The Stability of Martensite in Cu-Zn Alloys

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The enthalpy and entropy difference between the β phase and the martensite has been calculated for Cu-Zn binary and ternary alloys using a description in terms of pairwise chemical interaction energies. It is shown that the concentration dependence of M_s is mainly determined by fourth neighbour pair interactions. This result is also supported by the analysis of the critical stress which is necessary to transform the orthorhombic martensite to a fcc ordered lattice. In contrast to the strong effect which long range order has on the enthalpy of transformation, the entropy difference has been found to be quite insensitive to order.

Die Stabilität des Martensits in Cu-Zn-Legierungen

Die Umwandlungsenthalpie und Entropie zwischen β und Martensit in binären und ternären Cu-Zn-Legierungen wurde berechnet unter der Annahme paarweiser Atom-Atom-Wechselwirkungen. Es wird gezeigt, daß die Konzentrationsabhängigkeit von M_s hauptsächlich durch Wechselwirkungen zwischen viertnächsten Nachbarn bestimmt ist. Dieses Ergebnis wird gestützt durch die Analyse der Schubspannungen, die nötig sind, um den orthorhombischen Martensit in eine geordnete flächenzentrierte Struktur umzuwandeln. Im Gegensatz zum starken Einfluß der Ordnung auf die Umwandlungsenthalpie ist die Entropie kaum vom Ordnungsgrad abhängig.

Many copper based alloys show highly reversible phase transformations between the bcc β phase and a martensitic structure. In CuZn the difference between the temperature M_s at which martensite appears first on cooling and the temperature A_f at which the retransformation to β is completed on heating is of the order of 6°C[1]). Similarly, the resolved shear stress τ_M at which the martensite is induced above M_s and the stress τ_{Af} at which the martensite disappears again on unstressing differ by about 6 MN/m^2, being independent of temperature within experimental scatter[1]). The hysteresis is small compared to the influence of composition and temperature on the transformation[2]) [3]), and no appreciable error is committed if M_s and τ_M are approximated by the values at which the free energy difference ΔG between β and martensite is zero, $\Delta G = \Delta H - M_s \Delta S \simeq 0$. From measurements of M_s and the temperature dependence of τ_M, the transformation enthalpy and entropy can be determined[3]). It had been shown for binary CuZn that ΔS depends only weakly on composition[3]), whereas M_s and consequently the enthalpy difference ΔH changes sensitively with zinc content[2]).

It is desirable to have a knowledge of the factors that are responsible for contributing to ΔH and ΔS, not only for the intrinsic interest to understand the mechanism of the martensitic transformation, but also because these materials have technological applications[4]), and the choice of the CuZn system is particularly suited for this purpose as it is possible to produce and study various phases at a given alloy composition, and thus obtain more information on the relationship between structure and alloy stability. The phases that can be compared are the disordered β, the ordered β', the orthorhombic martensite, an ordered face centered structure obtained by deformation of the martensite[5]) and by extrapolation from lower zinc concentrations the primary disordered fcc phase. An additional fact that makes the Cu-Zn system interesting is that the different structures have closely the same atomic volume, and that in a free electron model the same Fermi surface is obtained.

The stability of the equilibrium alloy phases is controlled mainly by the electron concentration[6]). However, the M_s temperature can not be correlated with e/a[7]), but depends on long range order[8]), for the reason that at least in Cu-Zn-Al, Cu-Zn-Ga, Cu-Zn-Si and Cu-Zn, where X-ray data are available, M_s is proportional to the order induced distortion of the martensite lattice.

In this paper an attempt has been made to analyse the factors that contribute to the transformation. First the enthalpy of transformation will be discussed for the binary and the ternary Cu-Zn based alloys, followed by a discussion of the transformation entropy.

The enthalpy contributions

Long range order in the bcc beta phase:

The influence of order in the β phase has been successfully described in terms of atom pair interaction energies between first and second nearest neighbours[10]). The relevant quantity is the chemical interaction energy $w^{(i)}_{AB} = -2V^{(i)}_{AB} + V^{(i)}_{AA} + V^{(i)}_{BB}$ where $V^{(i)}_{AB}$, $V^{(i)}_{AA}$ and $V^{(i)}_{BB}$ are the interaction energies between A-B, A-A and B-B atom pairs in the i-th neighbour position.

The bcc lattice is usually divided into four sublattices denoted by I to IV, each of which having an atom occupation probability that is independent of the sublattice site. By using the Bragg-Willams-Gorsky model and taking into account short range disorder by a scaling parameter, it has been possible to relate order-disorder temperatures and specific heats to chemical interaction energies in many body centered systems[10]).

Although the distances of third and higher order neighbours in the β phase are more than 60% larger than that between first nearest neighbours, this fact alone does not justify neglecting their contribution to order-disorder changes. As will be shown in the course of this paper, interactions between atoms that correspond to third nearest neighbours in the β phase cannot be neglected. The first and second neighbour chemical interaction energies

which are determined from properties that depend only on the order-disorder change can thus be only effective energies, which will be denoted by $w_{AB}^{(i)}$(eff). However, a calculation that includes up to sixth neighbour interactions shows that the higher order terms are taken into account by writing:

$$w_{AB}^{(1)}(\text{eff}) = w_{AB}^{(1)} - 3w_{AB}^{(3)} + 3w_{AB}^{(4)} - 1.5w_{AB}^{(8)}, \quad (1)$$

$$w_{AB}^{(2)}(\text{eff}) = w_{AB}^{(2)} - 2w_{AB}^{(3)} + \frac{4}{3}w_{AB}^{(2)} - w_{AB}^{(6)}.$$

Therefore $w_{AB}^{(1)}$(eff) and $w_{AB}^{(2)}$(eff) are sufficient to describe order-disorder transformations in bcc alloys, in agreement with the observations.

The martensite transformation:

The enthalpy difference between β and the martensite will be split into three terms, (a) a "configurational" component ΔE_{conf}, which is structure insensitive and is given by the sum of the interaction energies between all atom pairs; (b) a vibrational part ΔE_{vib} from the phonon contribution and (c) an "electronic" structure sensitive term ΔE_{el} which describes the electronic changes that do not enter in the previous two terms. ΔE_{vib} can safely be neglected since the Debye temperatures of the two phases are very similar. The basic assumption of this paper is that in the Cu-Zn based alloys ΔE_{el} is so small that it can be approximated from a linear interpolation of the values for the pure elements. For free electron behaviour and no volume change ΔE_{el} can be expected to be zero. For alloy systems in which the constituent atoms are sufficiently similar, Cu and Zn for example, and for which the Fermi surface is only little distorted, the approximation should be reasonable. Thus it will be assumed that the chemical interaction energies depend only on distance between the atoms and not on the crystal structure. For example, since first neighbour distances in bcc and in martensite are practically unaltered, the corresponding nearest neighbour interaction energies remain constant.

The enthalpy can be evaluated by simply counting the number of A-A, A-B and B-B bonds and multiplying them by the corresponding pair interaction energies. This evaluation has been carried out to ninth neighbours in the martensite. Whereas the first and second neighbour contribution is the same for fcc and hex lattices, for higher neighbour interactions the actual martensite structure has to be taken into account. To a good approximation the martensite has a 3R structure, ABCBCACAB. Though it would present no problems in incorporating the actual structure in the calculations, the deviation from 3R contributes little to ΔH[3]) and for simplicity will be neglected.

Let the occupation probability of atom A on sublattice site J = I to IV be p_A^J. The influence of long range B2 order can best be described by defining $x_A = 1/4(p_A^{I} + p_A^{II} - p_A^{III} - p_A^{IV})$, which is zero when long range order is absent. The interaction energies in the β phase are denoted by $V_{AA}^{(i)}$, $V_{AB}^{(i)}$ and $V_{BB}^{(i)}$, and those in the martensite by $M_{AA}^{(i)}$, $M_{AB}^{(i)}$ and $M_{BB}^{(i)}$.

The corresponding chemical interaction energies are $w_{AB}^{(i)}$ and $m_{AB}^{(i)} = -2M_{AB}^{(i)} + M_{AA}^{(i)} + M_{BB}^{(i)}$. Let E^{β} and E^{M} be the energies respectively of the β phase and the 3R martensite per g-atom. The result of the calculation for the ternary Cu-Zn-X alloy, neglecting the nonlinear part in the electronic contribution ΔE_{el} can be written as follows:

$$E^{\beta} - E^{M} = \Sigma\,[\Delta E_A^{\circ} C_A + \Delta E_{AB}^{(1)}(C_A C_B + x_A x_B) + \Delta E_{AB}^{(2)}(C_A C_B - x_A x_B)] \quad (2)$$

where ΔE_A° are the hypothetical transformation energies from bcc to the orthorhombic 3R structure for the pure elements A = Cu, Zn and X, C_A the concentration of A and the sum in the last two terms is over all pairs.

$$\Delta E_{AB}^{(1)} = -3w_{AB}^{(2)} - 6w_{AB}^{(3)} + 2m_{AB}^{(1)} + 3m_{AB}^{(2)} + \frac{2}{3}m_{AB}^{(3)} + \frac{10}{3}m_{AB}^{(4)} + \frac{4}{3}m_{AB}^{(5)} + 4m_{AB}^{(6)} + \frac{8}{3}m_{AB}^{(7)} + \frac{4}{3}m_{AB}^{(8)}, \quad (3)$$

$$\Delta E_{AB}^{(2)} = -4w_{AB}^{(1)} + 4m_{AB}^{(1)} + \frac{20}{3}m_{AB}^{(4)} + \frac{8}{3}m_{AB}^{(5)} + \frac{16}{3}m_{AB}^{(7)} + \frac{8}{3}m_{AB}^{(8)}. \quad (4)$$

In table 1 are given the distances d in units of the face centered cubic lattice parameter a_{fcc} for i-th neighbours in the martensite lattice. Given are also the distance vectors to which they correspond in an fcc or hexagonal lattice:

For transformation temperatures sufficiently far below the order-disorder temperature, the order parameter x_A can be approximated, assuming that the alloy is in its highest long range ordered state. Then:

$$x_{Cu} = 1 - C_{Cu};\ x_{Zn} = -C_{Zn};\ x_X = -C_X.$$

The binary Cu-Zn system: In the small concentration range in which a martensitic transformation is observed[2]), $C_{Cu}C_{Zn} + x_{Cu}x_{Zn}$ car be approximated by

$$C_{Cu}C_{Zn} + x_{Cu}x_{Zn} = \varkappa_{CuZn}^{\circ} - \varkappa_{CuZn}^{(1)} C_{Zn}$$

$$(\varkappa_{CuZn}^{\circ} = 0.312,\ \varkappa_{CuZn}^{(1)} = 0.573).$$

Then $E^{\beta} - E^{M}$ can be rewritten as:

$$E^{\beta} - E^{M} = \Delta E_{Cu}^{\circ} + \Delta E_{CuZn}^{(1)} \varkappa_{CuZn}^{\circ} + (\Delta E_{Zn}^{\circ} - \Delta E_{Cu}^{\circ} - \Delta E_{CuZn}^{(1)} \varkappa_{CuZn}^{(1)} + \Delta E_{CuZn}^{(2)})\, C_{Zn}. \quad (6)$$

Experimentally, the M_s temperature varies linearily with concentration and is given by $M_s = 3280 - 8000\ C_{Zn}$ [K][2]), (C_{Zn} in atomic fraction). Using the measured entropy of transformation (3), the enthalpy difference is, correspondingly:

$$E^{\beta} - E^{M} = (510 - 1250\ C_{Zn})\ R' \quad (7)$$

(R' = k' · N, k' = the Boltzmann constant times 1 K, N = the Avogadro number).

It is not possible to describe the results in terms of only the measured first and second neighbour interaction energies in the β phase with $m_{CuZn}^{(1)} = w_{CuZn}^{(1)}$, as otherwise either an unreasonably high $\Delta E_{Zn}^{\circ} - \Delta E_{Cu}^{\circ}$ for the elements or a high electronic contribution ΔE_{el} has to be postulated, the latter is in contrast to the observation that the M_s temperature is not correlated with electron concentration in ternary alloys. An estimation of ΔE° for Cu and Zn can be made, using published values (1) for the energy difference between the bcc and hex phases of pure Cu and Zn, and approximating the orthorhombic martensite lattice by a mixture of a hexagonal and face centered phase. The values deduced in this way are ΔE_{Cu}° = 370 R' and ΔE_{Zn}° = 280 R'.

In order to describe the experimental results it is therefore necessary to include higher neighbour chemical interaction energies. For lack of data it will be supposed that $w^{(3)}_{CuZn} = m^{(3)}_{CuZn} = m^{(4)}_{CuZn}$, since the corresponding neighbour distances are approximately the same. As will be shown $w^{(3)}_{CuZn} < 0$, whereas $w^{(2)}_{CuZn} > 0$, and since $m^{(2)}_{CuZn}$ is intermediate in distance between second and third neighbours in β, $m^{(2)}_{CuZn}$ will be set to zero. Also the contributions from higher than fourth neighbours will be neglected.

complete shielding of the charged impurities by the conduction electrons with wave vector $k < k_F$, where k_F is the value at the Fermi surface. For free electrons the charge perturbation $\Delta\varrho$ at large distances r from the impurities oscillates and is according to Friedel: $\Delta\varrho = A \cos(2k_F r + \psi)/r^3$ where A and ψ are constants that characterize the impurity. Here it is assumed that the atomic volume of the impurity is the same as that of the matrix. Correspondingly, the chemical interaction energies for sufficiently large r can be rewritten as $w(r) = B \cos(2k_F r + \phi)/r^3$. These fluctuations have indeed been observed in various systems[12]). For Cu-Zn with an electron concentration of e/a = 1.396 the wavelength of the oscillations is $\Delta r = \pi/k_F = 0.57\, a_{fcc} = 0.21$ nm. If ϕ and B were known it would have been possible to improve the calculations of $\Delta E^{(1)}_{AB}$ and $\Delta E^{(2)}_{AB}$ within the free electron approximation. An estimate for various ϕ indicates however that the error in replacing $\Delta E^{(2)}_{CuZn}$ by $6\,2/3\, m^{(4)}_{AB}$ is small (a factor of 1.4 in the worst case). ϕ has a larger influence on $\Delta E^{(1)}_{CuZn}$, but since this constitutes only a relatively small contribution, especially to the concentration dependence of $H^\beta - H^M$, the error involved remains small.

Table 1. Distance d (in units of a_{fcc}) for i-th neighbours in the martensite lattice.

neighbour i =	1	2	3	4	5	6	7	8	9
d^2/a^2_{fcc}	1/2	1	1 1/3	1 1/2	1 5/6	2	2 1/2	2 5/6	3
d/a_{fcc}	0.7071	1.000	1.1547	1.2247	1.3540	1.4142	1.5811	1.6833	1.7321
fcc lattice	1/2<$\bar{1}$10>	<100>	–	1/2<112>	–	<110>	1/2<310>	–	<111>
hex lattice	1/3<$2\bar{1}\bar{1}$0>	1/6<40$\bar{4}$3>	<0001>	<01$\bar{1}$0>	1/3<$2\bar{1}$13>	2/3<$11\bar{2}$0>	1/6<$82\bar{6}$3>	<01$\bar{1}$1>	1/6<08$\bar{8}$3>
	1/6<02$\bar{2}$3>			1/6<24$\bar{6}$3>					

With these simplifications it is possible to determine $m^{(4)}_{CuZn}$ from the measured M_s temperatures, using as input data $w^{(1)}_{CuZn}$, $w^{(2)}_{CuZn}$ and $\Delta E^\circ_{Zn} - \Delta E^\circ_{Cu} = -90$ R', which is so small that an error has a negligible influence on the result. The best agreement between eq. (6) and (7) is obtained for $m^{(4)}_{CuZn} = -125$ k' and $\Delta E^\circ_{Cu} = 340$ R'. The latter value is in close agreement with the theoretical estimate derived earlier, and $m^{(4)}_{CuZn}$ is of a reasonable order of magnitude. The main contribution to the concentration dependence of $E^\beta - E^M$ comes from $\Delta E^{(2)}_{CuZn}$, with $6\,2/3\, m^{(4)}_{CuZn}$ as the leading term. If, in a cruder approximation $\Delta E^\circ_{Zn} - \Delta E^\circ_{Cu}$ and $\Delta E^{(1)}_{CuZn}$ had been set to zero, an $m^{(4)}_{CuZn} = -187$ k' would have been obtained from the concentration dependence of $E^\beta - E^M$ that is only 50% different from the more exact value. This result shows that (within a factor of 2) the contribution of first and second neighbour chemical interactions in β and martensite do not affect the results, provided reasonable estimates for the $w^{(i)}_{CuZn}$ and $m^{(i)}_{CuZn}$ are used. This seems to be surprising, but as seen from eq. (3) and (4) is due to the fact that the small $m^{(4)}_{CuZn}$ is associated with a large factor of $6\,2/3$ in $\Delta E^{(2)}_{CuZn}$, whereas in $\Delta E^{(1)}_{CuZn}$ only the differences $2m^{(1)}_{CuZn} - 3w^{(2)}_{CuZn}$ and $6w^{(3)}_{CuZn} - 2/3\, m^{(2)}_{CuZn} - 3\,1/3 m^{(4)}_{CuZn}$ contribute which remain small for reasonable choices of chemical interaction energies.

Hitherto, the transformation enthalpy has been written essentially as the sum of a linear mixing term for the pure components $\Delta E^\circ_{Cu} C_{Cu} + \Delta E^\circ_{Zn} C_{Zn}$ and an additional term which describes the influence of changes in the i-th neighbour pair population on transformation. It is instructive to split $E^\beta - E^M$ into three terms instead: The first, giving the linear mixing term as before but the second showing the contribution of pair redistribution in the disordered lattice ($x_A = 0$), and the third term describing the influence of order. In fig. 1 are shown the three contributions: curve (a) corresponding to the first term, (b) to the contribution in the disordered alloy and (c) the sum for the ordered alloy. It is seen here that long range order decreases substantially the enthalpy of transformation, thus making the β phase more stable with respect to the martensite. The concentration dependence of $E^\beta - E^M$ is also controlled mainly by the order contribution.

The large range over which the chemical interaction energies are different from zero is caused by the in-

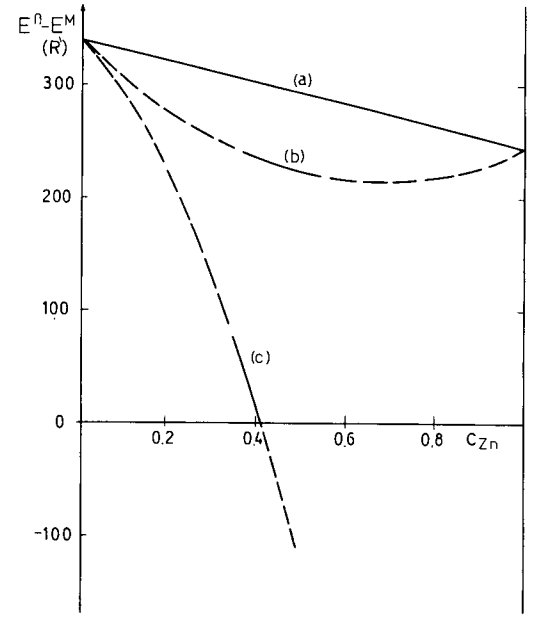

Fig. 1. The transformation enthalpy $E^\beta - E^M$ between the β phase and the martensite as a function of zinc concentration for binary Cu-Zn. Curve (a): The linear mixing term from the pure elements. Curve (b): The $E^\beta - E^M$ for the transformation from a disordered β phase. Curve (c): The result for the ordered alloy.

The ternary Cu-Zn-X systems: The influence of small concentrations of a third element X on the M_s temper-

ature had been determined experimentally by Pops[7]) and Pops and Ridley[13]). They present their results in the form M_s (K) = 3280 − 80Zn + 8 Ni − 30 Ag − 12 Au − 140 Cd − 90 Ga − 145 In − 80 Ge − 175 Sn − 120 Si − 150 Sb − 110 Al. The element symbols denote concentrations in atomic percent. For the present discussion it is more convenient to define a C°_{Zn} by the zinc concentration of the corresponding binary alloy with the same transformation temperature M_s, i.e. M_s = 3280 − 8000 C°_{Zn}. Then the influence of a third element X can be described by a parameter f_o: $C^{\circ}_{Zn} = C_{Zn} + f_o C_X$.

In order to compare these results with the calculations for ternary alloys (eq. (2) to (4)) approximations have to be made, since for most systems the chemical interaction energies with the third elements have not been measured. Therefore it will be assumed that the chemical interaction energies between Zn and the third element can be neglected. This approach should work well in Cu-Zn-Al where $w^{(1)}_{ZnAl}$ and $w^{(2)}_{ZnAl}$ in the β phase have been found to be approximately zero[14]), and for other Zn-X pairs, for which the binary Zn-X diagram does not indicate ordering tendencies. Thus, X = Ag and Au have to be excluded. Furthermore $\Delta E^{(1)}_{CuX}$ and $\Delta E^{\circ}_X - \Delta E^{\circ}_{Cu}$ will be neglected for lack of data. This introduces some error in the evaluation for $E^{\beta} - E^{M}$ but as in binary Cu-Zn still shows the correct trend. For B2 order, which is of concern here for small amounts of the third element, we find:

$$f_o = \frac{\Delta E^{(2)}_{CuX} + (\Delta E^{\circ}_X - \Delta E^{\circ}_{Cu}) - \Delta E^{(1)}_{CuX}\, \varkappa^{(1)}_{CuX}}{\Delta E^{(2)}_{CuZn} + (\Delta E^{\circ}_{Zn} - \Delta E^{\circ}_{Cu}) - \Delta E^{(1)}_{CuZn}\, \varkappa^{(1)}_{CuZn}} \cong \frac{m^{(4)}_{CuX}}{m^{(4)}_{CuZn}} \quad (8)$$

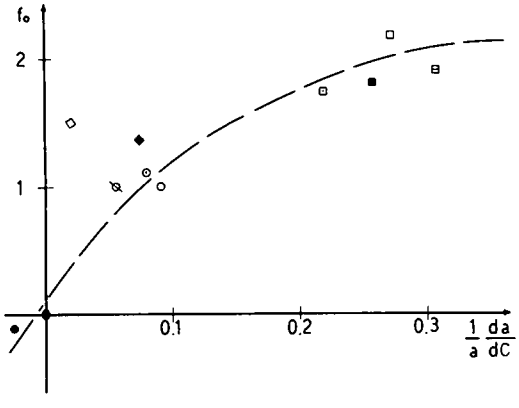

Fig. 2. The ratio $f_o = m^{(4)}_{CuX}/m^{(4)}_{CuZn}$ versus relative lattice parameter change due to X in a pure α phase Cu matrix. X = Ni (●), Si (◇), Zn (⊘), Al (◆), Ga (⊙), Ge (○), Cd (⊡), In (■), Sn (□), Sb (⊟).

here, again $C_{Cu}C_{Zn} + x_{Cu}x_{Zn}$ and $C_{Cu}C_X + x_{Cu}x_X$ have been linearised by $\varkappa^{\circ}_{AB} - \varkappa^{(1)}_{AB}C_B$. As in binary CuZn the influence of a third element of M_s is mainly controlled by the fourth neighbour chemical interaction energy. Independent measurements of $m^{(4)}_{CuX}$ for CuZn do not seem to exist. On the grounds that impurity atoms X in a pure fcc copper matrix produce charge fluctuations and cause variations in the interatomic distances, it has been attempted to correlate $m^{(4)}_{CuX}$ with the relative change in lattice parameter $1/a_{fcc}\,da/dC_X$ due to the addition of small concentrations of an element X.

If this reasoning is correct a relationship between $1/a_{fcc}\,da/dC_X$ in the copper matrix and f_o should hold. In fig. 2 are plotted the experimental values for f_o from the M_s determinations versus the lattice parameter change for the used ternary elements[15]), except Ag and Au. As can be seen there is indeed a reasonable correlation between f_o and $1/a_{fcc}\,da/dC_X$, the largest deviation occurring for Si.

Ni, which decreases the lattice spacing of Cu, also gives rise to a negative f_o. These results also compare favorably with the observation that in the martensite structure the change in lattice parameter, i.e. in the c/a ratio of the basic fcc martensite lattice varies linearly with the M_s temperature independent of the third element present, at least for X = Al, Si, Ga where X-ray measurements have been performed[8]).

The stress induced transformation of the martensite from the orthorhombic to the fcc structure: When a martensitic single crystal of appropriate orientation is stressed, a new face centered structure is induced[5]). The transformation from orthorhombic to fcc involves only changes in third and higher order atom neighbours. An analysis of the corresponding energy change gives important additive information about the contribution of more distant atom pairs.

The transformation occurs by a shear on the orthorhombic $(001)_o$ basal plane in a $[100]_o$ direction (in fcc notation $(111)_{fcc}\ \langle 11\bar{2}\rangle_{fcc}$) at a critical resolved shear stress τ_B which in Cu-Zn is strongly concentration dependent. Although τ_B can be higher than the equilibrium stress between the two phases due to a frictional component, it had been argued[5]) that the concentration dependence of τ_B and of the equilibrium stress are the same. This would make it possible to compare the results with calculated energy differences between the orthorhombic and the fcc structure. This energy difference has been calculated in the same way as before for the binary Cu-Zn alloy, using up to ninth neighbour chemical interaction energies:

$$E^{fcc} - E^{M} = \Delta(E^{fcc}_{el} - E^{M}_{el}) - \Delta^{(1)}E^{fcc\text{-}M}_{CuZn}\,(C_{Cu}C_{Zn} + x_{Cu}x_{Zn}) - \Delta^{(2)}E^{fcc\text{-}M}_{CuZn}\,(C_{Cu}C_{Zn} - x_{Cu}x_{Zn}) \quad (9)$$

with

$$\Delta^{(1)}E^{fcc\text{-}M}_{CuZn} = \frac{2N}{3}\,(-m^{(3)}_{CuZn} + m^{(4)}_{CuZn} - 2m^{(5)}_{CuZn} + 3m^{(6)}_{CuZn} + 2m^{(7)}_{CuZn} - 2m^{(8)}_{CuZn} + m^{(9)}_{CuZn}) \quad (10)$$

$$\Delta^{(2)}E^{fcc\text{-}M}_{CuZn} = \frac{2N}{3}\,(2m^{(4)}_{CuZn} - 4m^{(5)}_{CuZn} + 4m^{(7)}_{CuZn} - 4m^{(8)}_{CuZn}). \quad (11)$$

$\Delta(E^{fcc}_{el} - E^{M}_{el})$ includes the contributions that are not due to structure insensitive pair interactions. It can be decomposed into two terms

$$\Delta\,(E^{fcc}_{el} - E^{M}_{el}) = \frac{2}{3}\Delta\,(E^{fcc}_{el} - E^{hex}_{el}) + \Delta E_{el} \quad (12)$$

the first representing the contribution, if the orthorhombic lattice were just a mixture of a disordered fcc and hex lattice, the second term gives the deviations caused by the regularities of the 3R stacking and by the influence of order on the electronic properties. $\Delta^{(1)}E^{fcc\text{-}M}_{CuZn}$ and $\Delta^{(2)}E^{fcc\text{-}M}_{CuZn}$ is 2/3 of the difference between fcc and hexagonal up to ninth neighbours.

The total $E^{fcc} - E^{M}$ can now be split into three terms: a) the contribution of the disordered lattice if the martensite were a mixture of fcc and hex, b) the excess ΔE_{el} and c) the order contribution. The first term is proportional to

the stacking fault energy γ in the α phase, which has been measured[16] to [18]. The order contribution can be calculated using the $m^{(4)}_{CuZn}$ which was derived earlier. The γ which has been measured in the α phase contains probably a contribution from short range order at high Zn concentrations. Hence the γ which are required for an evaluation of the completely disordered phase are lower and are likely to lie somewhere between the actually measured γ as an upper limit, and the linearily extrapolated values from low concentrations shown as curve A of fig. 3. When the calculated order contribution is added to A, curve B is obtained, using $m^{(3)}_{CuZn} = m^{(4)}_{CuZn} = -125$ k', and $m^{(i)}_{CuZn} = 0$ for $i > 4$. The third curve C gives the lower limit of the stacking fault energy in the martensite phase corresponding to the stress τ_B as an upper limit of the equilibrium stress between fcc and 3R. When comparing curve B and C it is seen that B has a correct concentration dependence around $C_{Zn} = 0.40$, but is shifted to values lower than curve C. The energy difference (whose lower limits are indicated by a double arrow) then would be the additional term ΔE_{el}.

If as an upper limit the order contribution is added to the actually measured γ in the α phase, the data points (⊙) on curve C are closely reproduced without requiring a ΔE_{el} different from zero, although the slope of C results somewhat larger than predicted (fig. 3).

It is evident that, on the basis of this discussion, an electronic contribution ΔE_{el}, if it is not zero, makes the 3R structure less stable than a mixture of fcc and hex lattices with the same average stacking fault density. The reason for the frequent formation of the 3R martensite therefore seems not to be due to a higher stability of the 3R phase, but is probably due to compatibility requirements (an undistorted habit plane) imposed by the transformation mechanism, a view that has been expressed earlier[3].

Further work on ternary CuZnAl alloys is in progress[20].

The entropy contribution

An evaluation of the entropy of transformation not only serves to predict M_s temperatures when the transformation enthalpy is known, but is also useful to describe the temperature dependence of the critical stress which is necessary to induce martensite above M_s. This latter aspect has found application in the construction of heat engines[21] [22].

The entropy difference can be broken into $\Delta S = \Delta S_{vib} + \Delta S_{el} + \Delta S_{conf}$. Here ΔS_{vib} is the contribution from the lattice vibrations, ΔS_{el} the electronic component and ΔS_{conf} the configurational part. During the diffusionless martensitic transformation the configuration does not change, therefore $\Delta S_{conf} = 0$. Since the transformation occurs without volume change at a constant electron concentration and at a temperature far below the Fermi temperature ΔS_{el} can be neglected.

In the following it is attempted to calculate the transformation entropy for the binary Cu-Zn alloy in order to compare with the measurements which yielded $\Delta S = 0.31$ cal/g-atom $= 0.165\ R$[3]. It is convenient to separate ΔS into the sum of two terms

$$\Delta S = S^{\beta} - S^{M} = (S^{\beta} - S^{\alpha}_{dis}) + (S^{\alpha}_{dis} - S^{M}_{ord}). \quad (13)$$

$S^{\beta} - S^{\alpha}_{dis}$ is the entropy difference between the ordered β phase and the disordered face centered α phase and is measurable. $(S^{\alpha}_{dis} - S^{M}_{ord})$ is the remaining term. It had been shown that in martensitic Cu-Zn the stress which is necessary to transform the orthorhombic martensite into a face centered ordered lattice is temperature independent[5]. Consequently the corresponding transformation entropy $(S^{M}_{ord} - S^{\alpha}_{ord})$ is zero. It is justified therefore to replace $S^{\alpha}_{dis} - S^{M}_{ord}$ by $S^{\alpha}_{dis} - S^{\alpha}_{ord}$. Thus the influence of long range order on the entropy in the face centered lattice has to be evaluated.

In the Debye model the entropy change is related to the corresponding Debye temperatures Θ^{α}_D(ord) and Θ^{α}_D(dis) by $(S^{\alpha}_{dis} - S^{\alpha}_{ord}) = 3R \ln (\Theta^{\alpha}_D(ord)/\Theta^{\alpha}_D(dis))$. The Debye temperatures can be determined from the elastic constants c_{ik}. An approximation to calculate Θ_D from c_{ik} has been given by Blackmann for $c_{11} - c_{12} \ll c_{11}$[23] [24]:

$$\Theta_D = \frac{h}{k} c_m \left(\frac{3}{4\pi V_a}\right)^{1/3};$$

$$c_m^3 = \text{const}\,(c_{44}(c_{11} - c_{12})(c_{11} + c_{12} + 2c_{44}))^{1/2}$$

V_a the atomic volume. Thus

$$S^{\alpha}_{dis} - S^{\alpha}_{ord} = \frac{R}{2} \ln \frac{(c^{\alpha}_{44}(c^{\alpha}_{11} - c^{\alpha}_{12})(c^{\alpha}_{11} + c^{\alpha}_{12} + 2c^{\alpha}_{44}))_{ord}}{(c^{\alpha}_{44}(c^{\alpha}_{11} - c^{\alpha}_{12})(c^{\alpha}_{11} + c^{\alpha}_{12} + 2c^{\alpha}_{44}))_{dis}} \quad (14)$$

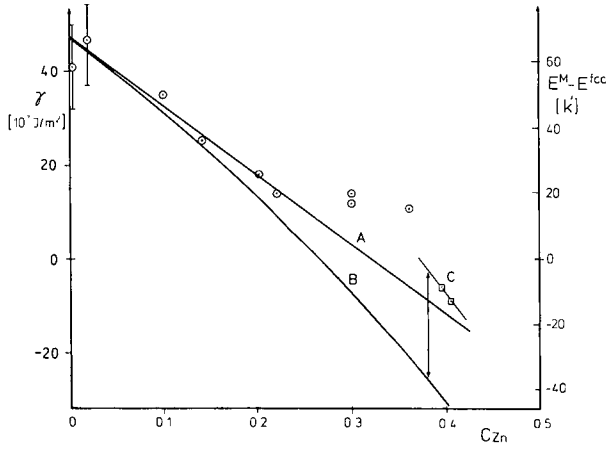

Fig. 3. Measured stacking fault energies γ for α phase Cu-Zn alloys (⊙).
Curve A: Linear extrapolation of γ-values for $c_{Zn} < 0.25$.
Curve B: Calculated order contribution to A.
Curve C: Lower limit of the energy difference between 3R and fcc martensite, deduced from measurements of the critical transformation stress. The scale in γ and $E^M - E^{fcc}$ correspond to each other.

In β brass the elastic constants have been measured through the order-disorder transformation range[25]. For the martensite phase the corresponding c_{ik} do not exist and therefore can only be deduced indirectly. In order to do this it will be assumed that long range order influences only the central force contribution of the elastic constants. Furthermore it will be postulated that the order effects can be derived from a relationship between chemical energy versus pair distance, which is structure insensitive and thus the same for the bcc and the fcc structure. In the following the effect of order on c_{ik} will be analysed first in the β phase. Subsequently the result will be applied to the fcc phase.

The influence of order on c_{ik} in the β phase:

The measured elastic constants[25]) have been plotted as a function of lattice spacings[26]) for 48.1 at.% Zn. The lattice spacing instead of the temperature has been used in order to eliminate the contribution due to the lattice parameter variation during the order-disorder transformation. It is found that disorder decreases c_{44}^{β} by 0.25 MN/cm^2 and $c_{11}^{\beta'} = c_{11}^{\beta} + c_{12}^{\beta} + 2c_{44}^{\beta}$ by 1.0 MN/cm^2.

The elastic constants can be expressed in terms of force constants[27]). In the general case two force constants α'', γ'' are needed to express the nearest neighbour contribution and two additional ones α, β for next nearest neighbours. For central forces $\alpha_{\beta}'' = \gamma_{\gamma}''$ and $\beta_{\beta} = 0$. The elastic constants are given by

$$c_{11}^{\beta} = -\frac{2}{a_{\beta}}(\alpha_{\beta}'' + \alpha_{\beta}); \; c_{44}^{\beta} = -\frac{2}{a_{\beta}}(\alpha_{\beta}'' + \beta_{\beta}); \qquad \frac{2}{a_{\beta}}(c_{12}^{B} + c_{44}^{B}) = -\frac{1}{2}\gamma_{B}'' \qquad (15)$$

Thus for central forces $c_{12}^{\beta} = c_{44}^{\beta} = 1/4\, c_{11}^{\beta'}$. The observed relationship between the change in c_{44}^{β} and $c_{11}^{\beta'}$ at the order-disorder transition is consistent with the assumption of central forces and negligible second neighbour contribution. In the ordered alloy the force constants are averages of the contributions from different atom bonds, and depend on the order parameters. Denoting by $\Delta\alpha \equiv -2\alpha_{CuZn} + \alpha_{CuCu} + \alpha_{ZnZn}$, etc., the difference in contribution from Cu-Zn and Cu-Cu, Zn-Zn bonds, a simple counting leads to $\alpha_{\beta}'' = 1/2x_{Cu}x_{Zn}\Delta\alpha''$; $\alpha_{\beta} = 1/2x_{Cu}x_{Zn}\Delta\alpha$.

In the following we set $\alpha_{\beta} = 0$, since it will not be needed for a discussion of the face centered lattice. $\Delta\alpha''$ is related to the chemical interaction energy by

$$\Delta\alpha'' = -\frac{1}{r}\frac{dw(r)}{dr} - \frac{a_{\beta}^2}{4r}\frac{d}{dr}\left(\frac{1}{r}\frac{dw(r)}{dr}\right). \qquad (16)$$

The contribution of $dw(r)/dr$ to $\Delta\alpha''$ can be neglected. This is seen by approximating $dw(r)/dr$ by the difference ratio using known first and second neighbour chemical interaction energies[10])

$$\frac{dw(r)}{dr} \cong \frac{w^{(1)}(r_1) - w^{(2)}(r_2)}{r_1 - r_2} \leqslant \frac{w^{(1)}(\text{eff}) - w^{(2)}(\text{eff})}{r_1 - r_2} \qquad (17)$$

contributing less than 13% to the $\Delta\alpha''$ value which was deduced from the experiment. This however lies within the error with which the change in c_{ik} could be determined experimentally. Therefore the change in c_{44} can be given by

$$\Delta C_{44}^{\beta} = x_{Cu}x_{Zn}\frac{a_{\beta}}{4r_1^2}\frac{d^2w(r_1)}{dr^2} \qquad (18)$$

The influence of order in the martensite

The same equations can now be derived for the face centered structure α taking into account only nearest neighbour central force constants[27]):

$$\Delta c_{44}^{\alpha} = \Delta(c_{11}^{\alpha} - c_{12}^{\alpha}) = \frac{1}{4}\Delta(c_{11}^{\alpha} + c_{12}^{\alpha} + 2c_{44}^{\alpha}) = -\frac{1}{3a_{\alpha}}\Delta\beta_{\alpha}'\, x_{Cu}x_{Zn} \qquad (19)$$

$\Delta\beta_{\alpha}'$ is the nearest neighbour force constant in the α phase, and is related to $w(r)$ by

$$\Delta\beta_{\alpha}' = -\frac{1}{r}\frac{dw(r)}{dr} - \frac{a_{\alpha}^2}{4r}\frac{d}{dr}\left(\frac{1}{r}\frac{dw(r)}{dr}\right) \qquad (20)$$

Neglecting again the term in $dw(r)/dr$, we obtain finally for Δc_{44}^{α}: $\Delta c_{44}^{\alpha} = a_{\alpha}/3a_{\beta}\,\Delta c_{44}^{\beta} = 0.4\,\Delta c_{44}^{\beta}$.

Δc_{44}^{β} for 48.1 at.% Zn was 0.25 MN/cm^2, for different concentrations we get then:

$$\Delta c_{44}^{\beta}(c_{Zn}) = \Delta c_{44}^{\beta}(48.1\text{ at.\%})\frac{x_{Cu}(c_{Zn})x_{Zn}(c_{Zn})}{x_{Cu}(48.1)x_{Zn}(48.1)}. \qquad (21)$$

For maximum long range order $x_{Cu} = -x_{Zn} = c_{Zn}$ and $\Delta c_{44}^{\beta} = 1 \cdot c_{Zn}^2$ (MN/cm^2). Thus $\Delta c_{44}^{\alpha} = 0.4\, c_{Zn}^2$ (MN/cm^2). The elastic constants of the α phase at 40 at.% Zn are obtained by extrapolating measured α phase values (in MN/cm^2): $c_{44}^{\alpha} = 7.1$; $c_{11}^{\alpha} - c_{12}^{\alpha} = 3.0$; $c_{11}^{\alpha} + c_{12}^{\alpha} + 2c_{44}^{\alpha} = 37.1$. Using these values we obtain for the entropy change on disordering in a Cu-40 at.% Zn fcc alloy: $S_{dis}^{\alpha} - S_{ord}^{\alpha} = 0.037$ cal/g-atom K $= 0.019$ R.

Comparing this value with the observed entropy change during the martensitic transformation, $S^{\beta} - S^{M} = 0.165$ R[3]), it can be concluded that order in the martensite affects the transformation entropy negligibly and therefore $S^{\beta} - S^{M}$ is approximately the same as that between the equilibrium β and α phases: $S^{\beta} - S^{M} \cong S^{\beta} - S^{\alpha}$.

This result is in complete agreement with the observation that $S^{\beta} - S^{M}$ does not depend or depends little on composition in Cu-Zn and CuZnAl in spite of the large influence of composition on order.

The evaluation of $S^{\beta} - S^{\alpha}$ is difficult due to the small difference in Debye temperatures for both phases. Debye temperatures have been determined from specific heat measurements at low temperatures for various α and β phase compositions of binary Cu-Zn[28]) [29]). Extrapolation to $c_{Zn} = 0.4$ yield a low temperature of $\Theta_D = 299 \pm 3$ K for the α phase and $\Theta_D = 265 \pm 3$ K for the ordered β phase. For the Debye model an entropy difference of $S^{\beta} - S^{\alpha} = 3$ R ln $(\Theta_D^{\alpha}/\Theta_D^{\beta}) = 0.36$ R is thus obtained from the low temperature Debye temperatures. Though this value is of the correct order of magnitude it is higher by a factor of two. It is known that Debye temperatures depend on temperature and on the physical quantities from which they are evaluated at higher temperatures. In order to derive more reliable transformation entropies calorimetric data are therefore required.

Summary

The enthalpy difference between the high temperature bcc β phase and the martensite, and between the orthorhombic 3R martensite and the stress induced fcc phase has been calculated and compared with experimental results for binary Cu-Zn and some ternary Cu-Zn based alloys. In addition, the entropy difference ΔS between β and martensite has been estimated.

It is shown that the enthalpy difference $E^{\beta} - E^{M}$ between β and martensite is mainly due to long range order contribution from fourth nearest neighbour atom pairs in the martensite phase.

The fourth neighbour chemical pair interaction energy $m_{CuX}^{(4)}$ of Cu with third elements X of small concentrations in Cu-Zn matrix has been related to their influence on the transformation enthalpy $E^{\beta} - E^{M}$. It has been shown that

a correlation exists between $E^{\beta} - E^{M}$ (and thus $m^{(4)}_{CuX}$) and the change in lattice spacing in the α phase fcc pure Cu matrix due to small additions of X.

The concentration dependence of the stress which is necessary to induce an fcc ordered phase in a martensitic single crystal has also been analysed. It is shown that the addition of the long range order contribution from fourth neighbours to the measured and extrapolated stacking fault energies in the disordered fcc α Cu-Zn phase can reproduce the measured concentration dependence of the critical stress.

It is shown that long range order has a negligible effect on the transformation entropy ΔS, in agreement with the observed insensitivity of ΔS against changes of long range order.

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