by direct cooling. This phenomenon is referred as stabilisation. The degree of stabilisation increases with the time for which the specimen is held at the intermediate temperature. Slight variations in the amount of transformation with cooling velocity are also attributed to stabilisation. There is no general agreement on whether or not stabilisation results from halting the cooling above $M_s$ temperature.
3.1 Martensitic Transformation In Copper Based Shape Memory Alloys

Martensitic transformation in copper-based alloys was discovered in several laboratories approximately 60 years ago. Greninger and Mooradian in 1938 [2] first suggested the use of the term "martensite" to describe the structural transformation in copper-based alloys in an investigation of β-phase changes in Cu-Sn and Cu-Zn alloys. After that, similar transformations were found in other β-phase Cu-based alloys including Cu-Al [41], Cu-Al-Ni [42], Cu-Zn-Sn, Cu-Zn-Al, Cu-Zn-Si [43], Cu-Zn-Ga and Cu-Au-Zn [44]. The structures of martensite in these alloys are similar to the martensite which forms in steels during rapid cooling, and Warlimont [45] reported that a number of different martensitic phases are formed in β-phase Cu-based alloys and the martensite phases formed at similar concentrations are structurally similar.

Most Cu-based alloys have been found to transform martensitically in the bcc β-phase range of compositions which occur at an electron concentration e/a near to 3:2. The β-phase is stable over a wide range of compositions at high temperatures but the stability decreases with decreasing temperature leading to a constriction of the range of solid solution. In most pertinent alloy systems, the β-phase range is closed towards lower temperatures by eutectoid equilibrium between β, the fcc terminal solid solution, and a solute rich intermetallic γ-phase.

Martensitic transformations occur by co-ordinated atom movements which convert the initial lattice into the final lattice as described by a total lattice strain. The total lattice strain can be resolved into the shape strain (which is an invariant plane strain together possibly with a small dilation), and a lattice invariant strain. The total lattice strain transforms the matrix lattice into the martensite lattice, whereas the lattice invariant strain corresponds to heterogeneities in the martensite. For copper-based alloys, the heterogeneities may occur in two ways depending on the change in crystal structure. In
one way, the lattice strain transforms the bcc \( \beta \)-phase structure into a fcc structure and the lattice invariant strain is manifest as slip which may introduce stacking shifts ranging from random to periodically ordered (long stacking structure) and may even lead to alternating layers of different crystal structure. In the other, the total lattice strain converts the \( \beta \)-phase to a hcp structure and the invariant strain consists of twinning [46].

Generally, the two types of martensitic phase are designated \( \beta \)-type martensite, in which the lattice invariant deformation appears as stacking faults, and \( \gamma \)-type martensite, in which the lattice invariant deformation is twinning.

Apart from stacking faults or twins, the ordered atom positions have to be considered if the parent lattice is ordered. Ordering effects are responsible for orthorhombic and monoclinic distortions of the martensitic structure, and may be compared to the effect of anisotropic distortion due to carbon atoms in the structure of some ferrous alloys.

Different superscripts have been used to describe the superlattice structure of the different martensites, such as \( \beta' \), \( \beta'' \), \( \gamma' \). For example, ('') indicates that the martensite is derived from an Fe\textsubscript{3}Al type superlattice in the parent phase and the transformation product consists of one structure, and ('') indicates that transformation product is a lamellar composite of two structures.
3.1.1 The Forward Martensitic Transformation

A martensitic transformation involves diffusionless formation of one phase from another of the same composition. The prominent characteristics of martensitic transformation [47] include the following:

(a) The transformation is diffusionless, which means that the parent and product phases have no compositional differences and ordered phases transform to ordered martensites.

(b) The transformation is usually athermal, that is, it occurs only on cooling between \( M_s \) and \( M_f \) (the temperatures at which transformation to martensite starts and finishes) and the amount of product is not linearly related to temperature. The transformation may not be completed even at very low temperatures, possibly due to the severe distortion induced in retained parent phase. The relationship between temperature on cooling between \( M_s \) and \( M_f \), and the percentage of parent phase that transforms to martensite during forward martensitic transformation is represented in Figure 3.1.

(c) Martensite may be induced at temperatures above \( M_s \) by mechanical deformation up to a limiting temperature, termed \( M_d \). Strain above \( M_d \) can lead to mechanical stabilisation of the parent phase against subsequent transformation during cooling.

(d) There is a change in shape for the transformed volume and this appears as tilting and rumpling on prepolished surfaces.

(e) The parent and product phases are at least semi-coherent across the interface habit plane which must be restricted to certain crystallographic planes which give a good fit between the two structures.
Although in general, most transformations considered to be martensitic have the majority of these characteristics, the one characteristic that they all possess is that which involves a shape change corresponding to a homogeneous strain.

Since the martensite phase has a different crystal structure from the parent phase, there is therefore a change in volume of the transformed region. This change in volume, $\delta V$ was defined by Kakeshiita, et al [48] as $\delta V = V_m - V_p$, where $V_m$ and $V_p$ are the volumes per atom in the martensite and parent phases respectively. If the change in volume, $\delta V$ is large, then coherency of the interface will be difficult to sustain during transformation [8].
For most martensitic transformations, the overall change in macroscopic volume is in the range 0 to 4% and in many cases, regions of single orientation in the parent phase transform typically to many different, self accommodating arrangements of martensite variants [49]. Each separate arrangement commonly consists of four martensite variants (plates), back to back as shown in the schematic diagram in Figure 3.2. This arrangement results in the martensite having a characteristic "spear like" or "diamond" morphology which is adopted to minimise the strain energy associated with the transformation.

![Schematic diagram of martensite variants](image)

Figure 3.2: A schematic representation of the four variants of martensite found in a spear like plate group [7].

Saburi and Wayman [7] reported that in the $\gamma_1'$ martensite of Cu-Al-Ni alloy, the four variants were symmetrically disposed about the {100} family planes in the parent $\beta_1$ crystal structure. The four variants are collectively called a "plate group" and are twin related in a way which depends upon the specific {100} plane the group formed about. For example, in Figure 3.2, if the group formed about the (011) plane then A and C (and B and D) will be twin related. If the plate group formed about (100) then A and D (and B and C) will be twin related.
According to crystallographic theory, during the forward martensitic transformation, inhomogeneous shear must be accommodated by the martensite. Saburi and Wayman [7] reported that in $\beta_1'$ martensite this shear is accommodated by faulting on the martensite basal plane, and in $\gamma_1'$ martensite by transformation twinning on the same plane. In both cases, the basal plane in the martensite may originate from one of the six \{100\} planes of the parent bcc phase. For each of these six planes, there exists two possible shear directions resulting in twelve possible combinations. As there are two crystallographically equivalent habit planes, twenty four different variants of martensite may form from a single crystal of $\beta_1$ [7].

The martensitic transformation due to applied stress occurs by the same coordinated atomic movements. However, deformation between $M_d$ and $M_s$ causes nucleation of favourably orientated plates of martensite which grow during further deformation [2]. After complete transformation to martensite, further deformation results in the favourably orientated variants growing at the expense of other variants [50]. Deformation to low strain of a fully martensitic structure can occur by growth of favourably orientated twins if present in the structure of the martensite, or alternatively, by deformation twinning. High strain deformation occurs by growth of favourably orientated plates by motion of the interface with adjacent plates. In the extreme case, up to 17% recoverable strain occurs by transformation of the martensite to a new martensitic structure. These processes result in growth of the most favourably orientated of the many original variants of the martensite at the expense of other variants and can theoretically lead to the formation of a single crystal of martensite.
3.1.2 The Reverse Martensitic Transformation

In shape memory alloy systems, the reverse transformation from martensite to parent phase occurs upon heating between the $A_s$ and $A_f$ temperatures [2,7] as in Figure 3.3, or during reversal of stress. Each crystal of martensite transforms back into the original crystal of the parent phase, and the original shape is regained. The shape memory effect is associated with the reverse transformation and the term "marmem" (martensite memory [15]) was coined to describe the general behaviour.

For cases where the forward transformation is incomplete, for instance by cooling to between $M_s$ and $M_f$, some parent phase will remain untransformed. Heating in this state results in the reverse movement of existing interfaces [8,17,49], and the reverse transformation corresponds directly to the shape recovery process of the marmem behaviour [27]. The origin of shape recovery from a fully martensitic structure is far less clearly defined.

Clearly, investigation of shape recovery processes is very important in elucidating the mechanism of the marmem behaviour but it is evident that the reverse transformation has not been studied systematically compared with the forward transformation and deformation processes. Complete shape recovery can be realised only when two conditions are satisfied. First, each volume element of martensite reverts to the original orientation of the matrix phase by reverse transformation (ie. crystallographic reversibility), and secondly, all structural defects, which are associated with deformation in the wholly or partially martensitic state, are annihilated during the reverse transformation [8].

It has been suggested [15,51] that additional requirements for reverse martensitic transformation are that the matrix and martensite structure be ordered and that the martensite structure has lower symmetry than the matrix structure [51,52].
Figure 3.3: Schematic representation of the forward transformation between $M_s$ to $M_f$ and reverse transformation between $A_s$ and $A_f$.

Notwithstanding these suggestions, there is some evidence for accumulation of structural defects during forward and reverse transformations. Transmission electron microscopy [53] showed that after transformation cycling, parent crystals of Fe-Al contained dense dislocation networks, a few stacking faults along $\{111\}$ and the orientation relationships measured between the martensite and the reverse parent crystal were close to the orientation relationships for the austenite-martensite transformation [34]. These observations suggested that the crystallographic nature of the reverse transformation is basically the same as that for the forward austenite to martensite transformations and should be explained in terms of the crystallographic theory [53].
In other alloys, the reverse martensitic transformation produced high densities of dislocations in the parent phase [54] and Krauss [55] observed a complex dislocation structure in austenite formed during reverse transformation in Fe-Ni alloys. Kajiwara and Owen [56,57] found that austenite formed during reverse transformation in disordered Fe-Pt alloys also contained a high density of dislocations with a unique arrangement. In other cases again, it was reported [56,57] that very few dislocations are produced by reverse martensitic transformation in highly ordered Fe-Pt alloys and Cu-Zn alloys which undergo thermoelastic martensite transformation. Umemoto and Wayman [58] observed scattered dislocations lying on (100) planes in austenite formed during reverse transformation was in partially ordered Fe-Pt alloy in which the transformation behaviour was nearly, but not ideally thermoelastic.

These observations suggest that the density of dislocations produced by reverse martensitic transformation depends on the nature of the martensitic transformation. The dislocations in austenite formed during reverse transformation are quite different from the straight or smoothly curved dislocations in the retained austenite associated with the direct martensitic transformation [8].

Shimizu and Otsuka [8] found that the reverse transformation of $\gamma_1^*$ martensite in ordered Cu-Al-Ni alloys has available to it only one variant which will result in the generation of the ordered parent phase in the original orientation. It was also suggested that, as a consequence of the generation of the ordered parent, and the fact that the transformation is thermoelastic, all defects associated with the martensite, and the martensitic interface itself will be annihilated on reverse transformation.

Cockerill [59] argued that the high density of dislocations formed in the reverse transformation is a result of accommodation of the difference in atomic volume between the martensite and the parent phases. The dislocations become significant when the difference in volume is large enough to generate a sufficiently high dislocation density to
impede the motion of the parent-martensite interface during reverse transformation, as in the case for steels. Using this argument, if the density of dislocations produced is below the level required to effect the parent-martensite interface, then the effect on the reverse transformation will be minimal.

Michal and Sinclair [60] and Goldstein and Falleiros [61] also pointed out that exact reversibility of the interface for thermally induced martensite formed in Ni-Al alloys during cooling, generated the original parent structure but the path of the reverse transformation was not the path followed in the forward transformation. However, they observed that in a Cu-Al alloy, the parent phase nucleated as fine lamellae within thermally induced $\beta_1'$ martensite possibly in striations in that $\beta_1'$. Again, in this case, the forward formation path was not followed by the reverse transformation.

3.2 The Morphology Of Martensite Copper Based Shape Memory Alloys

The crystallography and morphology of the Cu-Al-Ni martensites has been well established compared with other marmem alloys such as Ag-Cd and Cu-Zn [62]. The Cu-Al-Ni alloy having composition near to $(\text{Cu},\text{Ni})_3\text{Al}$ has attracted considerable attention and is well-studied as it has interesting mechanical behaviour, such as the shape memory effect and superelasticity associated with a thermoelastic martensitic transformation [63]. Apart from this, the martensite has a morphology called spear-like form [64], which is considered to be responsible for its growth into a large crystal, as usually observed, without losing coherency at the boundary.

It is well-established that Cu-Al-Ni alloys [62] transformed directly from the $\beta_1$ parent phase to either $\beta_1'$ or $\gamma_1'$ martensite depending on composition. Additionally, Otsuka, Sakamoto and Shimizu [62] reported that a martensitic transformation occurs
between martensites in Cu-Al-Ni and it was proposed that observed transformation from \( \beta_1' \) to \( \gamma_1' \) occurred by the following steps. First, the \( \beta_1' \) martensite was stress-induced from a \( \beta_1 \) matrix single crystal at a temperature above \( A_f \). Secondly, the specimen was cooled while keeping the stress constant. Thirdly, the specimen was unloaded during which the martensitic transformation from \( \beta_1' \) martensite to \( \gamma_1' \) martensite occurred. It was suggested that martensite formed by stress-induced martensitic transformation may be different from the martensite formed by thermally induced transformation. In the case of Cu-Al-Ni with composition near to 14.2% Al and 4.3% Ni, acicular martensite appeared under stress while spear-like martensite appeared by cooling below \( M_s \) temperature.

3.2.1 \( \gamma_1' \) Martensite

The \( \gamma_1' \) martensite formed in copper based alloy is usually observed after slow cooling or stressing above the \( M_s \) temperature [8], and is described as having a diamond or spear-like morphology characteristic. It also occurs in single plate-like forms with 2H structure and stacking faults near the boundaries between the matrix and the martensite; the middle of the plate is nearly defect free, except for antiphase domain boundaries inherited from the matrix \( \beta_1 \). The "spear-like" form [64] consists of two parts divided by a ridge at the center. Otsuka and Shimizu [64] reported that the two halves are twin related with a \( (121)^{\gamma_1'} \) twinning plane as a plane of the ridge. This martensite has a hcp structure, or an orthorhombic distortion of that structure. The plate groups generally have dense, finely spaced striations or transverse markings on either side of a clearly visible mid-rib.
Saburi and Wayman [7] analysed the crystallography of these spear-like morphologies and found that they comprised of four separate twin related variants. The striations were found to be due to transformation twinning which provided the inhomogeneous shear required for the interface to remain invariant. The crystallographic relations between the variants are shown in Figure 3.4.

Figure 3.4: Crystallographic relationships between the four martensite variants in the \((01\bar{1})_{\beta_1}\) plate group for \(\gamma_1\) martensite. Solid lines: variant and twin boundaries \(\overline{1} = (01\bar{1})_{\beta_1}\).

Dashed lines: basal planes \(3 = (\overline{1}01), \ 4 = (101), \ 5 = (\overline{1}10), \) and \(6 = (110)\), related to the \(\beta_1\) matrix. The striations result from twinning on the \(3 = (\overline{1}01), \ 4 = (101), \ 5 = (\overline{1}10)\) and \(6 = (110)\) planes [7].
In cases where the martensite forms as a single variant rather than part of a plate group [8], the advancing interface often consists of many steps that result in a macroscopically curved appearance, Figure 3.5.

Figure 3.5: Scanning electron micrographs of a stepped interface between the β matrix and γ₁' martensite ((a) and (b)), with a schematic interface (c) as expected from the phenomenological theory [8].

Shimizu and Otsuka [8] suggested that, to support the phenomenological theory of martensite transformations, these steps were due to internal twinning, so that the interface would be an invariant plane. They noted that the twins became thinner and more densely spaced toward the interface resulting in a reduction of elastic energy, which is important near the interface. They also noted that internal twins may extend into the parent phase matrix as though they were independent martensite variants. This was attributed to stresses associated with coherency.
It should be noted that the internal twinning observed by Shimizu and Otsuka [8] is identical with the transformation twinning observed by Saburi and Wayman [7]. Internal twinning is shown in Figure 3.6 parallel to the single headed arrows. Thicker and more widely spaced twins may also occur in $\gamma_1$ martensite as a consequence of accommodation twins [7] and are also shown in Figure 3.6 parallel to the double headed arrows.

Figure 3.6: Photomicrograph of several plates of $\gamma_1$ martensite showing striations (traces of faults on the basal plane), parallel to the single headed arrows, and internal twinning, indicated by the double headed arrows [7].
3.2.2 β₁' Martensite

The β₁' martensite formed in copper-based alloys has been described as having an "acicular" morphology. Generally, β₁' martensite is formed during quenching below the Ms temperature or may be stress induced [8]. In Cu-Al-Ni alloys, the crystal structure of stress induced martensite was identified as 18R type long period stacking order structure with AB'CB'CA'BA'BC'AC'AB' stacking sequence [8] which is the same as the thermally formed β₁' martensite in a Cu-Al binary alloys.

Internal defects in the β₁' martensite are stacking faults on the basal plane and the habit plane is close to {155}β₁. The orientation relationship between matrix and martensite is consistent with that in stress induced β₁' martensite in Cu-Al-Ni alloy and thermally induced β₁' in a binary Cu-Al alloy.

3.3 Stress Induced Martensitic Transformation In Cu-Al-Ni Shape Memory Alloys

3.3.1 The β₁ To γ₁' Transformation

An ordered β₁ structure is formed when Cu-Al-Ni alloys are cooled from a homogenising temperature of 900° to 950° C to a temperature in the range between Ms and Af. Figure 3.7 [65] shows a vertical section of the Cu-Al-Ni ternary system and includes the region where the β-β₁ transformation occurs on quenching. Body centred cubic β phase can transform to two types of ordered structures identified by the structure symbols (strukturbericht) [66] B2 and DO₃.
Figure 3.7: Vertical section of the Cu-Al-Ni ternary system at 3% Ni where the transformation $\beta \rightarrow \beta_1$ occurs when quenching through the ordering temperature [65].
The B2 structures are formed when the composition is approximately 50 at.% Cu and is the simple CsCl type comprising a copper atom at the cell corner sites and a solute atom at the cell centre site.

The DO₃ structure is formed when the composition is stoichiometric and is complex comprising eight cells with copper atoms at all corner sites and at the centre sites of four cells with solute atoms at the other four cell centre sites.

Martensite can be stress-induced from the ordered β₁ when an alloy of suitable composition is deformed between the Mₐ and Mₛ temperatures. The stress induced martensite inherits the ordered structure and has the 2H orthorhombic structure in Ramsdell notation [64, 67, 68, 69].

The 2H structure is usually formed in either a thick plate morphology [64] or a thin plate morphology [70] and contains twins and stacking faults [71]. It is usually designated γ₁ as it is derived from DO₃ order and has an AB'AB'..... stacking sequence. This structure is almost close packed hexagonal but it is usually orthorhombic. The crystal structure of the β₁ and γ₁ phases and the proposed [71] lattice correspondences of the two phases are shown schematically in Figure 3.8.
closed circles: Al atoms
open circles: Cu or Ni atoms.

Figure 3.8: Diagrammatic illustration showing the lattice correspondence [71] in transformation from the $\beta_1$ parent phase to $\gamma_1'$ martensite:

(a) DO$_3$ type ordered structure of the $\beta_1$ matrix.

(b) Orthorhombic unit cell derived from delineated part of DO$_3$ cell outlined.
3.3.2 Lattice Parameters For The $\beta_1$ And $\gamma_1'$ Phases

The lattice parameters for a Cu-14.2%Al-4.3%Ni alloy were determined by Otsuka and Shimizu [63] for thermally induced martensite using selected area diffraction from specimens onto which TiCl was evaporated as a standard. Otsuka, et al [72] found that the lattice parameter for $\beta_1$ was 583.6 pm and that the lattice parameters for $\gamma_1'$ stress induced martensite were the same as for thermally induced martensite as shown in Table 3.1.

Table 3.1: Lattice parameters for stress induced and thermally induced orthorhombic $\gamma_1'$ martensite [72].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Thermally and stress induced martensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>438.2 pm</td>
</tr>
<tr>
<td>$b$</td>
<td>535.6 pm</td>
</tr>
<tr>
<td>$c$</td>
<td>422.2 pm</td>
</tr>
</tbody>
</table>

Kennon and Dunne [6] made accurate determination of the lattice parameters for the $\beta_1$ and $\gamma_1'$ phases in a Cu-Al-Ni alloy using CrK$_\alpha$ X-ray diffraction powder patterns obtained from needle shaped specimens that were either cooled or lightly deformed to produce martensite at the tips. The results are given in Table 3.2.
Table 3.2: Lattice parameter for $\beta_1$ and $\gamma_1'$ of stress induced and thermal induced martensite [6].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thermally induced martensite</th>
<th>Stress induced martensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\gamma_1')$ a</td>
<td>439.7 pm</td>
<td>439.3 pm</td>
</tr>
<tr>
<td>$(\gamma_1')$ b</td>
<td>536.3 pm</td>
<td>535.7 pm</td>
</tr>
<tr>
<td>$(\gamma_1')$ c</td>
<td>422.0 pm</td>
<td>421.5 pm</td>
</tr>
<tr>
<td>$(\beta_1)$ a</td>
<td>292.05 pm</td>
<td>292.00 pm</td>
</tr>
<tr>
<td>volume ratio g</td>
<td>0.998723</td>
<td>0.996028</td>
</tr>
</tbody>
</table>

The value of g is defined as the volume ratio per atom in the final and initial structures.

3.3.3 Shape Strain Associated With Stress Induced Martensite In Cu-Al-Ni Alloys

When a specimen of a Cu-Al-Ni alloy is stressed at an appropriate temperature, $\gamma_1'$ martensite plates are formed in the $\beta_1$ matrix. The shape strain $S_R$ for these $\gamma_1'$ plates is assumed to be an invariant plane strain defined by the habit plane $p'$ and the magnitude $m$ and direction $d$ of the displacement vector, together possibly with a small isotropic dilatation $\delta$ [6] and can be written in matrix notation as:

$$S_R = \frac{I}{\delta}(I +mdp')$$  \hspace{1cm} (3.3.3)
Kennon and Dunne [6] determined the elements of the shape strain for thermally-induced plates and for stress-induced plates in a Cu-14%Al-3.4%Ni alloy. For thermally induced plates they used surface tilt method to obtain the elements shown in Figure 3.9 (a) and Table 3.3. For stress induced plates they used scratch displacement method and the habit plane, direction of atom movements, and magnitude were determined for the assumption that $\delta = 1$, as shown in Figure 3.9 (b) and Table 3.4 [6].

Figure 3.9: Stereographic projection showing habit planes near $\{\overline{3}31\}_B$ and displacement vectors near $[\overline{1}10]_B$ and for:

(a) Five thermally induced plates of $\gamma'_1$ martensite, and

(b) fifteen stress induced plates of $\gamma'_1$ martensite [6].
Table 3.3: Crystallographic measurements for thermally induced martensite represented in Figure 3.9 (a) [6].

<table>
<thead>
<tr>
<th>Plate</th>
<th>Magnitude, $m$</th>
<th>Dilatation, $\delta$</th>
<th>$\cos^{-1}(p'.d)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.089172</td>
<td>1.000076</td>
<td>90.67</td>
</tr>
<tr>
<td>2</td>
<td>0.088351</td>
<td>1.000542</td>
<td>89.77</td>
</tr>
<tr>
<td>3</td>
<td>0.097178</td>
<td>0.996503</td>
<td>96.93</td>
</tr>
<tr>
<td>4</td>
<td>0.078050</td>
<td>1.000118</td>
<td>90.68</td>
</tr>
<tr>
<td>5</td>
<td>0.085350</td>
<td>1.002481</td>
<td>85.85</td>
</tr>
<tr>
<td>Average</td>
<td>0.087620</td>
<td>0.999944</td>
<td>90.78</td>
</tr>
</tbody>
</table>
Table 3.4: Crystallographic measurements for stress induced martensite represented in Figure 3.9 (b).

<table>
<thead>
<tr>
<th>Plate</th>
<th>Magnitude, m</th>
<th>$\cos^{-1} (\mathbf{p} \cdot \mathbf{d})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.085887</td>
<td>90.85°</td>
</tr>
<tr>
<td>2</td>
<td>0.096102</td>
<td>90.76°</td>
</tr>
<tr>
<td>3</td>
<td>0.081004</td>
<td>90.96°</td>
</tr>
<tr>
<td>4</td>
<td>0.081785</td>
<td>90.89°</td>
</tr>
<tr>
<td>5</td>
<td>0.093063</td>
<td>89.92°</td>
</tr>
<tr>
<td>6</td>
<td>0.090690</td>
<td>90.81°</td>
</tr>
<tr>
<td>7</td>
<td>0.092125</td>
<td>90.79°</td>
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<tr>
<td>8</td>
<td>0.080560</td>
<td>90.90°</td>
</tr>
<tr>
<td>9</td>
<td>0.076806</td>
<td>89.30°</td>
</tr>
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<td>10</td>
<td>0.083539</td>
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<tr>
<td>11</td>
<td>0.090674</td>
<td>90.81°</td>
</tr>
<tr>
<td>12</td>
<td>0.086449</td>
<td>90.85°</td>
</tr>
<tr>
<td>13</td>
<td>0.085625</td>
<td>90.85°</td>
</tr>
<tr>
<td>14</td>
<td>0.096186</td>
<td>90.76°</td>
</tr>
<tr>
<td>15</td>
<td>0.098769</td>
<td>90.74°</td>
</tr>
<tr>
<td>Average</td>
<td>0.088018</td>
<td>90.66°</td>
</tr>
</tbody>
</table>
From the measurements, it was concluded that there was no significant difference between the two shape strains with habit planes scattering near \((\overline{3} \overline{3} 1)_{\beta}\), and displacement vectors scattering near \([\overline{1} 1 0]_{\beta}\). The strain magnitude was approximately 0.087 for both martensites.

Further work by Kennon, Dunne and Middleton [73], using the same Cu-Al-Ni shape memory alloy, strongly confirmed that the dilatation parameter is not significantly different from unity for both thermally-induced martensite and stress-induced martensite. Their direct estimates of the dilatation parameter are given in the Table 3.5.

As a result of their findings, \(\delta = 1\) will be applied to the analysis presented in this thesis for calculations of the shape strain elements for the forward and reverse martensitic transformations. Therefore, the shape strain is assumed to be an invariant plane strain very close to a simple shear as \(p'.d = 0\) [6].

Collectively, results presented in this section indicate that the elements of the shape strain for both stress-induced and thermally-induced martensitic transformation in Cu-Al-Ni alloys have been well-established [6,73].
Table 3.5: Direct estimates of the Dilatation Parameter

<table>
<thead>
<tr>
<th>Thermally induced plates</th>
<th>Stress induced plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_1 )</td>
<td>( \delta_2 )</td>
</tr>
<tr>
<td>1.0004</td>
<td>0.9994</td>
</tr>
<tr>
<td>0.9996</td>
<td>0.9966</td>
</tr>
<tr>
<td>1.0009</td>
<td>1.0036</td>
</tr>
<tr>
<td>0.9961</td>
<td>0.9986</td>
</tr>
<tr>
<td>1.0013</td>
<td>0.9997</td>
</tr>
<tr>
<td>0.9982</td>
<td>0.9982</td>
</tr>
<tr>
<td>1.0011</td>
<td>1.0008</td>
</tr>
<tr>
<td>1.0004</td>
<td>0.9984</td>
</tr>
<tr>
<td>0.9986</td>
<td>0.9991</td>
</tr>
<tr>
<td>0.9986</td>
<td>0.9961</td>
</tr>
<tr>
<td>0.9973</td>
<td>0.9982</td>
</tr>
<tr>
<td>0.9985</td>
<td>0.9991</td>
</tr>
<tr>
<td>0.9985</td>
<td>0.9977</td>
</tr>
<tr>
<td>Average</td>
<td>0.9990</td>
</tr>
</tbody>
</table>
3.4 Methods For Determining The Shape Strain Elements In Martensitic Transformations

The shape strain accompanying martensitic transformation is specified by the habit plane \( p' \), the direction of atom movements \( d \), the magnitude of atom movements \( m \) and dilatation parameter \( \delta \). For the case that \( \delta = 1 \) the shape strain may be expressed in matrix notation:

\[
S_R = I + mdp
\] (3.4.0)

Methods that may be used to determine the elements of the shape strain include:

(a) single surface analysis

(b) two tilt analysis

(c) three tilt analysis

These three analyses will be described briefly in this section. Comparison of the analyses will be made and relative benefits analysed to determine the most appropriate method for a particular application.

3.4.1 Single Surface Analysis

The location of a plane cannot be determined from the trace in a single surface but traces of three or more variants of a particular plane in a reference surface can be used to determine the general crystallographic identity of those planes. For each trace, the zone in stereographic projection contains all possible solutions to the normal to the plane. In general, each trace will pass through nine stereographic triangles, which for cubic crystals are crystallographic equivalent. Therefore, if each segment for each of three traces is plotted in a single stereographic triangle, a common intersection defines the plane
for which it is a variant. Experimental error of measurement will usually ensure that the segments do not share a common intersection.

The shape strain elements, other than the habit plane, can be determined in the single surface method from measurements of the tilt of the surface and displacements of two or more non-parallel fiducial reference lines (scratches) lying in this tilted surface. The experimental procedures for determining the strain direction and strain magnitude involves the measurement of initial and final directions of these scratches. A plane that contains the strain direction, together with the strain magnitude, is determined explicitly for the case that the shape strain is exactly an invariant plane strain, that is, the dilatation parameter $\delta$ is unity. The initial and final directions of a second fiducial line define a second plane that contains the strain direction which is therefore located at the intersection of the two planes and the strain magnitude has an associated explicit value [74]. For three or more scratch displacements, the problem is over determined and statistical methods can be used to assess the accuracy of the results [75].

For multiple scratch measurements, it is estimated that the single surface analysis is capable of providing a determination of the habit plane to within 1°, the strain direction to within 2° and the strain magnitude to within 5% of the correct value [76].

### 3.4.2 Two Tilt Analysis

In the two tilt analysis, traces of a (habit) plane in a reference surface and an additional surface determined the location of that plane with precision which depends upon the accuracy with which measurements of the trace angles ($\alpha$, $\beta$) and interfacial angle ($\sigma$) are made.
The magnitude and direction of the shape strain for a particular martensite plate can be determined from the tilt of the plate in two surfaces using the method described by Dunne and Wayman [76]. In this method, the two tilt displacements define a plane which contains the shape strain direction and the values for \( m \) and \( d \) can be obtained from the equation:

\[
\mathbf{n}'S_{R}^{-1} = \mathbf{A}f' \tag{3.4.2}
\]

where \( \mathbf{n}' \) is the normal to original surface, \( S_{R} \) is the shape strain, \( \mathbf{A} \) is a scalar quantity and \( f \) is the normal to the tilted surface. The equation can be expanded and equivalent terms equated to obtain expressions for \( m_{d1}, m_{d2} \) and \( m_{d3} \) where \( d = [d_{1}d_{2}d_{3}] \).

To obtain a unique solution for the magnitude and direction of the shape strain it is necessary to evaluate \( m_{d1}, m_{d2} \) and \( m_{d3} \) which are specified in terms of the dilatation parameter. In the present work it was assumed that the dilatation parameter \( \delta \) was unity, consequent upon previous work on the same alloy.

### 3.4.3 The Three Tilt Analysis

The traces of a habit plane in three surfaces, which are approximately orthogonal, can be measured to determine the habit plane with high precision. The tilt of the plate in each surface defines the final direction of each of the three edges between the surfaces and so defines three planes containing the direction of the shape strain. Three solutions for the directions and magnitudes of the strain vector (and of the dilatational parameter) are obtained from the intersections of those planes and will differ only because of experimental error. Best fit solutions for the strain direction and the strain magnitude have been reported [70,76] for this method.
The three tilt analysis gives the most precise determination of the shape strain elements as it is possible to use interference microscopy to measure the tilt angles more accurately than any other method and for measuring the direction of a fiducial line on the tilted surface of a plate. Angular measurements of the habit plane traces in the three adjoining surfaces, the tilts of those plates, the interfacial angles for the specimen and the volume ratio can all be obtained with comparable precision. Thus, solutions for the shape strain elements can be obtained with considerable precision without invoking any assumptions.

The three tilt analysis is similar in many respect to the two tilt method but provides better accuracy in determination of the shape strain elements. However the three tilt analysis is restricted to systems in which a single martensite plate can develop relief effects in three surfaces of an approximately orthogonal specimen. Due to this limitation, the scratch displacement method or two tilt analysis offers more general applicability, but with less accuracy. It has been argued that the three tilt analysis of shape strain determination yield results of comparable accuracy [96] but this accuracy is governed largely by the martensite plate quality.

As the accuracy of all the analyses is reasonably good, choice of a particular analysis is governed either by the geometry of the specimens, or the conditions under which the martensitic transformations occur. The three tilt analysis is suitable for thermally induced martensitic transformation but not for the stress-induced martensitic transformation for which two tilt analysis is more appropriate.
4.0 CRYSTALLOGRAPHY OF MARTENSITIC TRANSFORMATION

Crystallographic features of martensitic transformations have been studied since the early 1950's and have been incorporated in the development of the phenomenological theories. The most obvious geometrical characteristics of a martensitic transformations are:

(a) a change in the shape of the transformed region manifest as well-defined surface relief effects (tilting) when a crystal of parent phase having a smooth surface transforms into a martensite product,

(b) a defined lattice orientation relationship between the lattices of the martensitic phase and the parent phase,

(c) the existence of a plane, known as the habit plane or interface plane, which separates the parent and martensitic phases, and

(d) the occurrence of martensite as plates or laths which are not homogeneous but contain arrays of twins, stacking faults, dislocations or other defects.

In 1953, Weschler, Lieberman and Read [12] (denoted as WLR) in the United States of America, and Bowles and Mackenzie [10, 11] (denoted as BM) in Australia independently developed a successful phenomenological theory. The WLR theory was developed for a specific transformation in steels and non-ferrous metals. On the other hand, BM developed a general theory to be applied to a variety of transformations in steels and non-ferrous metals. The phenomenological theory is based on intrinsic assumptions of a lattice correspondence and a lattice invariant shear (to account for
heterogeneity). These provide a means of predicting the habit plane, orientation relationship, shape deformation and other parameters of a transformation from the lattice parameters and crystal structures of the parent and martensite phases. The mathematical approaches using matrix algebra by BM and WLR were distinctly different, but fundamentally the two theories are the same.

Using the same principle as BM and WLR, Bullough and Bilby [77] developed a surface dislocation approach. Bilby and Frank [78] devised a prism-matching analysis in which triangular prismatic structural units of the two phase are fitted together at the habit plane. Wayman [79], Bilby [80] and Christian [81] have since provided excellent reviews of the crystallographic theory of martensitic transformations.

The BM theory is more general and easily applicable for non-ferrous alloys thus it is used for the work described in this thesis.

4.1 The Phenomenological Theory

4.1.1 The Bowles-Mackenzie Theory

The BM theory [10, 11] is based on the assumption that the lattice strain can be expressed in terms of the shape strain and a complementary strain which is a simple shear on a twinning plane or in twinning direction of the martensite lattice. Therefore, the complementary strain is a part of the twinning shear of the martensite, but this strain must occur inhomogeneously on a macroscopic scale. In a physical sense the parent lattice is converted into an intermediate lattice by the shape strain, \((I/\delta)P_1\), then the intermediate lattice is transformed into the martensite lattice by the complementary strain.
The complementary strain $P_2$ is regarded as a combination of shears accompanied by localised inhomogeneities which counteract any macroscopic change in shape. These localised inhomogeneities leave the martensite lattice unchanged and so there can only be slip displacements on closely spaced planes parallel with the twinning plane, or a system of reverse shears which produce twin orientations.

The general composition of the total lattice strain, $S_t$, which converts the initial lattice into the final lattice, is established by the observed nature of the component shape and complementary strains. The total lattice strain, $S_t$, can be expressed by the matrix equation:

$$S_t = \left( I/\delta \right) P_2 P_1 \quad (4.1.1)$$

where $I/\delta$ is a pure dilatational strain.

In a homogeneous strain, such as the total lattice strain, there is always at least one line which is unrotated by the strain and, by removing an appropriate dilatation, this line can be converted into an invariant line $x_i$, and the total lattice strain $S_t$ can be converted into invariant line strain $S$. An invariant line strain $S$ is the resultant of two invariant plane strains (in this case, the strain $P_1$ and complementary strain $P_2$) because the line of intersection of their invariant planes is obviously invariant throughout. So the invariant line $x_i$ is the direction of intersection of the invariant planes of the strains $P_1$ and $P_2$. The plane which contains the directions of the two invariant plane strains has an invariant normal $n_i$. Therefore, the condition that restricts the nature of the total lattice strain is that the twinning shear plane should contain the invariant line and the twinning direction should lie in the plane with the invariant normal $[82]$.

If the invariant line strain $S$ is known, it can be resolved into two invariant plane strains $P_1$ and $P_2$ on arbitrary planes containing the invariant line $x_i$ by considering the total displacements of vectors or plane normals which are invariant in one of the invariant
plane strains. The two invariant plane strains $P_1$ and $P_2$ are determined uniquely if either the planes or directions of the two strains are specified. Then, all other features of the transformation can be specified.

In order to find the total lattice strain $S_t$, it is necessary that the correspondence between the parent lattice and martensite lattice be specified. Lomer [83] proposed that the correct correspondence is that which leads to the smallest principal strains in the pure strain component of the homogeneous strain and thereby allows the correspondence to be found by trial and error without using the orientation relationship [84]. Jaswon and Wheeler [85] proposed that the correct correspondence is that which involves the smallest atom displacements in the associated strain. This criterion has been confirmed in observed superlattices [10] and the positions of interstitial atoms [86] in a number of transformations, and it can often be applied by inspection of the orientation relationship [78]. Therefore, the total lattice strain can be determined provided that the parameters of the parent and martensite phases and their relative orientations are known. The accuracy with which the total lattice strain can be determined depends upon the accuracy of the measurement of the orientation relationship and experimental errors are approximately $0.5^\circ$. This error can cause large movements of unrotated lines and planes and, as a result the invariant line of the total lattice strain will not lie in the habit plane. Consequently the factorisation cannot be carried out with confidence.

Alternatively, the total lattice strain $S_t$ can be converted into an invariant line strain $S$ by removal of suitable dilatation. As the strain $S_t$ can be expressed by

$$S_t = RM$$

(4.1.2)

the strain $S$ becomes,

$$S = \delta RM$$

(4.1.3)
where $M$ represents the pure strain which extends all lattice vectors to their final lengths without rotating the principal axes and $R$ represents that rotation which rotates the principal axes into their corresponding directions in the martensite lattice. The principal axes of a homogeneous strain is that set of orthogonal axes that remain orthogonal after application of the strain.

The strain $S$ can be calculated by making use of the relationship between the invariant line strain and the initial positions of the twinning direction, $u$, and the normal of the twinning plane, $h$. Therefore, the invariant line $x_i$ lies in the plane with normal $h$ and the invariant normal $n_i$ lies in the zone of the direction $u$. The possible positions of $x_i$ and $n_i$ can be determined by the condition that their lengths are not changed by the strain $S$. The further condition that $x_i$ and $n_i$ are not rotated by the strain $S$ determines the pure rotation $R$.

Since the rotational part $R$, of $S$ does not change the length of any vector, all changes in length must be due to the strain $\delta M$. From these consideration, BM deduced that there are four possible ways for choosing to identify the pair of vectors $x_i$ and $n_i$ [10]. For each combination, the rotation $R$ is uniquely specified because the strain $\delta M$ rotates the vectors $x_i$ and $n_i$ without changing either the lengths or the angle between them, and they can always be restored to their original directions by the rotation [10].

Since the direction $x_i$ and the normal $n_i$ are not rotated by strain $S$, the required rotation $R$ is that which exactly reverses the rotations of $x_i$ and $n_i$ by the strain $\delta M$. 
4.2 Crystallographic Features Of The Martensitic Transformation

4.2.1 The Lattice Correspondence

Martensitic transformation is based on the concept of a lattice correspondence which can be illustrated by labelling atoms in the parent phase and martensite phases as shown in Figure 4.1 [45].

Figure 4.1: Diagram showing a lattice correspondence relating two structures. The atoms O, A, B., O, P, Q., etc. define corresponding lattice vectors and planes for a simple homogeneous structural deformation [45].
This diagram illustrates the lattice correspondence relating the two structures in two dimensions and which defines the unique relationship between any lattice point in the initial lattice and the point it becomes in the final lattice. This relationship specifies the structural unit (which may consist of more than one unit cell) in the parent phase which is transformed into a unit corresponding to the product phase [79]. Consequently, the unique relationship between unit cells or lattice vectors and planes in the two structures is referred to as the correspondence [87].

A relationship of this kind may be regarded physically as a homogeneous deformation of one lattice into the other. The change does not preserve angular relationship between pairs of vectors or pairs of planes, and it does not imply a rational orientation relationship between parent and martensite phase. A description of the correspondence is complete when three non-coplanar vectors of one structure are related to the corresponding set of vectors in the other structure; it is evident from Figure 4.1 that this description is not changed by any relative rotation of the two structures.

For the transition of bcc structure into a hexagonal close-packed martensite structure, the corresponding unit cells are related by the lattice correspondence, Figure 4.2 [88]. The basal planes of the orthorombic and hexagonal product cells, \{001\}_o and \{00.1\}_h, are derived from a \{011\}_b plane. The specific correspondences given in Figure 4.2 for the two equivalent variants of unit cells yield (1\overline{1}0)_b // (001)_o // (00.1)_h. Close-packed directions \langle111\rangle_b are also preserved in these planes during the transformation and become \langle2\overline{1}0\rangle_h, and \langle1\overline{1}0\rangle_o directions. The correspondence of lattice sites in the \{110\}_b, \{00.1\}_h and \{001\}_o planes provides the derivation of the ordered atom distribution in corresponding planes of the martensite from the parent structure.
Figure 4.2: Diagram showing the lattice correspondence for the bcc to orthorhombic and hcp transformation. The subscripts refer to bcc (b), orthorhombic (o) and hcp (h) structures [88].
4.2.2 The Orientation Relationship

In general, the orientation relationship between the lattices of the matrix and martensitic phases is related to the lattice correspondence. The exact orientation relationship is the particular final orientations of directions and plane normals determined by applying the pure lattice strain $\mathbf{M}$ and the rotation $\mathbf{R}$ (in terms of the phenomenological theory) to the lattice vectors to be considered. Characteristic stereographic projections of orientation relationships are shown in Figure 4.3 [89] for a $\gamma'$ type martensite. Since $\mathbf{M}$ and $\mathbf{R}$ are functions of the rotation it is possible to derive the expected positions of characteristic poles as functions of either axial ratios and principal distortions. Orientation relationships have been determined for numerous martensitic transformations in Cu-based alloys.

Duggin and Rachinger [67] worked on Cu-14.5%Al-3%Ni alloys for which the parent and martensite structures were ordered bcc and orthorhombic respectively. The orientation relationship between the parent and martensite phases was found to be $(101)_{\beta_1}[010]_{\beta_1} // (001)_{\gamma'}[010]_{\gamma'}$. The interphase boundary was found to lie between $(221)_{\beta_1}$ and $(331)_{\beta_1}$.

Thermoelastic and spearlike $\gamma'$ Cu-14.2%Al-4.3%Ni martensite was studied using electron microscopy and electron diffraction by Otsuka and Shimizu [64] who found the crystal structures of martensite and parent structure to be identical with that reported by Duggin and Rachinger [67] for $\gamma_1'$ martensite. Otsuka and Shimizu proposed that the orientation relationship was $(110)_{\beta_1}[1\overline{1}\overline{1}]_{\beta_1} // (121)_{\gamma'}[2\overline{1}0]_{\gamma'}$. 
Figure 4.3: Stereographic projection showing orientation relationships between lattices of γ₁'-Cu-Al martensite and matrix β₁. The projection shows the basal planes, active twinning planes and common close-packed directions of four γ₁' orientations contained in one set of parallel martensite plates whose common habit plane is also given. Superscripts A and B refer to different martensite plates, subscripts 1 and 2 refer to their internal twin orientations; b refers to the matrix [89].
An investigation of stress-induced acicular γ\textsuperscript{1} martensite in Cu-14.2\%Al-4.3\%Ni alloy was carried out by Otsuka, Nakamura and Shimizu [90] by transmission electron microscopy and selected area electron diffraction. They found that the stress-induced acicular γ\textsuperscript{1} martensite was quite different from the spearlike martensite formed thermally even though both had the same crystal structure and lattice parameters. The orientation relationship for stress-induced acicular γ\textsuperscript{1} martensite was found to be (110)\textsubscript{β} \{11\overline{1}\}\textsubscript{β} // (121)γ \{0\overline{1}2\}γ and habit plane was roughly located between (321)\textsubscript{β} and (33\overline{2})\textsubscript{β}.

Greninger [89] made detailed studies on γ martensite of Cu-13.6\%Al alloy and found that the orientation relationship between parent and martensite phase was (011)\textsubscript{β} \{11\overline{1}\}\textsubscript{β} // (001)γ \{110\}γ.

The above results indicate that the orientation relationships determined between the parent and martensitic phases in Cu-14.2\%Al-4.3\%Ni are specified differently but have some similarities. The different parallelism for planes and directions in the parent and martensite phases could be due to nature of formation γ\textsuperscript{1} martensite, the means whereby the relationships were determined or perhaps to the accuracy of the determinations.

**4.2.3 The Shape Strain**

The lenticular or plate-like shape of martensite crystals terminating within or at the boundaries of grains are due to constraints imposed by the parent phase. All martensitic transformations have interfaces which are approximately planar and produce essentially the same kind of distortion or shape change at the surface [44]. When a volume of the parent phase transforms to a single region of martensite, the macroscopic change of shape may be recognised by the tilting of an originally flat surface [45]. Figure
4.4 shows the schematic shape change. Thus, on a macroscopic scale, the change of shape is such that straight lines are deformed into straight lines and planes into planes and so can be described by a homogeneous strain which is called the shape strain [79,82].

Mackenzie [82] found that there is little or no plastic deformation of the matrix particularly for single-interface transformations, so it appears that the habit plane is not rotated by the shape strain. He [82] also pointed out that the shape strain can only differ from a strain in which all lines in the habit plane are invariant, that is, both unrotated and unchanged in length, by a pure dilatation and such a strain is called an invariant plane strain (IPS).

An invariant plane strain (on the plane $p'$) has a matrix representation of the form:

$$ P = I + mdp' \quad (4.2.3) $$

where $I$ is the identity matrix, $d$ is the direction of the displacement and $m$ is the magnitude of the displacement.

Figure 4.4: Diagram showing idealised martensite plate formed in a single crystal of the parent phase matrix [82].
4.2.4 The Habit Plane

The habit plane is the interface plane or contact between the matrix and the martensitic phases. In analysing the surface relief effects accompanying martensitic transformations, Bowles and Mackenzie [10, 11] pointed out that the formation of martensite plates left continuous reference scratches but changed in direction as they crossed the interface. If the shape deformation had caused any significant rotation of the habit plane, the distortion of the matrix adjacent to a martensite plate would manifest as additional displacements of the scratches in the parent phase. Since plastic deformation of the adjacent material was not observed, it was concluded that the habit plane was an unrotated plane. Metallographic and interferometric evidence also indicated that the habit trace is not rotated out of the surface by more than a few minutes of arc and, since the habit plane trace represents random directions in the habit plane, it follows that all lines in the habit plane are essentially unrotated. In addition, the observation that scratches crossing the interface in Figure 4.4 appears to be continuous implies that lines in the habit plane cannot change in length by more than a few percent [9]. These observations also indicated that the habit plane is an unrotated plane and can differ from an undistorted plane only by a uniform distortion of not more than a few percent [9].

A frequent feature of γ-type martensite plates is that they tend to grow in groups of two or four [8, 92, 93]. The central junction plane is approximately parallel to \{110\}_B, whereas other junction planes can be nearly parallel with the habit plane as shown schematically in Figure 4.5. Considering this figure in more detail, the plane through [100]_B and [011]_B is a mirror plane [0 1 1]_B of the parent lattice. The arrows indicate that the shear planes parallel to [011]_B compensate each other completely whereas there is a residual shear parallel to [100]_B.
The magnitude of strain due to shear increases with increasing size of the martensite plates so that a formation of group of plates having a shear component in the opposite direction is favoured. The habit plane normals have been determined for numerous martensitic transformations in Cu-based alloys. Some characteristic results are presented in Figure 4.6 from which it can be seen that the habit planes of \( \gamma \)-type martensite are located near to \( \{122\} \) \( B \) and \( \{133\} \) \( B \).

Generally, the habit plane can be determined by using the two surface trace analysis method provided that the orientation of the parent phase has been determined. Normally, optical microscopy is used to measure the angles between the traces of a martensite plate and the reference line defined by the intersection of the two prepared surfaces. For martensite plates greater than 0.1mm in length [45], this technique yields results with an experimental scatter of about 1° in the habit plane position. However, for plates less than 0.1mm in length, the accuracy of the two surface trace analysis method decreases.

For very small plates, TEM can be used to determine the habit plane by a single surface trace analysis using measured angles between the different traces of several martensite plates in the thin foil specimen and reference direction. On the other hand, a three surface method can be used for some materials to obtain the habit plane with higher precision.

In the work described in this thesis, the habit plane determination was carried out by the two surface trace analysis method for both the \( \beta_1 \) to \( \gamma_1 \) forward transformation and the strained \( \gamma_1 \) to \( \beta_1 \) reverse transformation.
Figure 4.5: Schematic representation of a group of four martensite plates forming a self-accommodating system. The arrows indicate shear directions: the indices refer to the bcc matrix lattice.

Figure 4.6: Stereographic projection showing the habit plane normals of $\beta_1'$ and $\gamma_1'$ type martensite plates in Cu-based alloys [89].
PART B: EXPERIMENTAL WORK
5.0 INTRODUCTION

The shape memory effect is generally associated with a thermoelastic martensitic transformation. This type of transformation occurs in Cu-Al-Ni alloys which, after deformation, have the capacity to return to their original shape upon heating or release of stress.

In the work described in this thesis, a single crystal of Cu-15%Al-3%Ni alloy was used to study the strain induced forward and reverse transformations. Upon quenching, this alloy was ordered $\beta_1$ which transformed to the martensitic $\gamma_1'$ phase either during continued cooling or under applied (compressive) stress. Upon heating, the reverse martensitic transformation occurred to regenerate the original $\beta_1$ structure.

The experimental work comprised three parts. First, the crystallographic properties of the forward transformation were determined from measurements made on a partially (strain induced) transformed specimen. Secondly, the same transformation was completed by additional strain and the fully martensitic specimen was further strained to produce what was probably a near single crystal of martensite. Thirdly, the specimen was reheated to partially reverse the transformation and measurements made to determine the crystallography of the reverse transformation from the strained martensite.

The microstructural changes that occurred during the forward and reverse transformations are shown in Figure 5.1 and Figure 5.2 respectively. It should be noted that these figures refer to slightly different regions of the same specimen. The $\beta_1$ to $\gamma_1'$ and $\gamma_1'$ to $\beta_1$ martensitic transformations have been studied before and are well-documented. In the present work the $\beta_1$ to $\gamma_1'$ forward transformation and strained $\gamma_1'$ to $\beta_1$ reverse transformation in the same alloy were consistent with previous measurements.
on strain induced transformation made without additional strain to the martensitic structure. The additional strain, studied in this work, was accompanied by additional shape deformation so that the total (forward) shape strain was composed of the shape strain due to the forward transformation and the shape strain due to strain of the martensite. Since reverse transformation regenerated the original structure the total (forward) shape strain should be the exact inverse of the reverse shape strain accompanying transformation of the strained martensite back to the original $\beta_1$ phase. For this condition, the elements of the shape strain accompanying the additional strain in the martensite were obtained by numerical analysis of the relevant strain matrices. Determination of those elements and examination of the significance of them were main objectives of the work described in the thesis.
Reference surface

Side surface

(a)

(b)

(c)

(d)

(e)
Figure 5.1: Photomicrographs showing the forward martensitic transformation:

(a) the parent phase $\beta_1$; (b), (c), (d) progressive transformation to $\gamma_1'$ martensite by applied compressive strain; (e) transformation to a (near) single crystal of strained $\gamma_1'$ martensite by additional strain.
Figure 5.2: Photomicrographs showing the reverse martensitic transformation:
(a) near single crystal of strained $\gamma_1^\prime$ martensite; (b), (c), (d) partial transformation to the parent phase $\beta_1$ by slowly heating between $A_s$ and $A_f$; and (e) formation of the original parent phase after complete reverse transformation.
6.0 EXPERIMENTAL PROCEDURES

6.1 Specimen Preparation

A single crystal of a Cu-Al-Ni alloy had been prepared using the Bridgeman method. The specimen was heated to 900°C for one hour then water quenched to retain the ordered β as the ordered β₁ at the room temperature (RT) which was greater than Mₚ. The specimen was approximately 8.5mm x 9.0mm x 14.5mm, and was prepared for quantitative metallographic examination by grinding and polishing two surfaces designated as the reference surface and the side surface. Grinding and polishing were carried out unidirectionally to sustain sharp angle of about 90° between the two surfaces. The reference surface (RS) or plane 1 and the side surface (SS) or plane 2 intersected along the reference direction R'.

6.1.1 The Forward β₁ To γ₁' Martensitic Transformation

The single crystal specimen of β₁ was subjected to compressive stress parallel to the reference direction to obtain the γ₁' martensitic transformation. The specimen was clamped in a bench vice, and stress applied by tightening the vice jaws to obtain partial transformation so that a martensite plate occurred in the two metallographically prepared surfaces. Figure 6.1 shows a typical martensite plate in the two surfaces and Figure 6.2 diagrammatically identifies the reference surface or plane 1, side surface or plane 2 and the reference direction R'. The angle, α, subtended by the traces of the plate in the reference surface and β for the side surface are also shown together with the interfacial angle σ and the tilt angles φ₁ and φ₂. The
positive sense of the angles $\phi$ is defined as a right hand rotation about the habit plane traces $t_1$ and $t_2$. Measurement of the then angles $\alpha$, $\beta$, $\sigma$, $\phi_1$ and $\phi_2$ is described in Section 6.3.

Figure 6.1: Photomicrographs showing a $\gamma'_1$ martensite plate in the reference surface and side surface planes, unetched, oblique illumination, 3.2X.

6.1.2 The Reverse (Strained $\gamma'_1$ Martensite To $\beta_1$) Transformation

The specimen prepared as described in section 6.1.1, was then subjected to a continued applied stress to complete the transformation of the $\beta_1$ to $\gamma'_1$ martensite and to then strained the martensite plates to a (near) single crystal.

The specimen comprising of the single crystal of martensite was then heated slowly by controlled dipping into hot water. Upon reaching to the $A_S$ temperature, the reverse transformation commenced and the $\beta_1$ phase was formed by martensitic
transformation of the strained $\gamma_1'$. After partial reversion, the transformation was halted to provide a specimen of $\beta_1$ and $\gamma_1'$ as shown in Figure 6.3.

Figure 6.2: Schematic diagram showing the specimen geometry for the two surface analysis method.
Figure 6.3: Photomicrographs showing the product of the martensitic transformation and parent phase for reverse transformation in the reference surface and side surface planes. It must be noted that the two bands of $\gamma_1'$ is the parent phase for the reverse transformation and that the original $\beta_1$ phase, which has formed from the $\gamma_1'$, is the product phase for the reverse transformation. Unetched, oblique illumination, 3.2X.

In summary, the cycle of the forward and reverse transformations is as follows:

(a) **The forward martensitic transformation**

Stress was applied to the single crystal $\beta_1$ specimen using a bench vice to form $\gamma_1'$ martensite plates in two adjacent metallographically polished surfaces. Angular measurements were made on these plates to obtain the data needed for a two tilt surface analysis of the forward martensitic transformation.
(b) **Single crystal of martensite phase**

After angular measurements were made, further stress was applied to the specimen to complete the forward transformation and strain the $\gamma_1'$ martensite into a near single crystal.

(c) **Reverse martensitic transformation**

The near single crystal of strained martensite $\gamma_1'$ was heated slowly to obtain partial reversion to the $\beta_1$ phase. Angular measurements were made on the $\beta_1$ (plates) to obtain the data needed for a two tilt surface analysis of the reverse transformation.

(d) **Single crystal of parent phase**

The specimen was heated to a temperature above $A_f$ so that all the martensite phase transformed back to the original single crystal of $\beta_1$ phase, hereby establishing complete reversibility of the cycle.

The experimental work comprised repetition of sequence of (a) to (d) until several sets of angular measurements were obtained. The reverse martensitic transformation corresponded directly with the forward martensitic transformation and the results were then used to calculate the elements of the relevant shape strains.

6.2 **X-Ray Measurement**

The orientation of the lattice of the $\beta_1$ relative to the external geometry of the specimen was obtained from the specimen in the $\beta_1$ condition using the back-reflection Laue method. The estimated accuracy of determination was about 0.5% [70, 94]. The specimen was further strained to produce martensite which was then strained additionally
and finally heated to cause the reverse transformation which reverted the structure to the original $\beta_1$. This procedure was repeated many times to obtain the three sets of data.

Measurements of the geometry of the specimen after numerous cycles indicated that the shape recovery was complete to within the accuracy of measurements. Back reflection Laue patterns taken during the cycling indicated that the orientation of the lattice of the $\beta_1$ had not changed to within the $1-2^\circ$ accuracy of the method.

These observations established that, for the specimen used in the work, the shape recovery and crystallographic recovery were perfect.

6.3 Metallographic Measurement

Metallographic methods were used to measure the traces of habit planes of the martensite plates and to obtain other data from which the direction and magnitude of the shape strain were calculated. The angular measurements which were made are shown schematically in Figure 6.2.

6.3.1 Measurements Of Habit Plane Traces

As shown in Figure 6.2, $\alpha$ and $\beta$ were respectively, the angles between the reference direction, $R'$ and the traces of the habit planes in the reference surface or plane 1 and side surface or plane 2. Measurements of angles $\alpha$ and $\beta$ for the forward transformation and reverse transformations were made using the graduated rotating stage of a Leitz MM6 metallograph.
At least five measurements of each angle were made. The range of measurements was approximately $0.5^\circ$ and the estimated error of the measurement was $\pm 1.0^\circ$ [95].

### 6.3.2 Measurements Of Interfacial Angle

The interfacial angle $\sigma$, (refer to Figure 6.2) is the angle between the normal to the reference surface and the normal to the side surface of the specimen and was measured using a Unicam S25 single crystal goniometer with an estimated error of $0.05^\circ$.

### 6.3.3 Determination Of Habit Plane

The habit plane for a particular plate was determined in stereographic projection from the measured angles $\alpha$, $\beta$ and $\sigma$ and the measured orientation of the lattice of the parent $\beta_1$ phase. Additionally, the habit plane was calculated numerically using the mathematical procedure set out in Appendix A.

By addition of the estimated errors of all angular measurements, the accuracy of the habit plane determination was less than $\sim 1.5^\circ$.

### 6.3.4 Measurement Of Tilt Angles

The positive sense of the angles $\phi$ is defined as a right rotation about the relevant habit plane trace, $t_1$ or $t_2$. The surface tilt angles of a martensite plate were determined by quantitative interference microscopy using Mirau interference equipment and a Zeiss incident light microscope. The interferometer was adjusted so that the width of the
interference bands on the phase adjacent to a plate was infinite, and for this condition, the tilt angle for a plate is given by the relation:

$$\tan \phi = \frac{n\lambda}{2L}$$  \hspace{1cm} (6.3.4)

where $\lambda$ is the wavelength of illumination (546$\mu$m) and $n$ is the number of fringes in length $L$ ($\mu$m) of tilted surface [96]. The dimension $L$ for a particular number of fringes was measured utilising a photomicrograph of a stage micrometer with 10$\mu$m spacing taken at the same magnification as the interferogram.

Typical interferograms of surface tilts are shown in Figure 6.4 (a) and (b).

Figure 6.4 (a): Photomicrograph showing the fringes on a martensite plate in the reference surface; tilt angle $\phi_1 = -3.070^\circ$
Consistent measurements of the tilt angle for a martensite plate can be difficult when:

(a) the surface of the plate is slightly buckled, possibly due to accommodation strains, or

(b) transverse markings, with associated local changes of surface tilt, are present on the plate.

The estimated error of measurements resulting of these distortions is approximately 0.1% [95].

To obtain the tilt angle $\phi_1$, measurement of fringes was made on the plate in reference surface. Similarly, to obtain the tilt angle of $\phi_2$, fringes were measured on the plate in the side surface.

Measurements of tilt angles were carried out on several fields on each martensite plate. The average of the tilt angles from various fields of a particular plate was then used.
to obtain the magnitude of atom movement; \( m \), and the direction of atom movement; \( d \), as elements of the relevant shape strain.

### 6.3.5 Determination Of The Shape Strain Elements

Calculations of the shape strain elements; \( p \), \( m \) and \( d \) for the forward and reverse martensitic transformations were made using the angular measurements of \( \alpha \), \( \beta \), \( \sigma \), \( \phi_1 \) and \( \phi_2 \). Figure 6.2 shows the input and output data obtained from the two tilt surface analysis methods given in Appendix A which provides a mathematical analysis for calculating the elements in the \( J \) (habit plane) basis.
The J basis is defined by:

\[ j_1 = [100]_J \] parallel to the trace \( t_1 \) in plane 1,

\[ j_3 = [001]_J \] parallel to the normal to plane 1, and

\[ j_2 = [010]_J = j_3 \times j_1 \]

Conversion from the basis J to the parent phase basis B was carried out in stereographic projection. The basis B is defined as:

\[ b_1 = [100]_B, \]

\[ b_2 = [010]_B, \] and

\[ b_3 = [001]_B, \]

which are the crystallographic axes of the bcc unit cell of the \( \beta_1 \) phase parent crystal.
7.0 EXPERIMENTAL RESULTS

Precise angular measurements of angles $\alpha$, $\beta$, $\sigma$, $\phi_1$ and $\phi_2$ have been rigorously carried out using experimental methods, techniques and procedures as described in Section 6.0.

As mentioned in Section 6.0, the specimen was prepared and transformed to the $\gamma'_1$ martensite during the forward martensitic transformation by applied stress. Later, the $\gamma'_1$ was subjected to additional stress to obtain a (near) single crystal of martensite. The strained $\gamma'_1$ martensite phase reverts to partial $\beta$-phase when heated slowly to, and above, the $A_s$ temperature and untransformed martensite is fully transformed to the original $\beta$ phase when heated to above $A_f$.

Three martensite plates for the forward and reverse martensitic transformations have been analysed to obtain the habit plane; $p$, magnitude of atom movements; $m$, direction of atom movements; $d$ and thus, the shape strain, for relevant transformations.

The product phase ($\beta_1$) formed during reverse transformation corresponded with the martensite ($\gamma'_1$) which appeared during forward transformation (see Figures 5.1 and 5.2) and, on one cycle, the same pairs of martensite plates were measured. Similar structures were formed during separate cycles so that the sets of data attained for three cycles were similar.

For angular measurement purposes, at least five measurements were made on each plate of martensite, and the average value was used for calculating the elements of the shape strain for the relevant transformations.
7.1 Forward Martensitic Transformation

7.1.1 Angular Measurement

Measurements of the angles $\alpha$, $\beta$, $\sigma$, $\phi_1$ and $\phi_2$ were required to determine the elements of the shape strain, and the experimentally measured angles are shown in Table 7.1 for three plates of $\gamma_1'$ martensite. At least five independent measurements of the interfacial angle, $\sigma$, and martensite trace angles, $\alpha$ and $\beta$ were made to minimise experimental errors.

For the tilt angle determination, five separate fields of plate on each surface were photographed. Each interferogram was analysed and five measurements of each field were obtained to attain the tilt angle using equation 6.3.4 (page 80). The average value of tilt angles $\phi_1$ and $\phi_2$ were used for calculating the magnitude of the atom movements, $m$ and direction of the atom movements, $d$. The accuracy of measurement for the tilt angles $\phi_1$ and $\phi_2$ was required to be high as small errors can result in substantial errors for the calculated values of both $m$ and $d$.

Table 7.1: Experimentally measured angles used to calculate the elements of the shape strain for the forward transformation.

<table>
<thead>
<tr>
<th>Angles</th>
<th>$\gamma_1'$ Martensite Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>56.87°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>57.10°</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>89.00°</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>-3.09°</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>+0.52°</td>
</tr>
</tbody>
</table>
7.1.2 The Shape Strain For The Forward Transformation

The elements of habit plane; \( p \), direction of atom movements; \( d \), magnitude of atom movements; \( m \) and dilatation parameter; \( \delta \) were needed to specify the forward shape strain; \( S_F \). In the present work, the dilatation parameter was assumed to be unity as has been reported from previous work on the same alloy [6, 73]. Therefore, based on this assumption, the shape strain was obtained using the elements of the shape strain; \( p, d \) and \( m \) as follows:

\[
S_F = (1 + mdp')
\]  

(7.1.2)

According to the numerical procedure, determination of the tilt angle \( \phi \) in each surface leads to solutions for \( m \) and \( d \) provided that the volume ratio; \( g \) is known. The value of \( g \) is the ratio of the final to initial volume per atom and for the stress induced forward martensitic transformation which has been determined experimentally to be 0.996028 [6].

The results for \( p, d \) and \( m \) obtained using the two tilt surface analysis are shown in Table 7.2. Figure 7.1 shows the results for \( p \) and \( d \) in standard stereographic projection of the \( \beta_1 \) phase indexed so that the habit planes \( p \) are near the \((0\bar{1}1)_B\) symmetry plane and the directions \( d \) are near \([0\bar{1}1]_B\).
Table 7.2: Calculated elements of the shape strain for the forward martensitic transformation.

<table>
<thead>
<tr>
<th>The elements of shape strain</th>
<th>Plate 1</th>
<th>Plate 2</th>
<th>Plate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habit plane; $p'$</td>
<td>(+0.000000)</td>
<td>(+0.000000)</td>
<td>(+0.000000)</td>
</tr>
<tr>
<td>($p'$ ; $J$)</td>
<td>(-0.875705)</td>
<td>(-0.875605)</td>
<td>(-0.879103)</td>
</tr>
<tr>
<td></td>
<td>(+0.482847)</td>
<td>(+0.483028)</td>
<td>(+0.476633)</td>
</tr>
<tr>
<td>Habit plane; $p'$</td>
<td>(-0.174050)</td>
<td>(-0.164937)</td>
<td>(-0.198867)</td>
</tr>
<tr>
<td>($p'$ ; $B$)</td>
<td>(+0.727053)</td>
<td>(+0.748450)</td>
<td>(+0.729518)</td>
</tr>
<tr>
<td></td>
<td>(+0.664154)</td>
<td>(+0.642354)</td>
<td>(+0.654412)</td>
</tr>
<tr>
<td>Direction; $d$</td>
<td>[-0.449675]</td>
<td>[-0.480344]</td>
<td>[-0.467394]</td>
</tr>
<tr>
<td>[$d$ ; $J$]</td>
<td>[+0.474676]</td>
<td>[+0.462885]</td>
<td>[+0.461903]</td>
</tr>
<tr>
<td></td>
<td>[+0.756621]</td>
<td>[+0.744987]</td>
<td>[+0.753783]</td>
</tr>
<tr>
<td>Direction; $d$</td>
<td>[-0.250160]</td>
<td>[-0.301520]</td>
<td>[-0.266981]</td>
</tr>
<tr>
<td>[$d$ ; $B$]</td>
<td>[-0.706487]</td>
<td>[-0.683843]</td>
<td>[-0.712565]</td>
</tr>
<tr>
<td></td>
<td>[+0.662039]</td>
<td>[+0.664413]</td>
<td>[+0.648824]</td>
</tr>
<tr>
<td>Magnitude; $m$</td>
<td>0.079</td>
<td>0.087</td>
<td>0.085</td>
</tr>
<tr>
<td>$\cos^{-1} p'.d$</td>
<td>91.74°</td>
<td>92.02°</td>
<td>92.41°</td>
</tr>
</tbody>
</table>

Note: 1. The habit plane $p$ for plates 1, 2 and 3 are very similar but not parallel as the values for $\alpha$ and $\beta$ were distinctly different. Similarly, the directions; $d$ (and magnitudes; $m$) for plates 1, 2 and 3 are similar but not parallel due to different values of tilts angles $\phi_1$ and $\phi_2$.

2. The bases $J$ for the three plates were slightly different due to differences in the angles $\alpha$. 
Figure 7.1: Stereographic projection of the $\beta_1$ phase showing (•) habit planes; $p$ and directions of atom movements; $d$ for the three plates together with the average values (•) $p_F$ and $d_F$, (where the subscript refers to the forward transformation).
It is clear from Figure 7.1 that the habit planes of the martensite plates all lie within about 3° of the \(<110> - <111>\) boundary near \(\{133\}\)\(\beta\). Furthermore, the average value \(\mathbf{p}'\) is:

\[
\mathbf{p}'_F = (-0.179319, 0.735145, 0.653763)\mathbf{B}
\]

The directions of atom movements all lie within about 2° near \(\{133\}\)\(\beta\) and the geometrical average value of \(\mathbf{d}\) is:

\[
\mathbf{d}_F = [-0.272977, -0.701196, 0.658642]\mathbf{B}
\]

The magnitude of the shape strain accompanying the forward martensitic transformation, and shown in Table 7.2, was determined using the procedure described in Appendix A. The mean value of \(\mathbf{m}_F\) is \(0.084 \pm 0.004\) with 95% confident limits and is comparable with the mean value of 0.087 reported by Kennon and Dunne [6].

The average values \(\mathbf{p}_F\) and \(\mathbf{d}_F\) are given in Table 7.3 and for each plate, the shape strain for the forward martensitic transformation \(\mathbf{S}_F\), obtained in the J basis from \(\mathbf{p}_F, \mathbf{d}_F\) and \(\mathbf{m}_F\) is given in Table 7.4.

It should be noted that the J bases for the forward transformation for the three plates, and the reverse transformation for the three plates, differed by up to 10°. Consequently, to compare the six different shape strain, the elements \(\mathbf{p}\) and \(\mathbf{d}\) were referred to a common basis which was chosen to be the J basis for the forward transformation for plate 1. This basis is termed \(\mathbf{J}_{F1}\).
Table 7.3: The average values of the habit plane; $p_F$, direction; $d_F$, and magnitude; $m_F$, of atom movements for the forward transformation.

<table>
<thead>
<tr>
<th>Elements of the shape strain</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{F1}(basis)$</td>
</tr>
<tr>
<td>Habit plane; $p_F$</td>
<td>(+0.000000)</td>
</tr>
<tr>
<td></td>
<td>−0.876809</td>
</tr>
<tr>
<td></td>
<td>+0.480839</td>
</tr>
<tr>
<td>Direction; $d_F$</td>
<td>[−0.465851]</td>
</tr>
<tr>
<td></td>
<td>+0.466544</td>
</tr>
<tr>
<td></td>
<td>+0.751872</td>
</tr>
<tr>
<td>Magnitude; $m_F$</td>
<td>0.084 ± 0.004</td>
</tr>
<tr>
<td>$\cos^{-1} p_F \cdot d_F^{**}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: * These results were obtained stereographically.

** The value of 92.06° indicates that a small volume decrease accompanied the strain.
Table 7.4: Calculated shape strain, $S_F$ for the forward transformation using the elements of the shape strain $p_F$, $d_F$ and $m_F$.

<table>
<thead>
<tr>
<th>Plate</th>
<th>Shape strain $S_F$ in average $J_{F1}$ basis</th>
</tr>
</thead>
</table>
| 1     | \[
\begin{pmatrix}
1 & +0.031069 & -0.017131 \\
0 & +0.967204 & +0.018083 \\
0 & -0.052277 & +1.028824 \\
\end{pmatrix}
\] |
| 2     | \[
\begin{pmatrix}
+1.002091 & +0.034479 & -0.019055 \\
-0.002274 & +0.962493 & +0.020929 \\
-0.003450 & -0.056898 & +1.031445 \\
\end{pmatrix}
\] |
| 3     | \[
\begin{pmatrix}
+1.000767 & +0.034093 & -0.018489 \\
-0.000794 & +0.964756 & +0.019384 \\
-0.001267 & -0.056249 & +1.030505 \\
\end{pmatrix}
\] |

Note that the three strains are very similar because the three plates examined were very similar to the plate shown in Figure 5.1.

### 7.2 The Reverse Martensitic Transformation

#### 7.2.1 Angular Measurement

The angles $\alpha$, $\beta$, $\sigma$, $\phi_1$ and $\phi_2$ needed to determine the elements of the shape strain for the reverse martensitic transformation were measured experimentally in the same way as measurements were conducted for the forward transformation. The measured angles are shown in Table 7.5 for the three $\beta_1$ plates which corresponded
directly with the three $\gamma_1$ martensite plates measured of the forward transformation. For the reverse transformation, the $\beta_1$ plates were measured relative to parent $\gamma_1$. At least five independent measurements of the interfacial angle $\sigma$ and of the martensite trace angles $\alpha$ and $\beta$ were made to minimise experimental error and the average values used to calculate the habit planes. For the tilt angle measurements, five separate fields of each martensite plate in each surfaces were photographed to obtain an accurate measurements of $\phi_1$ and $\phi_2$. Suitable interferogram was analysed and five measurements of each field of the plate were obtained and calculations of $\phi$ were made using equation 6.3.4.(page 80).

The average values of $\phi_1$ and $\phi_2$ was used for the calculation of magnitude of atom movements; $m$ and the direction of atom movements; $d$. High accuracy of the tilt angles $\phi_1$ and $\phi_2$ were required so that determinations of the magnitude $m$ and the direction $d$ of atom movements could be made precisely.

Table 7.5: Experimentally measured angles used to calculate the elements of the shape strain for the reverse martensitic transformation.

<table>
<thead>
<tr>
<th>Angles</th>
<th>$\beta_1$ plate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>64.17°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>56.68°</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>89.00°</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>+3.16°</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>-1.44°</td>
</tr>
</tbody>
</table>
7.2.2 The Shape Strain For The Reverse Transformation

The crystallographic information needed to specify the reverse shape strain $S_R$ is the habit plane; $p$, the direction of the atom movements; $d$, the magnitude of atom movements; $m$ and $\delta$ which is assumed to be unity.

The numerical procedure set out in Appendix A was used to calculate the elements of the shape strain using the value of $g^{-1} (= 1/g)$ of 1.003988 for the reverse transformation. The results for $p$, $d$ and $m$ for each plate, obtained using the two tilt surface analysis are shown in Table 7.6 and Figure 7.2.

Figure 7.2: Stereographic projection of $\beta_1$ phase showing ($\circ$) habit planes; $p$ and directions of atom movements; $d$ for the reverse martensitic transformation together with the average values (*) $p_R$ and $d_R$. (where the subscript refers to the reverse martensitic transformation).
Table 7.6: Calculated values for the elements of shape strain for the reverse transformation.

<table>
<thead>
<tr>
<th>The elements of shape strain</th>
<th>Plate 1</th>
<th>Plate 2</th>
<th>Plate 3</th>
</tr>
</thead>
</table>
| Habit plane; \( p' \) \((p' ; J)\) | \((+0.000000)
-0.857722
(+0.514113)\) | \((+0.000000)
-0.839304
(+0.543661)\) | \((+0.000000)
-0.834696
(+0.550712)\) |
| Habit plane; \( p' \) \([p' ; B]\) | \((-0.334017)
+0.701349
(+0.629715)\) | \((-0.416070)
+0.715618
(+0.561050)\) | \((-0.368444)
+0.729220
(+0.576617)\) |
| Direction; \( d \) \([d ; J]\) | \([+0.535716]
-0.469522
-0.701824\) | \([+0.621044]
-0.462350
-0.632879\) | \([+0.572399]
-0.484152
-0.661783\) |
| Direction; \( d \) \([d ; B]\) | \([+0.139648]
+0.684323
-0.715682\) | \([+0.130552]
+0.713394
-0.688494\) | \([+0.174057]
+0.677183
-0.714932\) |
| Magnitude; \( m \) | 0.095 | 0.091 | 0.101 |
| \( \cos^{-1} p'.d \) | 90.99° | 85.99° | 89.00° |

Note: 1. The habit planes \( p \) for plates 1, 2 and 3 are very similar but not parallel as the values for \( \alpha \) and \( \beta \) were distinctly different. Similarly, the directions; \( d \) (and magnitude; \( m \)) for plates 1, 2 and 3 are similar but not parallel due to different values of tilt angles \( \phi_1 \) and \( \phi_2 \).

2. The bases \( J \) for the three plates were slightly different due to differences in the angles \( \alpha \).
Clearly, from Figure 7.6, the habit planes of the martensite plates all lie within 5° near the \((0\bar{1}1)B\) symmetry plane and the directions lie within about 2° near \([0\bar{1}1]B\). The average values of habit plane \(p_R\), and the direction of atom movements \(d_R\), for the reverse transformation are as follows:

\[
p_R = (-0.373241, 0.716157, 0.589754)B
\]

\[
d_R = [0.148142, 0.691895, -0.706637]B
\]

and the mean value of the magnitude of atom movements \(m_R\) is 0.096 ± 0.005.

Table 7.7 shows the average values of the reverse shape strain elements. Calculations to obtain \(p\), \(d\) and \(m\) for the reverse transformation were made with the same procedure used to obtain \(p\), \(d\) and \(m\) for the forward transformation. The calculated the shape strains \(S_R\) for the reverse transformation are given in Table 7.8.
Table 7.7: The average value of habit planes $p_R$, direction $d_R$, and magnitude $m_R$, of atom movements for the reverse transformation.

<table>
<thead>
<tr>
<th>Elements of the shape</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habit planes; $p_R$</td>
<td>$J_{F1}(\text{basis})$</td>
</tr>
<tr>
<td></td>
<td>(+0.000000)</td>
</tr>
<tr>
<td></td>
<td>(-0.844056)</td>
</tr>
<tr>
<td></td>
<td>(+0.536256)</td>
</tr>
<tr>
<td>Direction; $d_R$</td>
<td>[+0.576994]</td>
</tr>
<tr>
<td></td>
<td>[-0.472506]</td>
</tr>
<tr>
<td></td>
<td>[-0.666197]</td>
</tr>
<tr>
<td>Magnitude; $m_R$</td>
<td>0.096 ± 0.005</td>
</tr>
<tr>
<td>$\cos^{-1} p'_R \cdot d_R$**</td>
<td>88.66°</td>
</tr>
</tbody>
</table>

Note: * The results were obtained stereographically.

** The value of 88.66° indicates that a small volume increase accompanies the strain.
Table 7.8: Calculated shape strain, $S_R$ for the reverse transformation using the elements of shape strain, $p'$, $d$ and $m$.

<table>
<thead>
<tr>
<th>Plate</th>
<th>Shape strain $S_R$ in average $J_{FI}$ basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( +1.006130, -0.047859, +0.028921 )&lt;br&gt; ( -0.004125, +1.032198, -0.019458 )&lt;br&gt; ( -0.007280, +0.056831, +0.965658 )</td>
</tr>
<tr>
<td>2</td>
<td>( +1.005821, -0.050640, +0.033018 )&lt;br&gt; ( -0.003376, +1.029362, -0.019146 )&lt;br&gt; ( -0.005502, +0.047850, +0.968801 )</td>
</tr>
<tr>
<td>3</td>
<td>( +1.005581, -0.051809, +0.034380 )&lt;br&gt; ( -0.003776, +1.035044, -0.023256 )&lt;br&gt; ( -0.005949, +0.055214, +0.963360 )</td>
</tr>
</tbody>
</table>

Note: the three strains are very similar because the three plates of $\beta_1$ examined are very similar to the structure shown in Figure 5.2.
7.3 Shape Strain For The Strained $\gamma_1'$ Martensite Formed By Additional Strain In Martensitic Transformation

In present work, the parent phase $\beta_1$ was strained to $\gamma_1'$ and the associated forward shape strain $S_F$ determined as set out in Table 7.4. The transformation was completed and the $\gamma_1'$ martensite subjected to additional strain to produce what appeared to be a (near) single crystal strained of martensite. This strain was accompanied by an additional shape deformation termed $S_A$. Thus, the total shape deformation associated with the formation of, and additional strain to, the $\gamma_1'$ martensite is a combination of $S_F$ and $S_A (=S_A S_F)$. The strained $\gamma_1'$ was then reheated to form the original structure of $\beta_1$ and this transformation was accompanied by the reverse shape strain $S_R$ as set out in Table 7.8.

As the original $\beta_1$ was exactly regenerated on heating, $S_R$ must be the exact inverse of $S_A S_F$ and in matrix notation:

$$S_R = (S_A S_F)^{-1} = S_F^{-1} S_A^{-1}$$

Thus $S_A^{-1}$ is obtained as the matrix product $S_F S_R$ as shown in Table 7.9.

This definition of the strain $S_A$ imposes the condition that it must be an invariant line strain. Since $S_F$ and $S_R$ are both invariant plane strains, the two invariant planes $p_F$ and $p_R$ intersect along a line that is invariant in $S_F S_R$. Additionally, the two directions of atom movements, $d_F$ and $d_R$, identify a plane which has an invariant normal in $S_F S_R$. Thus, $S_F S_R$ leaves one line and one normal invariant and so is an invariant line strain.
Table 7.9: Calculated shape strains $S_A$ for the additional strain to the martensite.

<table>
<thead>
<tr>
<th>Plate</th>
<th>$S_A^{-1} = S_F S_R$ in average $J_{F1}$ basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(+1.006127 \ -0.016763 \ +0.011774)\n-0.004121 \ +0.999374 \ -0.001358\n-0.007274 \ +0.004509 \ +0.994509)$</td>
</tr>
<tr>
<td>2</td>
<td>$(+1.007913 \ -0.016167 \ +0.013966)\n-0.005651 \ +0.991861 \ +0.001580\n-0.008953 \ -0.009039 \ +1.000240)$</td>
</tr>
<tr>
<td>3</td>
<td>$(+1.006334 \ -0.017582 \ +0.015802)\n-0.004557 \ +0.999676 \ -0.003790\n-0.007192 \ -0.001256 \ +0.994012)$</td>
</tr>
</tbody>
</table>
8.0 DISCUSSION

The single crystal Cu-Al-Ni specimen was strained to form $\gamma'_1$ from the $\beta_1$ and strained further to form a (near) single crystal martensite. The strained $\gamma'_1$ martensite reverted to the original structure of $\beta_1$ during subsequent heating. The elements of the shape strains for the forward $\beta_1$ to $\gamma'_1$ stress induced martensitic transformation and reverse strained $\gamma'_1$ to $\beta_1$ transformation have been determined.

The average values of the measured of $\mathbf{p}$, $\mathbf{d}$ and $\mathbf{m}$ for each forward and reverse shape strain are set out in Table 8.1 and shown in stereographic projection in Figure 8.1.

By comparison of the results in Table 8.1 and Figure 8.1, it is clear that the habit planes for the forward and reverse transformations were significantly different and the two directions of atom movements were approximately antiparallel.

The differences in the habit planes necessarily arises from the effect the additional strain in the martensite which was applied before the reverse transformation occurred.

For the forward transformation, the elements of the shape strain were as follows:

$$\mathbf{p}_F = (-0.179319, 0.735145, 0.653763)\mathbf{B}$$

$$\mathbf{d}_F = [-0.272977, -0.701196, 0.658642)\mathbf{B}$$

$$\mathbf{m} = 0.084 \pm 0.004$$

which are very similar to results reported in the literature [51].
Table 8.1: Calculated average values of the elements of the shape strain for the forward and reverse transformations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Forward ($\beta_1$ to $\gamma_1'$) transformation</th>
<th>Reverse (strained $\gamma_1'$ to $\beta_1$) transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habit plane; $p$ in J basis ($p; J$)</td>
<td>$\begin{pmatrix} +0.000000 \ -0.876809 \ +0.480839 \end{pmatrix}$</td>
<td>$\begin{pmatrix} +0.000000 \ -0.844055 \ +0.536256 \end{pmatrix}$</td>
</tr>
<tr>
<td>Habit plane; $p$ in B basis ($p; B$)</td>
<td>$\begin{pmatrix} -0.179319 \ +0.735145 \ +0.653763 \end{pmatrix}$</td>
<td>$\begin{pmatrix} -0.373241 \ +0.716157 \ +0.589754 \end{pmatrix}$</td>
</tr>
<tr>
<td>Direction $d$ in J basis ($d; J$)</td>
<td>$\begin{pmatrix} -0.465851 \ +0.466544 \ +0.751872 \end{pmatrix}$</td>
<td>$\begin{pmatrix} +0.576994 \ -0.472506 \ -0.666197 \end{pmatrix}$</td>
</tr>
<tr>
<td>Direction; $d$ in B basis ($d; B$)</td>
<td>$\begin{pmatrix} -0.272977 \ -0.701196 \ +0.658642 \end{pmatrix}$</td>
<td>$\begin{pmatrix} +0.148142 \ +0.691895 \ -0.706637 \end{pmatrix}$</td>
</tr>
<tr>
<td>Magnitude; $m$</td>
<td>$0.084 \pm 0.004$</td>
<td>$0.096 \pm 0.005$</td>
</tr>
<tr>
<td>$\cos^{-1} p'.d$</td>
<td>$92.06^\circ$</td>
<td>$88.66^\circ$</td>
</tr>
</tbody>
</table>
Figure 8.1: Stereographic projection showing the average habit plane normal and direction of shape strain for the forward (\(*F\)) and reverse (\(*R\)) transformations.
For the reverse transformation, the elements of the shape strain were as follows:

\[
\mathbf{p}_R = (-0.373241, 0.716157, 0.589754) \mathbf{B}
\]

\[
\mathbf{d}_R = [0.148142, 0.691895, -0.706637] \mathbf{B}
\]

\[
\mathbf{m}_R = 0.096 \pm 0.005
\]

These results are to be compared with the results for the reverse transformation from unstrained \( \gamma_1 \) to \( \beta_1 \) which have been reported before [51], using an obvious notation:

\[
\mathbf{p}_R(u) = (-0.704669, 0.680241, 0.201777) \mathbf{B \text{ unstrained}}
\]

\[
\mathbf{d}_R(u) = [-0.661206, 0.726637, 0.186563] \mathbf{B \text{ unstrained}}
\]

\[
\mathbf{m}(u) = 0.091 \pm 0.002
\]

For the two sets of results:

\[
\mathbf{p}_R \cdot \mathbf{p}_R(u) = 8.3^\circ
\]

\[
\mathbf{d}_R \cdot \mathbf{d}_R(u) = 3.0^\circ, \text{ and }
\]

\[
\Delta \mathbf{m} = 0.005 \sim 5\%
\]

It is possible that the two sets of data are crystallographically equivalent and that the differences are a consequence of accumulated experimental error. On the other hand it is possible that the two sets are significantly different because of the nature of the
martensite from which the transformation occurred. This latter possibility is supported by comparison of the shape strain elements determined in the present work which show that:

(a) the habit planes $p_F$ and $p_R$ differ by $11.8^\circ$ which is more than the accumulated experimental error of about $\pm 1.0^\circ$,

(b) the directions $d_F$ and $d_R$ are approximately antiparallel, differing by $7.7^\circ$ which is probably more than the accumulated experimental error, and

(c) the $m_F$ and $m_R$ differ by 0.012.

The cycle of forward and reverse transformations can be simplified as:

(a) the forward ($\beta_1$ to $\gamma'_1$) transformation with accompanying shape strain $S_F$ calculated using $g = 0.996028$,

(b) deformation of martensite to strained martensite by additional strain with accompanying shape strain $S_A$, and

(c) the reverse (strained $\gamma'_1$ to $\beta_1$) transformation with accompanying shape strain $S_R$ calculated using $g' = 1.003988$ (where $g' = 1/g$).
The matrix $S_A$ represents the shape deformation associated with the strain to which the $\gamma'$ martensite had been subjected. Clearly, the mechanism by which the strain occurred was exactly reversible as the deformation was totally recovered by reverse transformation during subsequent heating. Reversible deformation of a martensitic structure can occur only by motion of coherent or semicoherent interfaces and is most commonly accommodated by growth of favourably orientated transformation twins, by mechanical twinning or by motion of junction planes of some kind. For each of these mechanisms, the deformation can be represented by an invariant plane strain.

It has been established that the matrix $S_A$ should represent an invariant line strain (see Section 7.3). In this case the strain is a combination of two invariant phase strains and:

(a) the two strain planes should intersect along the invariant line of $S_A$, and

(b) the two strain directions should define a plane which has an invariant normal in $S_A$.

Under this condition the invariant normal $n_i$ and invariant line $x_i$ are defined by:

$$n_i' = n_i 'S_A^{-1}$$  \hspace{1cm} (8.6)$$

and,$$
x_i = S_A x_i$$  \hspace{1cm} (8.7)$$

For the three strains $S_A$ (Table 7.9) the equations (8.6) and (8.7) do not have solutions so that $x_i$ and $n_i$ cannot be identified. It is probable that this result is a consequence of two experimental problems:
(a) the planes \( p_F \) and \( p_R \) differ by only 11.8\(^\circ\), and the directions \( d_F \) and \( d_R \) differ by only 7.7\(^\circ\) so \( p_F \times p_R \) and \( d_F \times d_R \) will respectively define \( x_i \) and \( n_i \) imprecisely, and

(b) experimental error in determination of \( p_F, p_R, d_F \) and \( d_R \) will exacerbate the difficulty in obtaining accurate matrices for the strain \( S_A \).

Consequently, the calculated matrices \( S_A \) probably lacked the numerical precision for equations 8.6 and 8.7 to have solutions. Nevertheless, \( S_A \) must be an invariant line strain (since \( S_A^{-1} = S_F S_R \)), so that even approximate solutions to the equations might provide some information about the additional strains.

Since \( S_A \) must be invariant line strain, the additional strain in the martensite should occur by a combination of two shears (since \( g = 1 \)) and could be:

(a) growth of two favourably oriented twins, or

(b) growth of one twin and stacking faulting, or

(c) growth of one twin and some other shear.

For these possibilities, the invariant line \( x_i \) should be parallel to \( p_F \times p_R \) and the invariant normal \( n_i \) should be parallel to \( d_F \times d_R \). To make further progress with this analysis it will be necessary to determine the solution for \( x_i \) and \( n_i \) which should be related to the mechanism by which the recoverable additional strain occurs in the martensite. This further work was beyond the scope of the present study.
9.0 CONCLUSION

Precise quantitative metallographic methods and X-ray techniques have been used for the calculation of the shape strains associated with the forward stress induced ($\beta_1$ to $\gamma_1'$) transformation and reverse (strained) $\gamma_1'$ to $\beta_1$ transformation for the Cu-15%Al-3%Ni alloy used in this present work.

The following conclusions were evident from this work:

(a) The habit planes for the forward and the reverse transformations differed by 11.8°.

(b) The direction of atom movements for the forward and reverse transformations was antiparallel to within 7.7°.

(c) The magnitude of the atom movements in the forward transformation was $0.084 \pm 0.004$ and in the reverse transformation was $0.096 \pm 0.005$.

(d) The elements of the shape strain for the forward transformation $S_F$ are very similar to elements reported previously [51].

(e) The elements of the shape strain for the reverse transformation $S_R$ are similar to the results for reverse transformation from unstrained martensite reported before [51].
(f) The magnitudes of the shape strains accompanying the forward and reverse transformations were similar and differed by 0.01 thereby suggesting that there was no large scale microstructural change during deformation of the $\gamma_1$ martensite.

(g) The shape strain accompanying deformation of the martensite $S_A^{-1} = S_F S_R$ is not invariant plane strain but may be an invariant line strain indicating that deformation may occur by a combination of two shears.
10.0 REFERENCES


11.0 APPENDIX A

Numerical Procedure For Calculating The Elements Of The Shape Strain \((m, d \text{ and } p')\)

The elements of the shape strain for the forward and reverse transformations were determined using a two surface analysis of habit plane trace and tilt angles.

The analysis involves several bases but the results are obtained in the J Basis (defined in Section 8) and the so-called habit plane basis \(H\) defined as:

\[
\begin{align*}
h_1 & \; \text{parallel to } j_1, \\
h_3 & \; \text{parallel to the habit plane normal} \\
h_2 & \; = h_3 \times h_1
\end{align*}
\]

The habit plane traces \(t_1 \times t_2\) (Figures A1 and A2) are attained in the J basis using the angles \(\alpha, \beta, \sigma\) and the habit plane normal is then parallel with

\[
(\mathbf{p} ; J) = (0, \sin \psi, \cos \psi)j
\]

In the basis \(H\):

\[
(\mathbf{p} ; H) = (001)_H
\]

\[
[H ; D] = [d_1d_2d_3]_H
\]
thus a shape strain $S$ is given by

$$
\begin{vmatrix}
1 & 0 & \text{md}_1 \\
0 & 1 & \text{md}_2 \\
0 & 0 & 1 + \text{md}_3
\end{vmatrix}
$$

thus $l_s I = g = (1 + \text{md}_3)$

and

$$\text{md}_3 = g - 1$$

(A1)

Equations for $\text{md}_1$ and $\text{md}_2$ are obtained as follows:

The tilted normal to the reference surface can be specified in terms of the tilt angle $\phi_1$ and
by $n_R'S^{-1}$ which after expansion and equating equivalent terms leads to

$$\text{md}_2 = \cot \psi \cdot \text{gcot} (\psi - \phi_1)$$

(A2)

Similarly, the tilted normal to the side surface can be specified in term of the tilt angle $\phi_2$
and by $n_S'S^{-1}$ in leading to:

$$\text{md}_1 = s_3/s_1 - gA t_2/s_1 - (\text{md}_2)s_1/s_2$$

where $(s_1 s_2 s_3)$ and $(t_1 t_2 t_3)$ represent $n_S$ and $n_S'S^{-1}$ in an invariant basis with $A$ as a
constant.

The magnitude $m$ is then,

$$m = ( (\text{md}_1)^2 + (\text{md}_2)^2 + (\text{md}_3)^2 )^{1/2}$$

and the direction $d$ is

$$d = 1/m [\text{md}_1 + \text{md}_2 + \text{md}_3]$$
Figure A1: Diagram illustrating the geometry of a typical specimen for the two tilt analysis and the defined A, J, K and L bases. The angles of tilt are also defined.
Figure A2: Streographic projection for a hypothetical case as shown in Figure A1 and showing the bases:

J base; \( j_1 j_2 j_3 \)

K base; \( k_1 k_2 k_3 \)

L base; \( l_1 l_2 l_3 \)

A base; \( a_1 a_2 a_3 \)

\( \phi_1 = \) right hand rotation about \( +j_1 // l_1 \).