

## The Thermomechanical Behaviour of a Metastable Cu-Al-Ni Single Crystal Alloy

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**Abstract:** This paper presents the results from an experimental and theoretical analysis of the thermomechanical behaviour of a metastable  $\beta$ -phase single crystal alloy of composition Cu - 28.3at% Al - 3.8at% Ni. The stress-strain behaviour of this single crystal material was investigated experimentally by tensile testing and this data was used to characterise the stress/temperature martensite phase equilibria. The same alloy was also the subject of microcalorimetric measurements which enabled some of the enthalpies and entropies of transformation to be directly determined. This thermodynamic data was used to calculate the stress/temperature phase equilibria of the alloy. It is shown that the calculated equilibria agree well with those measured experimentally. It is also shown that such thermodynamic evaluations allow a direct interrogation of free-energy/stress/temperature space which provides a fundamental explanation for the change in stress-induced martensite type as the temperature of the alloy is increased. It is shown that the latter is due primarily to the difference in the shear strains associated with the  $\beta \rightarrow \gamma'$  and  $\beta \rightarrow \beta'$  martensitic transformations, with a smaller effect resulting from the entropy difference between the  $\gamma'$  and  $\beta'$  phases.

### 1. INTRODUCTION

In recent years there has been much interest in the thermomechanical behaviour of shape-memory effect materials. This is because (i) it has a direct influence on the introduction of the memory effect, and (ii) in superelastic alloys it can be directly exploited in applications ranging from spectacle frames to orthodontic wires. There has also been significant activity in attempting to understand the fundamental origin of this unusual behaviour. It is now well known that the thermomechanical behaviour of many memory alloys is associated with series of parent to martensite and martensite to martensite transformations. The phenomena associated with such transformations have now been characterised for a number of alloys [1]. However, less work has been carried out to analyse why changes in transformation behaviour occur as a function of external variables such as temperature.

A number of workers [2,3] have shown that the transformation behaviour of these alloys depends primarily on the thermodynamics of the first-order transformations. Thermodynamic approaches can therefore be employed to calculate the stress/temperature phase equilibria which are fundamental to all aspects of superelastic deformation. However, in order to fully understand such equilibria it is necessary to have well characterised stress/strain and thermodynamic data. The latter in particular has proved difficult to obtain due to the small heats exchanged during thermoelastic martensitic

transformation. In recent years a microcalorimetric technique has become available which enables the exchanged heats associated with thermoelastic martensitic transformations to be directly obtained. This technique has been described in detail in earlier publications [4]. In principle it is therefore possible to produce an accurate thermodynamic characterisation of the phases which give rise to superelastic deformation.

This paper presents a thermodynamic analysis of the martensitic phases responsible for superelasticity in Cu-Al-Ni alloys. It will show how thermodynamic data can be used to model the stress/ temperature phase equilibria which are at the origin of superelastic deformation. It will also show how such an approach generates equilibria which agree with those measured experimentally, and enables a fundamental explanation of the equilibria in terms of the relative stabilities of the martensitic phases.

## 2. EXPERIMENTAL DETAILS

The experimental part of this programme consisted of tensile testing of a single crystal of composition Cu - 28.3 at% Al - 3.8 at% Ni, and microcalorimetric measurements on the same material. Tensile testing was carried out over a range of temperatures using a screw-driven tensometer. The temperature range investigated was 150 - 280K which involved tests above and below the  $M_s$  temperature of the alloy (190K). The load cell output during such measurements was used to determine the forward (parent to martensite) stress-thresholds for stress-induced transformation, and this data was used to construct the experimental stress/temperature equilibria for the alloy.

Microcalorimetric measurements were carried out on the alloy using a technique which has been described previously [4]. The experimental aspects of this technique have been validated, however, recently there has been some discussion concerning the formalism required to convert experimentally measured heats to the enthalpies and entropies of transformation [5]. Much of these discussions have involved the validity of calorimetric measurements on materials which do **not** exhibit single interface transformation. In the current work measurements were carried out on a single crystal, and all data was determined whilst the sample was subjected to tensile stress. Although a multivariant transformation was induced within the material, the applied stress induced a number of **identical** variants within the single crystal. Thus transformation was as close as practically possible to the conditions of a single interface transformation. These measurements therefore minimised errors of the type discussed previously [5], and provided data which could be used with confidence later in the thermodynamic analysis.

## 3. EXPERIMENTAL RESULTS

Figure 1 shows the stress/temperature equilibria produced by tensile testing. This data is consistent with previously published measurements [6] and shows the forward transformation stress-thresholds for two parent to martensite and one martensite to martensite transformation. The phase fields in figure 1 were identified on the basis of comparison of the equilibria and transformation hystereses with previously published data [6]. The measurements of most interest in the context of this paper were the parent to martensite transformations which showed a transition in the stress-induced martensite from  $\gamma'$  to  $\beta'$  as the temperature increased. The interpretation of the latter phenomenon will form part of the thermodynamic analysis carried out in the following sections.

Table 1 contains the thermodynamic data measured directly by microcalorimetry. Unfortunately during work on this single crystal alloy it was only possible to directly measure data for the  $\beta \rightarrow \gamma'$  transformation. However, it was possible to calculate the missing data for  $\beta \rightarrow \beta'$  transformation using figure 1.

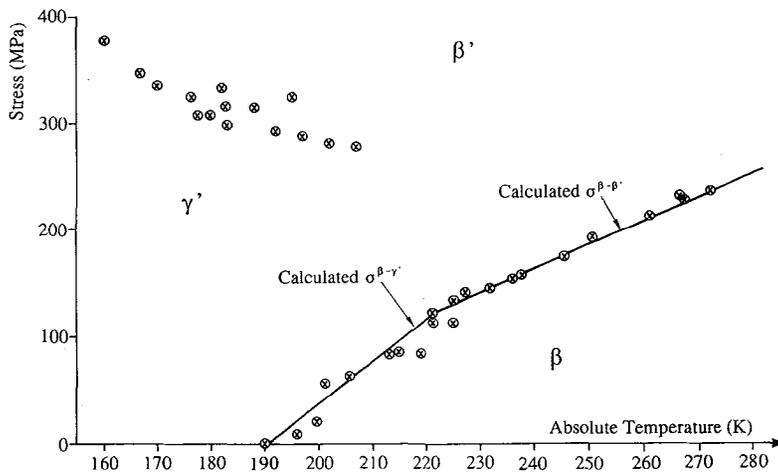


Figure 1 - Comparison of the Experimental Stress/Temperature Data to the Calculated Stress-Thresholds for Parent to Martensite Transformation

The entropy associated with  $\beta \rightarrow \beta'$  transformation was calculated by applying the Clausius-Clapeyron equation to the temperature dependence of the experimental stress-threshold for transformation. The only additional data required for this calculation were (i) the  $\beta \rightarrow \beta'$  shear strain, which was obtained from literature values for a similar alloy [7], and (ii) a calculated value for the molar volume of the alloy. The enthalpy change for  $\beta \rightarrow \beta'$  transformation was also calculated using figure 1. In this case the experimental stress-threshold for transformation was extrapolated to zero stress, and this effective  $M_s$  was used, along with the entropy of transformation, to calculate the  $\beta \rightarrow \beta'$  enthalpy change. These calculated entropy and enthalpy values are contained in table 1.

Table 1 - Thermodynamic Data for Cu - 28.3 at% Al - 3.8 at% Ni

Transformation	$\Delta H$ (Jmol <sup>-1</sup> )	$\Delta S$ (Jmol <sup>-1</sup> K <sup>-1</sup> )	$\gamma^{\beta \rightarrow m}$ [7]
$\beta \rightarrow \gamma'$ (directly measured)	-304.52	-1.5780	0.096
$\beta \rightarrow \beta'$ (calculated data)	-239.40	-1.4778	0.168

## 4. THERMODYNAMIC ANALYSIS

### 4.1. Thermodynamic Formalism

It is now widely accepted that because of the first-order nature of the martensitic transformations in  $\beta$ -phase alloys, the observed stress/temperature phase equilibria are controlled primarily by the thermodynamic properties of the martensitic phases [2,3]. Whilst details of these transformations, such as hysteresis, require consideration of further factors [5], it is possible in principle to calculate the phase equilibria from data of the type contained in table 1. The only problem associated with such analyses is the formalism employed for the effect of stress on the thermodynamics of the transformation. In most thermodynamic analyses the latter is usually considered in terms of an interaction between the applied stress and the strain resulting from stress-induced transformation. In such cases the transformation strain can be considered as a macroscopic strain [8], or the phenomenological shear strain associated with the stress-induced martensitic transformation. A number of recent papers [2] have presented an analysis of  $\beta$ -phase alloys using the latter approach. These show that the phase equilibria of such systems can be modelled successfully using the formalism shown below.

$$\Delta G^{A \rightarrow B} = \Delta H^{A \rightarrow B} - T \Delta S^{A \rightarrow B} - (0.5 \sigma V_m \gamma^{A \rightarrow B} \sin 2\theta \cos \alpha) \quad (1)$$

where:

$\Delta G^{A \rightarrow B}$	is the free energy difference between phases A and B
$\Delta H^{A \rightarrow B}$	is the enthalpy difference between phases A and B
$\Delta S^{A \rightarrow B}$	is the entropy difference between phases A and B
T	is the absolute temperature
$\sigma$	is the macroscopically applied stress
$V_m$	is the molar volume of the parent phase
$\gamma^{A \rightarrow B}$	is the transformation shear strain
$\theta$	is the angle between the axis of applied stress and the habit plane normal
$\alpha$	is the angle between the resolved shear stress and the direction of maximum shear

Thus only six material-specific parameters are required for the thermodynamic evaluation of a single stress-induced transformation.

### 4.2. Martensite Phase Equilibria

Using the above approach and the data contained in table 1, it is possible to calculate the parent to martensite phase equilibria for Cu - 28.3 at% Al - 3.8 at% Ni. The results of such an evaluation are contained in figure 1 where the calculated parent to martensite equilibria are compared to experimentally determined data. It is clear that there is good agreement between the experimental and calculated data, particularly for the  $\beta \rightarrow \gamma'$  transformation where no experimental stress/strain/temperature data was used in the evaluation of the thermodynamic parameters. This good agreement is interesting since it suggests that this simple thermodynamic model is an effective description of free-energy/stress/temperature space and can therefore be used to identify the fundamental reasons for transformation phenomena such as the change in stress-induced martensite type with temperature.

### 4.3. Temperature Dependence of the Stress-Induced Martensite

Figures 2(a) and (b) show such an interrogation of free-energy/stress/temperature space. This provides an explanation for the change in stress-induced martensite type from  $\gamma'$  to  $\beta'$  with increasing temperature. Figure 2(a) shows an isothermal section in the temperature range where  $\gamma'$  is stress-induced. This is clear since the lowest stress-threshold for transformation is that for  $\beta \rightarrow \gamma'$ . However, on increasing the temperature (figure 2(b)) a different equilibrium is established. In this case the lowest stress-threshold for transformation is  $\beta \rightarrow \beta'$ , as is observed experimentally. The reason for this change is easily seen by comparing figures 2(a) and (b).

Initially it may be thought that such a transition in martensite type is due to a change in the relative 'chemical' free-energies of the phases with temperature. Considering the data in table 1, this could be due only to the entropy difference between the two martensites. This entropy difference would alter the relative stabilities in the required way (ie move the stability of  $\beta'$  towards that of  $\gamma'$ ), however, the entropy difference is small and would not produce the required change in stability on its own. This is confirmed in figure 2 which shows that at both temperatures under stress-free conditions the ranking of the phases in order of decreasing stability is  $\beta, \gamma', \beta'$ . Thus within the temperature range of practical interest, in the absence of stress,  $\gamma'$  is always more stable than  $\beta'$ .

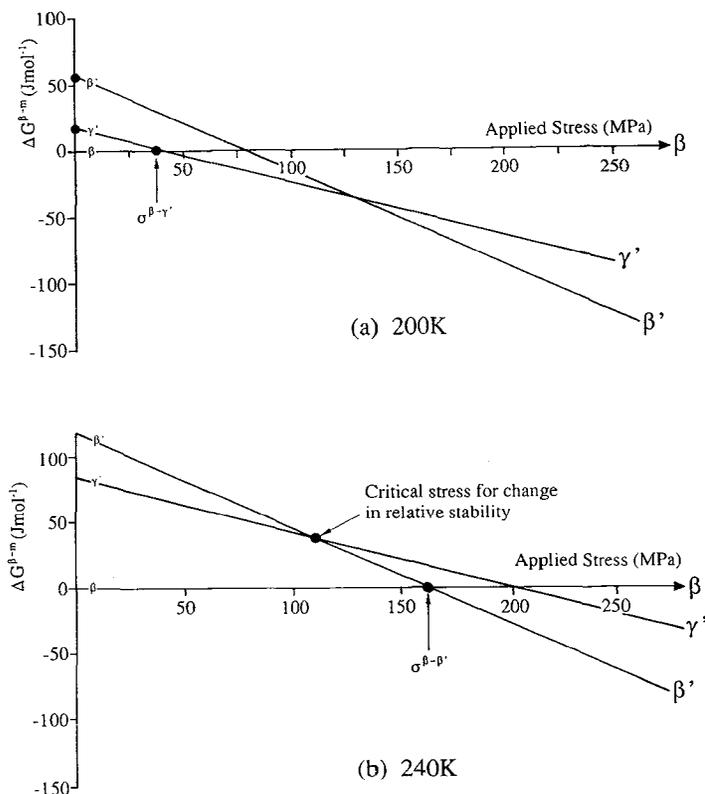


Figure 2 - Isothermal Sections through Free-Energy/Stress/Temperature Space at (a) 200K and (b) 240K

It is clear from figure 2 that the change in martensite type with temperature is only manifested when stress is applied to the system. It must therefore be the interaction between stress and the thermodynamic behaviour of the system which alters the relative stabilities of the phases. Under isothermal conditions equation 1 is linear with respect to stress and so differences in the behaviour of the two phases must be due to the different  $\gamma^{A \rightarrow B}$  terms. The larger value of this term for the  $\beta \rightarrow \beta'$  transformation clearly produces a greater change in free-energy under applied stress, and above a critical value of stress results in a change in the relative stabilities of the martensites (the critical stress level being dependent on the temperature). This is clear in figure 2(b). Thus the experimentally observed transition in stress-induced martensite type with temperature results primarily from the difference in the phenomenological shear strains of the  $\beta \rightarrow \gamma'$  and  $\beta \rightarrow \beta'$  transformations. At temperatures close to the stress-free  $M_s$  this effect is **not** manifested due to the relative instability of the parent phase (figure 2(a)). However, as the temperature is increased, the greater stability of the parent phase enables the shear strain effect to predominate and thus result in a change in the type of stress-induced martensite.

## 5. CONCLUSIONS

It is possible to calculate the stress/temperature martensite phase equilibria of metastable  $\beta$ -phase alloys using a simple thermodynamic formalism. Such evaluations allow the direct interrogation of free-energy/stress/temperature space which can provide a fundamental explanation for many aspects of these alloys' transformation behaviour. An example of the latter is the change in stress-induced martensite type with temperature. This arises primarily from the difference in the phenomenological shear strains associated with the  $\beta \rightarrow \gamma'$  and  $\beta \rightarrow \beta'$  martensitic transformations, with a smaller effect resulting from the entropy difference between the  $\gamma'$  and  $\beta'$  phases.

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