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THE INFLUENCE OF SHORT-RANGE DISORDER ON THE MARTENSITIC TRANSFORMATION IN Cu–Zn AND Cu–Zn–Al ALLOYS

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Abstract—The transformation temperature, M_s in Cu–Zn and Cu–Zn–Al alloys is changed by quenching from temperatures, $T_Q > M_s$. In Cu–Zn the quench from T_Q leads to an increase in M_s, whereas in Cu–Zn–Al, M_s is lowered compared to samples that are slowly cooled or have been aged at room temperature after the quench. The effect is ascribed to quenched-in disordered atom pairs in the long-range ordered matrix. The formation energies for disordered pairs have been calculated, and it is shown that in Cu–Zn nearest-neighbour pairs increase M_s, whereas in Cu–Zn–Al mainly Cu–Zn next-nearest-neighbour pairs control the change in M_s.

Résumé—On fait varier la température de transformation M_s dans Cu–Zn et Cu–Zn–Al en trempant à partir de températures $T_Q > M_s$. Dans Cu–Zn, la trempe à partir de T_Q produit une augmentation de M_s, alors que dans Cu–Zn–Al, M_s est abaissée par rapport aux échantillons refroidis lentement ou vieillis à l'ambiante après la trempe. Nous attribuons cet effet à des paires d'atomes trempées dans l'état désordonné, dans la matrice ordonnée à longue distance. Nous avons calculé les énergies de formation des paires désordonnées et montré que dans Cu–Zn les paires de premiers voisins augmentent M_s, alors que dans Cu–Zu–Al, ce sont essentiellement les paires Cu–Zn de seconds voisins qui contrôlent les variations de M_s.

Zusammenfassung—Die Umwandlungstemperatur M_s in den Legierungen Cu–Zn und Cu–Zn–Al wird durch Abschrecken von Temperaturen $T_Q > M_s$ verändert. In Cu–Zn führt Abschrecken von T_Q aus zu einem Anstieg in M_s, wohingegen M_s in Cu–Zn–Al, verglichen mit langsam abgekühlten oder bei Raumtemperatur nach dem Abschrecken ausgelagerten Proben, erniedrigt wird. Der Effekt wird entordneten, in die ferngeordnete Matrix eingeschreckten Atompaaren zugeschrieben. Die Bildungsenergien entordneter Paare wurden berechnet; es wird gezeigt, daß in Cu–Zn Paare nächster Nachbarn M_s erhöhen, in Cu–Zn–Al dagegen Cu–Zn-nächste Nachbarn die Änderung von M_s kontrollieren.

1. INTRODUCTION

In noble metal alloys the martensitic transformation is well characterized by the temperatures M_s, M_f, A_s and A_f. M_s and M_f are the temperatures for the beginning and completion of the martensitic transformation on cooling from the β phase, while A_s and A_f are the corresponding temperatures on reheating from the martensite phase. These transformation temperatures are changed by mechanical stresses. The critical stress $\sigma_T^{\beta\to M}$ which is necessary in order to induce the martensite and the temperature dependence of $\sigma_T^{\beta\to M}$ are further important parameters which are related to the entropy of transformation. A study of the factors that may influence these parameters is of interest, not only to better understand the underlying transformation mechanisms, but also to evaluate the conditions under which the properties of these materials are changed, an aspect which is important for their technological applications.

In an earlier paper [1] it had been shown that it is possible to change M_s and the stress $\sigma_T^{\beta\to M}$ in single crystuls of Cu–Zn–Al by a previous short-time heating ('flash heating') to 300°C followed by a rapid quench. However, on ageing at room temperature the stress $\sigma_T^{\beta\to M}$ again decreased to its normal value. Subsequently it was found [3] that M_s can be changed not only by flash heating but also by a longer time anneal at temperatures T_Q above room temperature, followed by a rapid quench.

The relationship between changes in the transformation temperature M_s and the annealing temperature T_Q have now been studied in more detail in Cu–Zn and Cu–Zn–Al single crystals. The results are reported in this paper and an interpretation is given in terms of quenched-in short-range disorder in a matrix that is essentially long-range ordered.

2. EXPERIMENTAL METHODS

The ternary Cu–Zn–Al alloy composition was Cu–20 at.% Zn–14 at.% Al. The selection was based on requiring an M_s temperature in the experimentally accessible range ($M_s = 180$ K for the present alloy) and on getting single-phase alloys which do not decompose on thermal treatments, thus limiting the composition to an electron concentration near 1.48. In addition a Cu–39.1 at.% Zn alloy with $M_s = 146$ K was studied. Both alloys were prepared by melting 99.99% pure metals in sealed quartz tubes with an

argon atmosphere. Single crystals were grown in sealed quartz tubes in the usual way by the Bridgman method. Subsequently these single crystals were spark-machined into cylindrical samples of 50 mm length and 2.5 mm dia, and annealed at 850°C for 24 h prior to all further treatments. All treatments of the ternary alloys were performed in air, since it had been shown that the zinc loss is negligible. The binary β Cu–Zn alloys, however, had to be encapsulated for each heat treatment due to the rapid loss of Zn at higher temperatures.

The influence of the heat treatment was followed by measuring changes in the electrical resistivity in the β phase at 0°C and by determining the transformation temperatures, also by electrical resistivity.

3. EXPERIMENTAL RESULTS

The temperatures M_s, M_f and A_f were determined immediately after quenching from the temperature T_Q. After each transformation the sample was reheated to 700°C prior to the next heat treatment at T_Q. This annealing process is essential in order to eliminate the effects of the martensitic transformation on the β phase [2]. The M_s temperatures that are measured after quenching from T_Q depend on T_Q and are different from those obtained after slow cooling. If, however, the specimen is annealed at 0°C (i.e. above M_s) after being quenched from T_Q, M_s depends on ageing time and converges to a value $M_s(0)$ which is independent of T_Q for quenches below $T_Q = 200$°C, and is identical to the M_s value for slowly cooled samples. For quenches from higher temperatures $T_Q > 200$°C, asymptotic values of M_s which differ by less than 4 K are found. The variation of M_s $(T_Q) - M_s(0)$ vs T_Q is shown in Fig. 1 for the Cu–Zn–Al alloy and in Fig. 2 for the binary Cu–Zn. It is found that by quenching from T_Q, M_s is depressed in Cu–Zn–Al but is increased in Cu–Zn, though to a smaller extent. It has also been verified that other Cu–Zn–Al alloys with $e/a = 1.48$ and M_s between 100 and 300 K showed the same effect. The change in M_s is independent of the number of the previous reheating and quenching cycles.

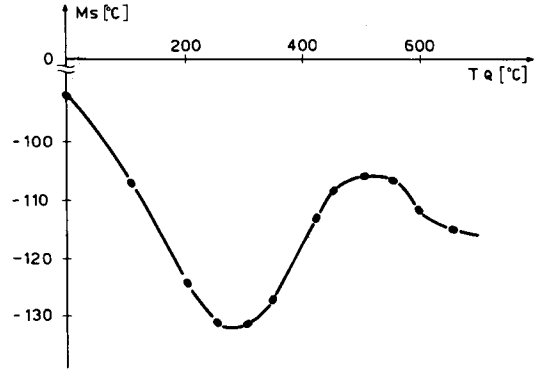

Fig. 1. Change of M_s temperature as a function of quenching temperature T_Q for Cu–20 at.% Zn–14 at.% Al.

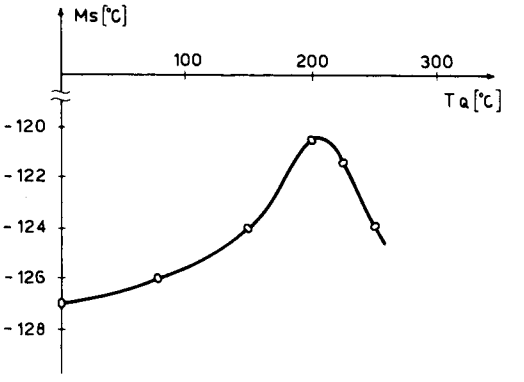

Fig. 2. Change of M_s after quench from T_Q for Cu–39.1 at.% Zn.

In previous publications [3, 6] the electrical resistivity measured at 0°C in the β phase has been found to show a similar dependence on the quenching temperature, although for both alloys this parameter increases by quenching. In Fig. 3 the difference $\rho(T_Q) - \rho(0)$ between the resistivity of the quenched ternary alloy and that after a long-time anneal at 0°C is plotted vs M_s $(T_Q) - M_s$ (0) for a T_Q range that spreads from room temperature to 660°C. The close relationship between the two parameters is evident. Within experimental scatter the temperatures M_f, A_s and A_f shift by the same amount as M_s, implying that the hysteresis is not changed by a quench from T_Q.

Transmission electron microscopic (TEM) studies have determined the time at which precipitates start

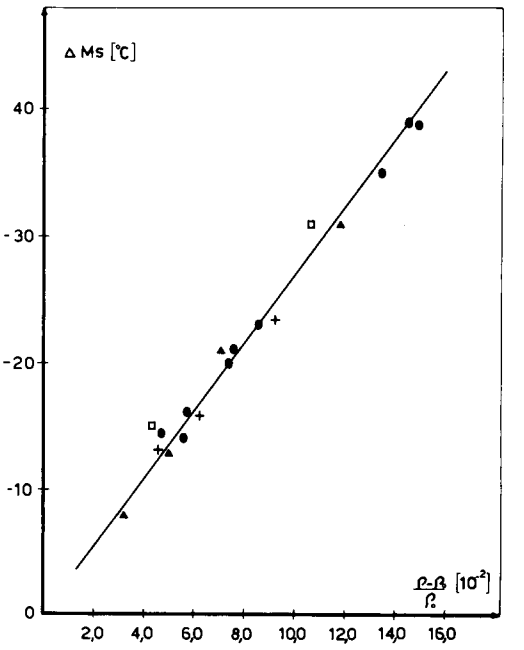

Fig. 3. Difference ΔM_s between M_s after quench from T_Q and after slow cooling to 0°C vs the corresponding change in resistivity for three Cu–Zn–Al samples of the same composition:

$T_Q \leqslant 200$°C (▲, □, ●) and $T_Q \geqslant 260$°C (+).

to be visible in the alloys at a given T_Q temperature [3]. For the present alloys the annealing times at T_Q are considerably shorter than the time for precipitation to start. This should preclude the appearance of new phases during the heat treatment at T_Q.

Some electrical resistivity measurements in the β phase Cu–Zn–Al have been made in addition to those reported in [3]. Samples were quenched from various $T_Q \leqslant 200°C$ to 0°C, and the increase in resistivity $\rho(T_Q) - \rho(0)$ was determined at 0°C. The $\rho(0)$ obtained after prolonged annealing at 0°C was independent of T_Q and agreed with the value obtained when the sample was slowly cooled from higher temperatures. However, when the sample had been quenched from a T_Q above the T_{DO_3} temperature, where ordering in next-nearest-neighbours to a DO_3 structure occurs [4], $\rho(0)$ after a 0°C anneal remained somewhat higher ($\Delta\rho = 3.10^{-7}\,\Omega$ cm) than the value for the slowly cooled sample. By TEM it was found [4] that samples quenched from above T_{DO_3} had a domain size of a few hundred Ångstrom whereas quenching from below T_{DO_3} resulted in considerably larger domains of 0.1 μ. During ageing at 0°C the domain size did not change. Thus domain boundaries have a negligible effect on ρ and M_s.

For specimens quenched from $T_Q \leqslant 170°C$ the quench velocity was not critical. This was tested by keeping the samples a few seconds in air before submerging them in water at 0°C. In all cases $\rho(T_Q)$ remained the same within the experimental scatter. Of course this result does not rule out the existence of an additional component which anneals out very rapidly. For $T_Q > 170°C$ the quenching velocity becomes increasingly important [6, 7] and quantitative evaluations become less reliable, unless the quenching velocities are measured precisely. For this reason results for T_Q below 200°C will be considered for the discussion that follows. In Fig. 4 is shown $\Delta\rho = \rho(T_Q) - \rho(0)$ for Cu–Zn–Al as a function of $1/T_Q$ in a semilogarithmic plot. The results of Fig. 4 can be described by a linear relationship with a slope of

$$Q_F^{\beta} = \mathrm{d}\ln\{\rho(T_Q) - \rho(0)\}/\mathrm{d}(1/T) = (1500 \pm 100)k,$$

where $k = 13.8 \times 10^{-24}$ J is the Boltzmann constant multiplied by 1 K.

4. DISCUSSION

The change in the M_s temperature after quenching from T_Q below 200°C is due to a change in the difference of the internal energy $\Delta H = H_\beta - H_M$ between the β phase and the martensite M, because neither the hysteresis given by $A_f - M_s$ nor the entropy difference $\Delta S = S_\beta - S_M$ between the two phases is affected by quenches from $T_Q < 200°C$. The latter result had been obtained by measuring the critical stress $\sigma_T^{\beta\to M}$ as a function of temperature for various T_Q [1].

The effect of quenching can either be due to changes in ΔH related to domain boundaries or to energy changes inside the ordered domains. It is unlikely that domain boundaries contribute significantly, for the following reasons: a large change in domain boundary area produces only small changes in M_s for ternary Cu–Zn–Al alloys after ageing at 0°C. In binary Cu–Zn the domain size after quenching from below T_{B_2} is so large that the increase of M_s with rising $T_Q < 200°C$ cannot be due to domain boundaries. Finally, the linear relationship between ΔM_s and $(\rho - \rho_0)/\rho_0$ of Fig. 3 is independent of T_Q, i.e. independent of the domain size, serving as a further indication that quenching effects change the properties within the domains. The fact that quenching effects anneal out at such low temperatures as 0°C suggests that only defects of atomic size can be responsible for the ageing effects in M_s and ρ. The most reasonable choice is quenched in short-range disorder in a long-range ordered matrix [3, 6]. For $T_Q < 200°C$ it will be shown later that the amount of quenched-in disorder is small and therefore it is possible to describe it approximately by non-interacting disordered pairs which are obtained from the long-range ordered matrix by interchanging the corresponding atom pairs.

The martensitic transformation is diffusionless and therefore the martensite inherits the disorder from the

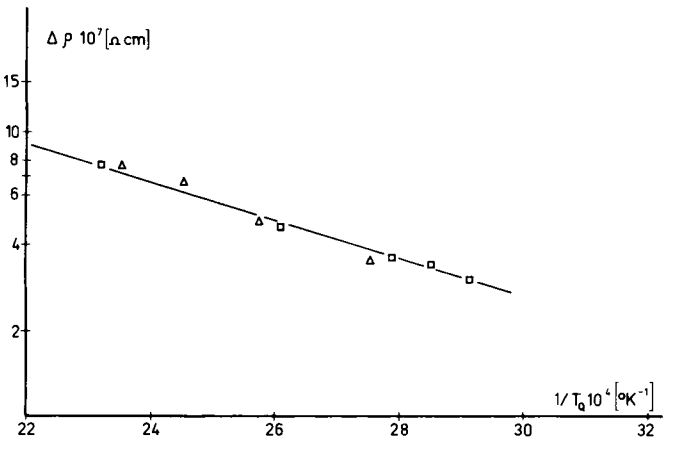

Fig. 4. Resistivity change referred to the resistivity at 0°C vs $1/T_Q$, where T_Q is the quench temperature.

β phase. Hence, for an evaluation of the enthalpy change on transformation it is necessary to evaluate the concentration of disordered pairs in the β phase and to determine the energy change of each pair during the transformation.

4.1 *Short-range disorder in the binary β phase Cu–Zn*

Clark and Brown [6] have measured the resistivity change $\rho(T_Q) - \rho(0) \equiv \Delta\rho$ for Cu–48.5 at.% Zn after quenching from various T_Q. They found that $\rho(T_Q)$ increases with T_Q for $T_Q \leqslant 230°C$, and obtain a 'formation energy' $Q_F^\beta = 0.31$–0.34 eV (i.e. $3.8 \times 10^3 k$–$4.1 \times 10^3 k$). They analyse their results in terms of single nearest-neighbour disordered Cu–Zn pairs in the long-range ordered matrix and calculate the formation energy for pairs by taking into account only nearest-neighbour interactions between atoms, and by estimating the corresponding chemical interaction energies from the ordering temperature in Cu–Zn they get a formation energy for pairs of 0.22 eV ($2.6 \times 10^3\, k$) which is considerably lower than the experimental value. The calculations can be improved if next-nearest-neighbour interactions are included and if the chemical interaction energies are used which have been determined recently by Inden [8]. The value of the formation energy for pairs E_F^β in this approximation is deduced as follows: the chemical interaction energy between atom A and B is defined as

$$w_{AB}^{(i)} = -2W_{AB}^{(i)} + W_{AA}^{(i)} + W_{BB}^{(i)},$$

where $W_{AB}^{(i)}$, $W_{AA}^{(i)}$ and $W_{BB}^{(i)}$ are the bond energies for AB, AA and BB atom pairs in next-neighbour ('nn', $i = 1$) or next-nearest neighbour ('nnn', $i = 2$) position, respectively. If p_{Cu}^{I} is the probability of having a Cu atom in the Cu-rich sublattice (for complete long-range order $p_{Cu}^{I} = 1$, if the concentration $C_{Zn} \leqslant 0.5$), the internal energy of a given atom distribution can be calculated by counting the number of bonds and multiplying them by the corresponding bond energies. This is the basis of the Bragg–Williams–Gorski model, which describes long-range order [8].

In the present case only the change in nn and nnn has to be considered. Doing this the formation energy of a wrong pair, obtained by an interchange of a nn Cu–Zn atom pair, is

$$E_F^\beta = (14\, w_{CuZn}^{(1)} - 12\, w_{CuZn}^{(2)})(p_{Cu}^{I} - 1 + C_{Zn}).$$

From [8] $w_{CuZn}^{(1)} = 955k$, $w_{CuZn}^{(2)} = 535k$, and if complete long-range order $P_{Cu}^{I} = 1$ is assumed, a formation energy for pairs of $E_F^\beta = 6950$ K. $C_{Zn} = 3370k = 0.29$ eV for Cu–48.5 at.% Zn is obtained. E_F^β depends on the temperature through P_{Cu}^{I} which decreases when T_Q approaches the order–disorder temperature T_{B2}. The decrease in E_F^β leads to a stronger increase in the number of disordered pairs than if E_F^β were constant. This can be seen as follows: the number of pairs n is proportional to $\exp(-E_F^\beta(T)/k_BT)$; the derivative of ln n with respect to $1/T$,

$$(\mathrm{d} \ln n/\mathrm{d}1/T) = (-E_F^\beta(T)/k_B) - \mathrm{d}E_F^\beta(T)/k_BT\, \mathrm{d}(1/T)$$

has an additional term that is due to the temperature dependent $E_F^\beta(T)$. Since E_F^β decreases with increasing temperature, $\mathrm{d}E_F^\beta(T)/\mathrm{d}(1/T) > 0$ and $|\mathrm{d} \ln n/\mathrm{d}(1/T)| > E_F^\beta(T)/k_B$. Far below the order–disorder temperature P_{Cu}^{I} is close to 1 and better approximations than the Bragg–Williams–Gorski model are required to obtain the value that has to be added to the calculated E_F^β in order to compare with measured Q_F. It is possible that this factor accounts for the small discrepancy between $E_F^\beta = 0.29$ eV and $Q_F = 0.31$–0.34 eV measured by Clark and Brown [6]. A second point has to be kept in mind: the difference $\Delta\rho = \rho(T_Q) - \rho(0)$ has been measured. If the correct contribution of the disordered pairs at 0°C had been added, the slope (in the semilogarithmic plot) would have been smaller. This contribution can be neglected for Cu–Zn because E_F^β is sufficiently high but becomes important for the ternary alloys with the lower E_F^β, as will be shown later. There is thus some confidence that the resistivity changes are due to isolated disordered nearest-neighbour Cu–Zn atoms, whose formation energy can be calculated from known chemical interaction energies.

4.2 *Short-range disorder in the ternary β phase Cu–Zn–Al alloys*

In the ternary alloys, ordering to a B2 and at lower temperatures to a DO_3 structure has been observed [4]. For the alloys used in the present investigation the B2 and DO_3 ordering temperatures are at 810 and 580 K, respectively. The evaluation of short-range disorder in the ternary alloys is more complex than in β phase Cu–Zn due to the larger numbers of pair combinations. In addition, atom interchanges between nnn positions have to be considered. As for Cu–Zn, it will be assumed that isolated wrong atom pairs exist in equilibrium in the long-range ordered matrix. This is a useful first approximation, which may become unreliable when the temperature gets close to the ordering temperature.

Long-range order in the ternary alloys is described with reference to a lattice which is divided into four sublattices I–IV, as shown in Fig. 5. In each of the four sublattices J, the occupation possibility P_A^J of having an atom A on its site is independent of the position on the sublattice. The P_A^J that corresponds to the maximum degree of long-range order in an alloy with Cu concentration $C_{Cu} > 0.5$, which are of interest here, are:

$$p_{Cu}^{I} = p_{Cu}^{II} = 1 \quad p_{Al}^{III} = p_{Cu}^{IV} = 0,$$

$$p_{Cu}^{III} = 4C_{Cu} - 2 \quad p_{Al}^{IV} = 4C_{Al}.$$

Several p_A^J are zero for perfect long-range order and can be expected to remain small at temperatures sufficiently below the order–disorder temperatures. Their contribution therefore will be neglected in the following discussion. Six disordered atom pairs are then

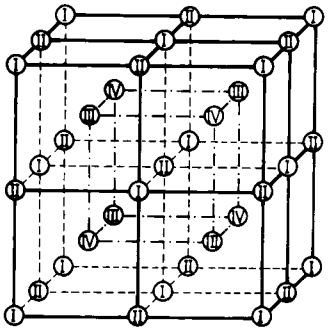

Fig. 5. Schematic drawing of the β phase lattice denoting by I–IV the four different sublattices.

considered and are listed together with their calculated formation energies. The atoms of the pairs are labelled by the sublattice on which they would be positioned in a perfectly ordered lattice, and whether they are nn or nnn pairs:

$$E_F^\beta(\text{nn Al}^{\text{IV}}\text{Cu}^{\text{I}}) = (w_{\text{CuZn}}^{(1)} + w_{\text{CuAl}}^{(1)} - w_{\text{ZnAl}}^{(1)}) \times (2p_{\text{Zn}}^{\text{III}} + 1.5p_{\text{Zn}}^{\text{IV}}) + 2w_{\text{CuAl}}^{(1)}(2p_{\text{Al}}^{\text{III}} + 1.5p_{\text{Al}}^{\text{IV}}) - 3(w_{\text{CuZn}}^{(2)} + w_{\text{CuAl}}^{(2)} - w_{\text{AlZn}}^{(2)})p_{\text{Zn}}^{\text{III}} - 6w_{\text{CuAl}}^{(2)}p_{\text{Al}}^{\text{III}}.$$

The formation energies for nn $Zn^{IV}Cu^{I}$ and $Zn^{III}Cu^{I}$ are obtained by interchanging the corresponding labels.

$$E_F^\beta(\text{nnn Zn}^{\text{IV}}\text{Cu}^{\text{III}}) = -5(w_{\text{CuZn}}^{(2)} + w_{\text{CuAl}}^{(2)} - Z_{\text{Zn}}w_{\text{AlZn}}^{(2)})Z_{\text{Al}} - 10w_{\text{CuZn}}^{(2)}$$

and correspondingly for nnn $Al^{IV}Cu^{III}$ and $Al^{IV}Zn^{III}$. The abbreviation $Z_A = \frac{1}{2}(p_A^{III} - p_A^{IV})$ has been used. The chemical interaction energies are listed in the table:

$w_{AB}^{(i)}$	CuZn	CuAl	AlZn
nn	$955k$	$(1345 \pm 25)k$	$(-50 \pm 100)k$
nnn	$535k$	$(825 \pm 15)k$	$(200 \pm 100)k$
Ref.	(8)	(4)	(4)

For the alloys with $M_s = 180$ K the following numerical values for the formation energies E_F^β are obtained (in units of 10^3k):

$Al^{IV}Cu^{I}$	$Zn^{IV}Cu^{I}$	$Zn^{III}Cu^{I}$	$Al^{IV}Cu^{III}$	$Zn^{IV}Cu^{III}$	$Al^{IV}Zn^{III}$
4.3 ± 0.2	3.5 ± 0.1	2.0 ± 0.1	2.6 ± 0.1	1.8 ± 0.2	0.7 ± 0.3

The calculations show that nn $Al^{IV}Cu^{I}$ and nn $Zn^{IV}Cu^{I}$ pairs have higher formation energies, and therefore are present only in negligible concentrations. On the other hand the nn $Al^{IV}Zn^{III}$ have a small energy of formation, whose value is quite uncertain, since mainly $w_{AlZn}^{(2)}$ contributes. The remaining pairs have similar values for the formation energies.

The predictions can be compared with the measurements summarized in Fig. 4. As has been discussed above, two points have to be kept in mind: first, only the difference $\Delta\rho \equiv \rho(T_Q) - \rho(0)$ can be measured and, second, the real formation energy E_F^β is in itself a function of temperature through the temperature-dependent long-range occupation probabilities p_A^i. For the pairs considered here E_F^β decreases with increasing temperature (except nn $Zn^{III}Cu^{I}$ pairs, whose E_F^β has been found to increase with temperature). Consequently the E_F^β are smaller than the Q_F deduced from the slope of the experimental curves. Comparing the experimental value of $Q_F = (1500 \pm 100)k$ with the calculations, it can be stated at this point that nn $Zn^{III}Cu^{I}$ and the nnn pairs can contribute to the resistivity change $\Delta\rho$. It will be shown later that of all the pairs the $Zn^{IV}Cu^{III}$ pairs are the most important in changing M_s.

4.3 *The influence of short-range disorder on the martensitic transformation*

The concentration of the disordered pairs is not changed during the transformation and is given by

$$n_{AB}^{(i)} = n_{AB}^{(i)}(0)\exp - E_F^\beta(A,B)/k_BT_Q,$$

where $n_{AB}^{(i)}(0)$ is the concentration of possible pair sites for nn ($i = 1$) or nnn ($i = 2$) interchanges of atoms A and B. $E_F^\beta(A,B)$ is the corresponding formation energy in the β phase. Due to the change in the crystal structure the energy of a disordered pair in general will be altered during the transformation.

If $\Delta E = E_F^\beta(A,B) - E_F^M(A,B)$ is the difference in the formation energy of a pair (A, B) between the two phases, then the change in internal energy is given by

$$\delta\Delta H = \sum_{A,B}[E_F^\beta(A,B) - E_F^M(A,B)]n_{AB}^{(i)}(0) \times \exp - E_F^\beta(A,B)/k_BT_Q.$$

The corresponding variation in M_s is $\delta M_s(T_Q) = \delta\Delta H/\Delta S$ (the sum is over all possible disordered pairs). The difference in M_s between a sample quenched from T_Q and slowly cooled to 0°C is then $\Delta M_s \equiv \delta M_s(T_Q) - \delta M_S(0°C)$. The observation that ΔM_s and $\rho(T_Q) - \rho(0)$ are proportional among themselves indicates that the same type of pairs are responsible for the resistivity changes and for ΔM_s. Therefore the results from the previous two paragraphs allow us to evaluate E_F^β.

The differences in pair formation energy $\Delta E_F \equiv E_F^\beta - E_F^M$ between the two phases have been calculated and are listed below. In the close-packed martensite structure nnn atom distances are considerably larger than nn distances, and the nn contribution to the pair

formation energies is expected to dominate E_F^M. Therefore chemical interaction energies between more distant nn neighbours for martensite have been neglected. If it is assumed that the interaction energies depend only on the distance between atoms and not on the crystal structure, then they should not be very different in the two phases, since the interatomic distances are only 2–3% larger in the martensite than in β. Equating the nn chemical interaction energies in the martensite with that of the β phase value $w_{AB}^{(i)}$, the following ΔE_F are obtained:

$$\Delta E_F(\mathrm{CuZn}) = (4w_{\mathrm{CuZn}}^{(1)} - 6w_{\mathrm{CuZn}}^{(2)})(p_{\mathrm{Cu}}^{\mathrm{I}} - 1 + 2C_{\mathrm{Zn}}).$$

For the ternary Cu–Al–Zn alloys, using the same labelling as before, one gets for the nn $\mathrm{Al^{IV}Cu^{I}}$ pair:

$$\begin{aligned}\Delta E_F(\mathrm{nn\ Al^{IV}Cu^{I}}) = (&2w_{\mathrm{CuZn}}^{(1)} - 3w_{\mathrm{CuZn}}^{(2)} \\ &+ 2w_{\mathrm{CuAl}}^{(1)} - 3w_{\mathrm{CuAl}}^{(2)} - 2w_{\mathrm{AlZn}}^{(1)} \\ &+ 3w_{\mathrm{AlZn}}^{(2)})p_{\mathrm{Zn}}^{\mathrm{III}} + 2(2w_{\mathrm{CuAl}}^{(1)} \\ &- 3w_{\mathrm{CuAl}}^{(2)})p_{\mathrm{Al}}^{\mathrm{III}}.\end{aligned}$$

An nnn pair in the β phase can transform to two different nnn pairs in the martensite, depending on whether the pair has its elongation parallel to the Bain axis or normal to it. The Bain axis is the $\langle 100\rangle_\beta$ direction in the β phase, which transforms into a $\langle 100\rangle_M$ direction of an f.c.c. martensite. Therefore the nnn pairs are labelled by the additional symbol N and P for pairs normal and parallel to the Bain axis, respectively:

$$\begin{aligned}\Delta E_F(\mathrm{nnn\ Zn^{IV}Cu^{III}}, N) = (&3w_{\mathrm{CuZn}}^{(1)} - 5w_{\mathrm{CuZn}}^{(2)} \\ &+ 3w_{\mathrm{CuAl}}^{(1)} - 5w_{\mathrm{CuAl}}^{(2)} \\ &- 3w_{\mathrm{AlZn}}^{(1)} + 5w_{\mathrm{AlZn}}^{(2)})Z_{\mathrm{Al}} \\ &+ 2(3w_{\mathrm{CuZn}}^{(1)} - 5w_{\mathrm{CuZn}}^{(2)})Z_{\mathrm{Zn}},\end{aligned}$$

$$\begin{aligned}\Delta E_F(\mathrm{nnn\ Zn^{IV}Cu^{III}}, P) = (&4w_{\mathrm{CuZn}}^{(1)} - 5w_{\mathrm{CuZn}}^{(2)} \\ &+ 4w_{\mathrm{CuAl}}^{(1)} - 5w_{\mathrm{CuAl}}^{(2)} \\ &- 4w_{\mathrm{AlZn}}^{(1)} + 5w_{\mathrm{AlZn}}^{(2)})Z_{\mathrm{Al}} \\ &+ (8w_{\mathrm{CuZn}}^{(1)} - 10w_{\mathrm{CuZn}}^{(2)})Z_{\mathrm{Zn}}.\end{aligned}$$

The ΔE_F for the other pairs are obtained by interchanging the labels correspondingly.

Specifically for binary CuZn ($M_s = 146$ K) in its long-range ordered state $p_{\mathrm{Cu}}^{\mathrm{I}} = 1$ we get $\Delta E_F(\mathrm{CuZn}) = 480\,k$. For the CuZnAl with $M_s = 180\,k$ the values are listed in the following table in units of k:

$\mathrm{Al^{IV}Cu^{I}}$	$\mathrm{Zn^{IV}Cu^{I}}$	$\mathrm{Zn^{III}Cu^{I}}$		$\mathrm{Al^{IV}Cu^{III}}$	$\mathrm{Zn^{IV}Cu^{III}}$	$\mathrm{Zn^{III}Al^{IV}}$
430 ± 130	220	950 ± 200	N	0 ± 65	−365 ± 170	365 ± 380
			P	−850 ± 75	−1100 ± 190	250 ± 420

The error limits have been calculated using the errors of the measured interaction energies $w_{\mathrm{CuAl}}^{(1)}$ and $w_{\mathrm{AlZn}}^{(4)}$ [4]. Since the error for $w_{\mathrm{CuZn}}^{(1)}$ is not known, it has been set to zero. In the formulas for ΔE_F enter the differences $2w_{AB}^{(1)} - 3w_{AB}^{(2)}$ for nn pairs, and $3w_{AB}^{(1)} - 5w_{AB}^{(2)}$ or $4w_{AB}^{(1)} - 5w_{AB}^{(2)}$ for nnn pairs. These are small quantities and consequently the resulting numerical values for ΔE_F have a long range of uncertainty. However, when comparing ΔE_F of the different pairs, one feature becomes evident: nearest-neighbour disordered pairs always have a lower formation energy in the martensite than in the β phase, whereas next-nearest-neighbour CuZn and CuAl pairs have a negative ΔE_F and thus a higher formation energy in the martensite.

The comparison with experimental results of Figs. 1–3 permits the following conclusions: the sign of the change in M_s temperature with T_Q is determined by the sign of ΔE_F. In binary Cu–Zn, M_s increases with $T_Q \leqslant 200$°C, in agreement with the predictions of a positive ΔE_F for nearest-neighbour pairs. The maximum change in M_s is about 6°C; this small effect is due to the high formation energy E_F in CuZn, which keeps the concentration of disordered pairs low. From the experimentally determined ΔM_s and an appropriate value for E_F^β, a ΔE_F can be deduced which can be compared with the calculated ΔE_F from above. Using the theoretical $E_F^\beta = 2720k$ for Cu–39.14 at.% Zn which had been calculated before, $\Delta E_F = (800 \pm 100)k$ is obtained, which agrees within a factor of two with the theoretical $\Delta E_F = 480k$. However, if the Q_F measured by Clark and Brown for Cu–48.5 at.% Zn are inserted for E_F^β, taking into account a correction corresponding to the different composition resulting in $2900k \leqslant E_F^\beta \leqslant 3200k$, a ΔE_F between $1200k$ and $2200k$ is deduced from the measured ΔM_s. This shows that the ΔE_F values are very sensitive to the exact E_F^β. As has been discussed before, the T_Q dependence of the electrical resistivity gives a Q_F that is only an upper limit to the real E_F^β. This would explain the better agreement in ΔE_F for the calculated E_F^β than for the measured Q_F.

In the ternary alloy a decrease of M_s by some 40°C for $T_Q \leqslant 200$°C is observed (Fig. 1). A decrease in M_s is predicted only for next-nearest-neighbour CuAl and CuZn pairs, indicating that the concentration of nnn pairs that are quenched from T_Q control the change in M_s. The calculations suggest that the contribution from nnn $\mathrm{Cu^{III}Zn^{IV}}$ pairs is larger than that from the nnn $\mathrm{Cu^{III}Al^{IV}}$ pairs, since ΔE_F is smaller and E_F^β is larger for the latter. This is further supported by the close relationship between ΔM_s and $\Delta\rho$ (Fig. 3), which is independent of T_Q. If different pair types were present in comparable amounts, their contributions to the electrical resistivity and to M_s would vary in different ways with temperature, and therefore a temperature-independent relationship between ΔM_s and $\Delta\rho$ would not be expected to hold. In the following, therefore, only the contribution from $\mathrm{Cu^{III}Zn^{IV}}$ nnn disordered pairs will be considered. Their con-

centration at 200°C in the β phase is 1.10^{-3}–2.10^{-3}, when using the calculated formation energies, and $n_{CuZn}(0) = \frac{1}{4}p_{Cu}^{III}p_{Zn}^{IV} = 7.10^{-2}$. Thus their concentration remains sufficiently small even at $T_Q = 200$°C, and a description by disordered pairs is justified. Alternatively, the small value makes it difficult to determine the pair concentration by an independent experimental method.

After the martensitic transformation, only $\frac{1}{3}$ of the $Cu^{III}Zn^{IV}$ pairs have their axis parallel to the Bain axis, therefore the average theoretical ΔE_F is

$$\Delta E_F = \tfrac{1}{3}\Delta E_F(Cu^{III}Zn^{IV}, P) + \tfrac{2}{3}\Delta E_F(Cu^{III}Zn^{IV}, N) = -610k.$$

Using the abbreviation

$$\Phi \equiv \exp(-E_F^\beta/k_B T_Q) - \exp(-E_F^\beta/273k_B),$$

the change in the transformation temperature M_s can be rewritten as

$$\Phi = \frac{\Delta S}{\Delta E_F n_{CuZn}(0)}\Delta M_s.$$

Φ has been calculated from the measured ΔM_s of Fig. 1 and is plotted in Fig. 6 as a function of $1/T_Q$ in a semilogarithmic plot (symbol ●). For the present alloy the calculated $\Delta E_F \equiv -610k$, $\Delta S = 0.155k_B$ from [5] and $n_{CuZn}(0) = 7.10^{-2}$ were used to evaluate the proportionality factor between Φ and ΔM_s. The data of Fig. 6 lie on a straight line with the slope $1400k$. The remaining two curves of Fig. 6 show the temperature dependence of Φ for two different E_F^β, denoted by □ for $E_F^\beta = 1370k$ and + for $E_F^\beta = 850k$. The corresponding slopes have the values $1600k$ and $1400k$, which are higher than E_F^β and quite insensitive to variations in E_F^β. Thus the E_F^β can be deduced from the measured temperature dependence of ΔM_s only within a large error margin.

The best agreement seems to exist between the

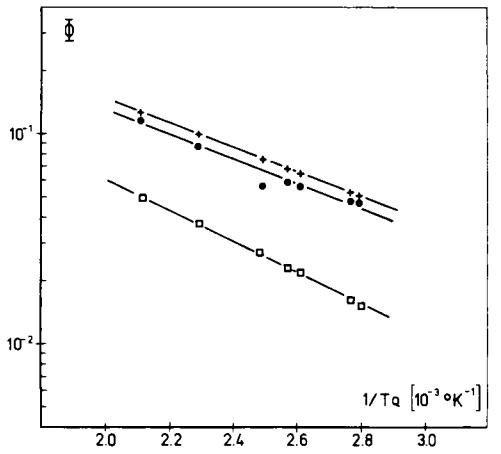

Fig. 6. Plot of Φ vs $1/T_Q$. (a) From measured ΔM_s (●). (b) Calculated from $E_F^\beta = 850k$ (+) and $1370k$ (□).

$\Phi(\Delta M_s)$ curve (●) and an $E_F^\beta = 900k$. This would imply, however, a discrepancy with the calculated E_F^β for $Cu^{III}Zn^{IV}$ pairs by a factor of two. If, on the other hand, an $E_F^\beta = 1370k$ were valid, corresponding to an upper limit of $1600k$ in the slope of $\Phi(\Delta M_s)$, according to the results of Fig. 4, then the ΔE_F in the proportionality factor between Φ and ΔM_s had to be increased by a factor of 2.5 in order to obtain agreement.

Thus it can be stated that E_F^β and ΔE_F agree by more than a factor of 2.5 with the calculated values. Taking into account the approximations made and the uncertainty in the measured chemical interaction energies, this is a highly satisfactory result, which indicates that the approach described in this paper is a valid one and permits a description of the influence of short-range disorder on the martensitic transformation in long-range ordered brass.

5. SUMMARY

(1) The electrical resistivity and the transition temperature M_s in Cu–Zn and Cu–Zn–Al alloys is changed by quenching from the temperatures T_Q above M_s. In Cu–Zn quenching leads to an increase in M_s smaller than 8 K, and in Cu–Zn–Al it produces a decrease of M_s up to 40 K.

(2) The results are interpreted by supposing that single disordered atom pairs in a long-range ordered matrix are produced in thermal equilibrium at T_Q and that they are retained after quenching. Their formation energies are calculated using existing data for chemical interaction energies between atoms. It is shown that in Cu–Zn the formation energy of nearest-neighbour Cu–Zn pairs is in good agreement with the experimental results of Clark and Brown [6]. In ternary Cu–Zn–Al mainly next-nearest-neighbour disordered pairs are quenched in.

(3) The formation energy of disordered nearest-neighbour pairs in the binary Cu–Zn martensite is smaller than in the β phase. The martensite becomes more stable with respect to β and M_s is increased by only a small amount because of the small concentration of the disordered pairs. Alternatively in Cu–Zn–Al mainly next-nearest-neighbour disordered CuZn pairs contribute to the change in M_s. Their presence increases the energy of the martensite with respect to β and thus lowers M_s. The formation energy of the pairs in the β phase is considerably smaller than for CuZn. Consequently the pair concentration is higher and quenching leads to larger variation in M_s. The measured formation energy in the β phase and its difference between β and martensite agrees by a factor of more than 2.5 with the calculated values.

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