Excess energy in quenched β-Cu-Zn-Al alloys: relation to the martensitic transformation

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The disorder-induced excess energy, δE_β, of a β-$Cu_{1-x}(ZnAl)_x$ (0.30 ≲ x ≲ 0.35) alloy, which shows a martensitic transformation at low temperature, after quenching from different initial temperatures, T_i, is calculated. Ordering energies for the different nearest and next-nearest neighbour atom pairs, obtained by fitting mean field expressions of order–disorder critical temperatures to experimental data, are used. The excess energy is related to the changes of the latent heat of the martensitic transformation, δL, observed just after quenching from T_i. It was found that the shift in latent heat correlates linearly with the calculated excess energy of the β-phase. Calorimetric measurements justify the results.

1. Introduction
A wide variety of noble metal β-phase binary or ternary alloys, transform martensically from bcc phases to close-packed martensitic structures [1]. The $Cu_{1-x}(Zn-Al)_x$ system with (0.30 ≲ x ≲ 0.35) is one such alloy, and has been the subject of continued experimental and theoretical work, because of its very interesting thermomechanical properties (shape memory effect, pseudoelasticity, high damping capacity) which are associated with the thermoelastic martensitic transformation (MT) [2]. Within this range of concentration the alloy shows B2 and DO3 ordered structures which appear, respectively, at the T_{c1} and T_{c2} ($< T_{c1}$) temperatures [3].

The MT in Cu-Zn-Al is quite sensitive to the state of atomic order present in the system [4]. A given atomic ordering state can be established by annealing at a temperature T_i, and then retained at lower temperatures by quenching. It has been shown experimentally that both the MT temperature (M_s) and the transition enthalpy change (L) are substantially modified by the quench, while the transformational entropy change (ΔS) is not modified [5]. This is consistent with the diffusionless character of the MT. In addition, it is also known that after a quench from T_i, some properties of the β-phase are modified with respect to their equilibrium values, in a similar way to the properties of the MT. For example, the change in electrical resistivity after quenching from T_i to T_f = 273 K, where T_f is the final temperature, measured at this temperature, has been found to be proportional to the corresponding change in M_s temperature [4]. The changes in resistivity have been associated with modifications in the atomic configuration after the quench.

The elastic constants of the system, and particularly the shear modulus $C' = 1/2(C_{11} - C_{12})$, are also affected by the quench. This is interesting, because C' measures the resistance against the $\{1\,1\,0\}\langle1\,\bar{1}\,0\rangle$ shear describing the structural change at the trans-

formation (at least to a first approximation), and the C' value near the transition point $T = M_s$ seems to play a very relevant role in determining the properties of the transition. This is so not only if the transition is thought to be driven by a local elastic instability near special lattice defects [6], but also if the low value of C' makes possible the existence of a first-order phase transition without the need of a mechanical instability [7]. From mean field considerations it has been proposed that C' depends linearly on the square of the long-range atomic order parameter (LRAOP) and that the changes δM_s and δL observed after a quench are proportional to the corresponding changes in C' [8, 9], i.e.

$$\delta M_s = a^{-1}\delta C' \tag{1}$$

where $a = (dC'/dT)_{T \geqslant M_s}$, which seems to be, in a first approximation, independent of the ordering state of the β-phase. Correspondingly, the shift δL is given by

$$\delta L = \delta M_s \Delta S = -a^{-1}\delta C'\Delta S \tag{2}$$

This result has been justified using data of elastic constants obtained by numerical simulations in a Cu-Zn binary alloy [10].

The aim of the present work is to study, from a thermodynamic point of view, the configurational changes of the β-phase in the Cu-Zn-Al alloy system after quenching from temperatures $T_i < T_{c2}$, for which experimental data are available.

To do this, the procedure given below is followed. In Section 2 we summarize the mean field model for a ternary alloy (zero-order approximation) used to describe the ordering state at each temperature. In this approximation all kinds of spatial fluctuations or contributions coming from short-range order are neglected. In spite of this simplification, the results obtained for bcc systems do not differ significantly from those obtained using more complicated techniques [11], at least outside the critical regions. In
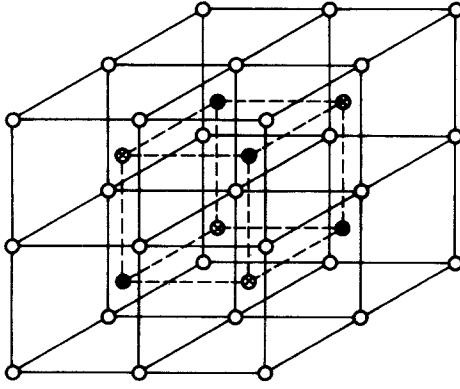
Figure 1 Unit cell of the DO3-type ordered structure, with three sublattice sites: (O) α, ($\bullet$) β and ($\otimes$) γ.

Section 3, the excess energy of the β-phase at T_f after quenching from different T_i will then be found as a function of the two LRAOPs describing the configurational state of the system. The results will finally be compared with calorimetric experiments, and correlated with the changes in thermodynamic properties of the corresponding MT.

2. Model and details of calculation

In order to describe the atomic configuration of the β-$Cu_{1-x}(ZnAl)_x$ alloy, the unit cell of the DO_3 superlattice is classified into three sublattices α, β and γ, as illustrated in Fig. 1. The B2-type superlattice is characterized by a complete equivalence between β and γ sites. In the ordered state the α-sites are occupied by copper atoms, whereas β and γ-sites are occupied at random by all the other species (copper, zinc, aluminium). Hence,

$$p_i^\beta = p_i^\gamma \quad i = Cu, Zn, Al \tag{3}$$

where p_i^j are the probabilities of finding an i-atom (copper, zinc, aluminium) on a j-type sublattice (α, β, γ).

For the DO_3-type superlattice, in the fully ordered state, α and β-sites are occupied by copper atoms, whereas zinc and aluminium atoms are on γ-sites. In this treatment it is assumed that zinc and aluminium atoms are equivalent with respect to ordering and should be located on the α- and β-sites with probabilities proportional to their own concentration, namely

$$\frac{p_{Zn}^j}{x_{Zn}} = \frac{p_{Al}^j}{x_{Al}} \quad \text{with } j = \alpha, \beta \tag{4}$$

where x_i is the atomic fraction of the i-compound (copper, zinc, aluminium). Taking into account these symmetry conditions, it results that both B2 and DO_3 structures require two LRAOPs, η_1 and η_2, to describe the occupation probabilities of three constituent atoms on three sublattice sites. We choose,

$$\eta_1 = 4(p_{Cu}^\alpha - x_{Cu}) \tag{5a}$$

$$\eta_2 = \frac{p_{Zn}^\gamma - x_{Zn}}{3x_{Zn}} \tag{5b}$$

In the zero-order mean field approximation the configurational free energy, F, is given, in a general form,

by

$$F = \sum_\mu \sum_{i=1}^n \sum_{j=1}^l \langle m_{ij} \rangle^{(\mu)} v_{ij}^{(\mu)} + k_B T \sum_{j=1}^l N_j \sum_{i=1}^n p_i^j \ln p_i^j \tag{6}$$

where

$$\langle m_{ij} \rangle^{(\mu)} = \frac{NZ^{(\mu)}}{2} \sum_{k,k'} p_i^k p_i^{k'}$$

n is the number of species, l the number of sublattices, $Z^{(\mu)}$ the coordination number of μth neighbours, and $v_{ij}^{(\mu)}$ are the corresponding pair-wise energies. The energy parameters are assumed to be independent of temperature and composition, at least in the range of compositions we are interest in.

Using Equation 6 and the symmetry relations Equations 3 and 4, we obtain, as a function of the two LRAOPs, η_1 and η_2, the free energies F_{B2} (η_1, η_2, T) and F_{DO_3} (η_1, η_2, T) for the B2 and DO_3 ordered structures, respectively. In our calculations, we have considered interactions between nearest (nn) ($\mu = 1$) and next-nearest neighbours (nnn) ($\mu = 2$).

The equilibrium conditions ($\delta F/\partial\eta_k$) $= 0$ (k $= 1, 2$), written explicitly for F_{B2} and F_{DO_3}, give two sets of non-linear equations describing the dependence of η_1 and η_2 with temperature in the B2 and DO_3 regions. In order to find their solution we must know the ordering energies for (nn) and (nnn)

$$V_1^{(\mu)} = (v_{Cu-Cu}^{(\mu)} + v_{Zn-Zn}^{(\mu)} - 2v_{Cu-Zn}^{(\mu)})/2$$

$$V_2^{(\mu)} = (v_{Cu-Cu}^{(\mu)} + v_{Al-Al}^{(\mu)} - 2v_{Cu-Al}^{(\mu)})/2 \tag{7}$$

$$V_3^{(\mu)} = (v_{Zn-Zn}^{(\mu)} + v_{Al-Al}^{(\mu)} - 2v_{Zn-Al}^{(\mu)})/2$$

($\mu = 1, 2$). The latter must be evaluated by fitting experimental information at hand to appropriate expressions given by the model. We have chosen the temperatures T_{c1} and T_{c2} at which the B2 and DO_3 structures, respectively, become unstable. T_{c1} is to be determined from the condition

$$\text{Det}\left[\left(\frac{\partial^2 F_{B2}}{\partial\eta_i\partial\eta_k}\right)_{\eta_1=\eta_2=0}\right] = 0 \quad (i, k = 1, 2) \tag{8}$$

and T_{c2} from the conditions

$$\left(\frac{\partial F_{DO_3}}{\partial\eta_2}\right)_{\eta_2=\eta_2^*} = 0 \tag{9a}$$

$$\left(\frac{\partial^2 F_{DO_3}}{\partial\eta_2^2}\right)_{\eta_2=\eta_2^*} = 0 \tag{9b}$$

In addition, the T_{c2} point must include the symmetry relations corresponding to both structures. This is equivalent to saying that Conditions 3 and 4 must be satisfied simultaneously, which leads to

$$\eta_2^* = \eta_2(T_{c2}) = \frac{\eta_1(T_{c2})}{12(X_{Zn} + X_{Al})} \tag{10}$$

Fitting the expressions of T_{c1} and T_{c2} to experimental data for alloys with different compositions [12], the model results in the following (nn) and (nnn) ordering energies for the β-Cu–Zn–Al alloy system

$$V_1^{(1)} = 333\,k_B \qquad V_1^{(2)} = 171\,k_B$$

$$V_2^{(1)} = 460\,k_B \qquad V_2^{(2)} = 280\,k_B$$

$$V_3^{(1)} = -13\,k_B \qquad V_3^{(2)} = -12\,k_B$$

3. Results and discussion

We are now interested in obtaining the β-phase configurational energy change after a quench from a temperature, T_i, to a final temperature, T_f, assuming that T_f is a temperature higher than M_s but close to it. In equilibrium at the temperature T_i, the ordering state of the system is characterized by the LRAOPs $\eta_1(T_i)$ and $\eta_2(T_i)$. The configurational excess energy δE_β of the system after quenching to T_f will then be given by

$$\delta E_\beta = E(\eta_1(T_i), \eta_2(T_i), T_i) - E(\eta_1(T_f), \eta_2(T_f), T_f) \tag{11}$$

In this paper we will only consider quenches from $T_i < T_{c2}$. For quenches above T_i, it has been argued [4] that the quenching rate has too strong an influence on the ordering state frozen at T_f. A partial ordering occurs during the quench, mainly due to a large free vacancy concentration at T_i. The situation becomes rather difficult to handle, both theoretically and experimentally.

From the model in the previous section, let us calculate δE_β as a function of the equilibrium values of the LRAOPs at T_i and T_f, respectively. The result is
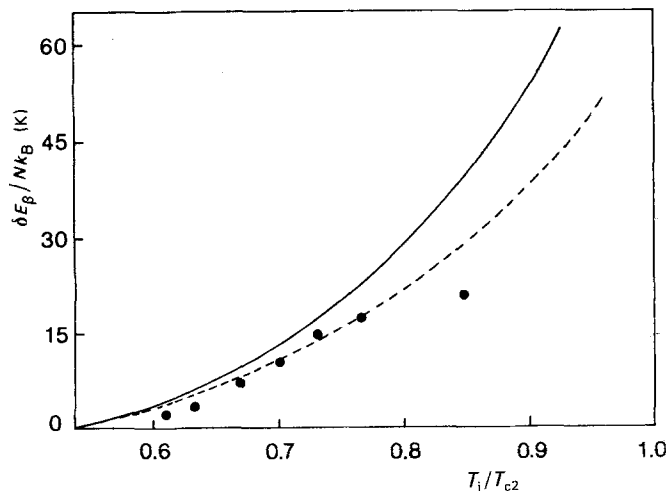
In Fig. 2, excess energies computed from Equation 12 (using the ordering energies evaluated previously and the appropriate values of the LRAOPs) are compared to experimental results [13], for a composition $x_{Cu} = 0.663$, $x_{Zn} = 0.244$, $x_{Al} = 0.093$. There is a good agreement between theoretical and experimental points for $\tau = T/T_{c2} < 0.8$. For $\tau > 0.8$, the agreement is much less satisfactory, probably due to the finite value of the quenching rate which hinders retaining the full equilibrium ordering state present in the system at the temperature T_i. This explanation is consistent with the fact that the experimental values are systematically smaller than the corresponding theoretical predictions.

In the DO_3 region ($0 < T < T_{c2}$) we have found that the variation of the LRAOP, η_1, is very small ($\Delta\eta_1 = [\eta_1^{max} - \eta_1(T_{c2})]/\eta_1^{max} < 0.050$ whereas $\Delta\eta_2 = [\eta_2^{max} - \eta_2(T_{c2})]/\eta_2^{max} \simeq 0.5$). It is then a good approximation to take η_1 as a constant, in this region. With this assumption the configurational energy change of the β-phase after a quench may be obtained as a function of only one LRAOP. It is interesting to define this LRAOP in such a way that it vanishes for

$$\delta E_\beta = \frac{-N[V_1^{(1)}x_B^2 + V_2^{(2)}x_c^2 + (V_1^{(1)} + V_2^{(1)} - V_3^{(1)})x_B x_c]}{8(x_B + x_c)^2} [\eta_1^2(T_i) - \eta_1^2(T_f)]$$

$$+ \frac{3N}{2}(V_1^{(2)}x_B^2 + V_2^{(2)}x_c^2 + (V_1^{(2)} + V_2^{(2)} - V_3^{(2)})x_B x_c)$$

$$\times \left\{ \frac{\eta_1^2(T_i) - \eta_1^2(T_f)}{8(x_B + x_c)^2} + \frac{3[\eta_1(T_i)\eta_2(T_i) - \eta_1(T_f)\eta_2(T_f)]}{(x_B + x_c)} - 18[\eta_2^2(T_i) - \eta_2^2(T_f)] \right\} \tag{12}$$

N is the total number of atoms in the system.

If the annealing temperature, T_f, is high enough, δE_β may be measured in a calorimeter as the energy dissipated during the isothermal ordering process at T_f following quenching from T_i. Actually, calorimetric measurements at constant pressure give the enthalpy change, δH, in the process. In our case, however, there are no significant volume changes during the ordering process. Hence

$$\delta E \simeq -\delta H = -[H(t \to \infty) - H(t = 0)]$$

$$= -\int_0^\infty \frac{dH}{dt} dt \tag{13}$$

where t is time.

$T > T_{c2}$. To do this, we define the LRAOP η as

$$\eta = \frac{1}{3x_B}(p_{Zn}^\gamma - p_{Zn}^\beta) = \frac{3}{2}\eta_2 - \frac{\eta_1}{8(x_B + x_c)} \tag{14}$$

This definition enables a formal treatment of the ternary alloy as if it were a binary alloy. Introducing the new LRAOP [14], and assuming that $\eta_1(T_f) \simeq \eta_1(T_i)$, Equation 12 takes the form

$$\delta E_\beta = -12N[V_1^{(2)}x_B^2 + V_2^{(2)}x_c^2 + (V_1^{(2)} + V_2^{(2)} - V_3^{(2)})x_B x_c][\eta^2(T_i) - \eta^2(T_f)] \tag{15}$$

In Fig. 2, δE_β calculated from Equation 15, is shown

Figure 2 Total energy released at $T_f = 300.5$ K plotted against T_i/T_{c2}. (———) Mean field theoretical expression (Equation 12), (— — —) the approximated expression (Equation 15). Points are experimental values obtained from calorimetric measurements.
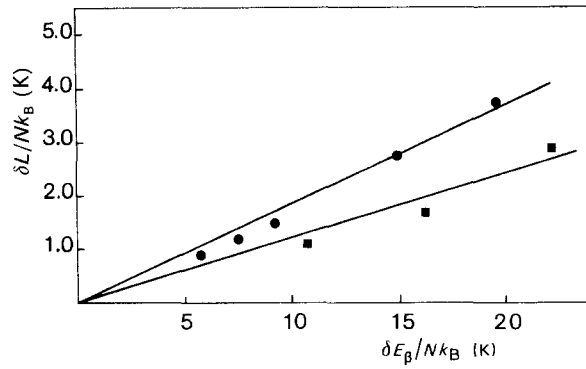
Figure 3 Experimental values of changes of latent heat, δL, for different β-phase ordering states plotted against the corresponding computed excess energy of the β-phase δE_β for the two alloys considered: (●) A and (■) B. In both cases we observe a good linear behaviour.

as a function of T_i. Apparently the agreement between the experimental data and the theoretical curve obtained from Equation 15 is better than the agreement with the non-approximated theoretical curve obtained from Equation 12. As previously mentioned, this is due to the finiteness of the quenching rate which is masked in the approximated method when considering $\eta_1 = \eta_1(T_f)$ ($< \eta_1(T_i)$) constant during the process.

It is interesting to note that in general δE_β depends quadratically on the LRAOPs [12], in the same way as the elastic constant, C', after the quench. This fact follows from the expression [5]

$$C'(\eta_1, \eta_2) = 2/3Nd \sum_{ij} \langle m_{ij} \rangle^{(2)} k_{ij} \qquad (16)$$

obtained in the framework of a mean-field theory within the harmonic approximation. k_{ij} corresponds to (nnn) interatomic force constants and d is the lattice parameter.

Moreover, if η_1 is assumed to be constant in the DO$_3$ region, δE_β and $\delta C'$ turn out to be mutually proportional

$$\delta E_\beta = \alpha \delta C' \qquad (17)$$

Comparing Equations 16 and 17 one can see that in this approximation $\alpha = 3Ndg$, where g is a parameter giving the relation between nnn interaction energies and force constants.

From Equations 1 and 2 we now obtain

$$\delta L = -(\alpha a)^{-1} \Delta S \delta E_\beta \qquad (18)$$

Fig. 3 presents experimental values of δL corresponding to different ordering states plotted against the corresponding δE_β computed from Equation 15 for two β-Cu–Zn–Al alloy systems (Alloy A: $x_{Cu} = 0.677$, $x_{Zn} = 0.193$, Alloy B: $x_{Cu} = 0.6932$, $x_{Zn} = 0.1364$). For these alloys $\Delta \eta_1 < 0.01$, and Equation 15 represents, therefore, a very good approach for computing

δE_β. A linear behaviour between δL and δE_β is observed, in agreement with Equation 18. It renders values of $(\Delta S/\alpha a)$ for the two alloys considered. Using that for Cu–Zn–Al, $a = 2.5 \times 10^6 \, \mathrm{N\,m^{-2}\,K^{-1}}$ [14], we evaluate the corresponding α-values. These values are summarized in Table I. It is also interesting to note that δL can be written in the form

$$\begin{aligned}
\delta L &= (E_M(\eta_i) - E_\beta(\eta_i)) - (E_M(\eta_f) - E_\beta(\eta_f)) \\
&= (E_M(\eta_i) - E_M(\eta_f)) - (E_\beta(\eta_i) - E_\beta(\eta_f)) \\
&= \delta E_M - \delta E_\beta \qquad (19)
\end{aligned}$$

where δE_M is the energy change of the martensitic phase (MP) following a quench from T_i. In writing Equation 19 we are implicitly considering that MP inherits the atomic configuration of the β-phase and that its crystallographic structure does not depend on the ordering state of the high-temperature phase. The former condition arises from the diffusionless character of the MT and is consistent with the fact that the ΔS does not depend on the state of order of the β-phase. The second condition is supported by experimental data [15]. It follows then that the energy change of the MP, δE_M, is given by

$$\delta E_M = \left(1 + \frac{\Delta S}{\alpha a}\right) \delta E_\beta \qquad (20)$$

In this approximation δE_M is proportional to the corresponding energy change of the β-phase. It is interesting to note that δE_M does not represent an excess energy in relation to the equilibrium configurational state of the MP. Experimental results [16] show that even when the β-phase is in its equilibrium state of order, the corresponding MP shows an ordering process to a different atomic configuration, if the temperature is high enough.

The equilibrium state of order in MP is not known. It would be very interesting to compare δE_M with calorimetric measurements of the excess energy in MP (which would always be measured in relation to the corresponding equilibrium state) in order to gain information about the equilibrium configuration in MP. Unfortunately, the excess energy in MP is very difficult to obtain experimentally, because of the slow ordering rate in this phase. Ordering requires diffusion and the rate of atomic ordering will depend on vacancy concentration and on vacancy mobility. The former may be considered similar for martensite and β, in a first approximation, but due to the close-packed character of martensite, the mobility of vacancies in this structure is much smaller than in the β-phase.

4. Conclusion

Quenching has a pronounced effect on the thermodynamic properties of the martensitic transformation

TABLE I Parameters involved in theoretical expressions for the two alloys considered. $\Delta S/\alpha a$ is obtained from Fig. 3. α is then calculated with the values of ΔS available in [5]. Its values is compared with that calculated from $\alpha = 3Ndg$.

	$\Delta S/\alpha a$	ΔS (J mol^{-1} K^{-1}) [5]	α (10^{-6} m^3 mol^{-1})	$3Ndg$
Alloy A	-0.19	-1.30	2.7	4.3
Alloy B	-0.13	-1.32	4.1	4.3

of Cu–Zn–Al alloy. A mean field model has been used to obtain the disorder-induced excess energy of the β-phase after a quench. The corresponding ordering energies for nearest and next-nearest pairs have been obtained by fitting mean field expressions of critical order–disorder temperatures to available experimental data.

The excess energy calculated after quenching from T_i temperatures below T_{c2} using these ordering energies, are in good agreement with calorimetric measurements of this quantity.

We have found that the β-phase excess energy is proportional to the corresponding shift of the latent heat of the martensitic transformation. This clearly demonstrates that the change of the ordering state of the β-phase after quenching is responsible for the changes of the thermodynamic properties of the martensitic transformation. Order could also affect the nucleation process. However, this local effect would be much less important than that described before.

The corresponding excess energy of the martensitic phase, is also proportional to the β-phase excess energy. This result comes from the diffusionless character of the martensitic transformation.

Acknowledgement

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