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A MODEL FOR THE RUBBER-LIKE BEHAVIOUR IN CU-ZN-AL MARTENSITES

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In a previous paper the rubber like behaviour of Cu-Zn-Al martensites was described and the crystallography of the corresponding transformation was analyzed. It was shown that the deformation of the martensite leads to the appearance of a new martensite variant of a structure identical to the original one. The new variant must have a higher free energy, in order that a force exists which moves the interface back on releasing the stress. Possible mechanisms which produce an increase in energy during the movement of the interface between the variants are: a) creation of defects or of a new structure at the moving interface, b) Transformation of existing dislocations or long range order domain boundaries into higher energy defects during the transformation and c) a change of short range disorder. The first two possibilities were rejected in (1), the third will be discussed in this paper. It will be shown that the contribution of short range disorder can account for the observed rubber like behaviour in Cu-Zn-Al alloys, and that the driving force which is calculated agrees well with the experimentally determined stress which is necessary to induce the martensite. The alloy that has been studied in ref. 1 (Cu-12 at % Zn-18 at % Al) has a long range ordered DO$_3$ phase at high temperatures up to 700 K. The martensite which forms by a diffusionless transformation inherits the long range order from the β phase. In figure 1 is drawn schematically the bcc lattice. The corresponding fcc martensite structure can be formally derived from the bcc lattice by a homogeneous lattice distortion parallel to one <100>$_\beta$, denoted by a in the figure (called "Bain distortion"). Long range order in the β phase can be accounted for by using four sublattices denoted I to IV in figure 1a, each of which has an occupation probability that is independent of location. A Bain distortion deforms the sublattices to the sublattices denoted by 1 to 4 of the ordered fcc structure (figure 1b).

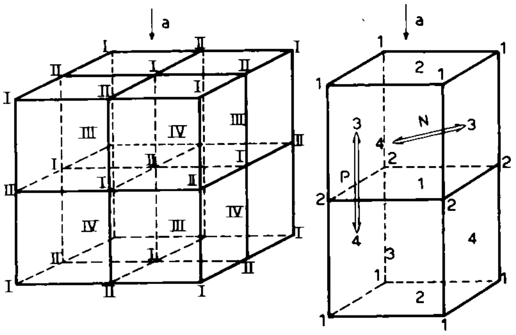

Fig. 1: Left: bcc structure with 4 sublattices denoted by I to IV. Right: fcc martensite after a homogeneous Bain distortion parallel a. Sublattice sites corresponding to the bcc structure denoted by 1 to 4. Double arrows connect atom pairs which were nnn in β and become nn (N) or nnn (P) in martensite.

Before entering into a detailed quantitative discussion, the main features of how short range disorder can contribute to the rubber effect shall be presented: Consider an fcc martensite lattice which has inherited its long range order from the β phase. Introduce now isolated disordered pairs by interchanging two different atoms on neighboring sites 3 and 4. The pairs are in nearest neighbour position if

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their axis (denoted by the double arrow in figure 1b) is normal to the Bain distortion $\underline{a}$ and next nearest neighbours when parallel. Both configurations have distinct formation energies, and in thermal equilibrium are present in different concentrations. If now the martensite variant is transformed into the variant with the pair axis normal to the initial one, then the nnn 3-4 pair changes to an nn pair, one nn pair becomes nnn, and one pair remains nn. This implies that during shear a nonequilibrium disordered pair concentration is induced, which changes the energy contribution from the value for thermal equilibrium. Only if equilibrium can be established again is the energy difference between the variants reduced and the force that drives the interface back on unloading disappears. A back driving force should also be absent if after transformation from β no reordering in the martensite is possible. These predictions of the model have been verified experimentally (1).

For a quantitative evaluation of the pair contributions the energies of the different types of disordered pairs in the martensite will now be calculated. Several approximations will be made:

1) The original β phase has perfect long range order, corresponding to T=OK. This is a reasonable approximation as long as the behaviour sufficiently below the critical temperature for disorder-order is of interest (For the alloys studied T_{DO_3}=700K).

2) The martensite inherits the long range order of the β phase. Experimentally no evidence has been found from transmission electron microscopy, that a different long range ordered lattice forms during aging of the martensite at room temperature, neither is a re-ordering expected that would require long range correlated atom interchanges at these low temperatures.

3) It is assumed that the concentration of the disordered pairs is sufficiently small, so that they can be treated as isolated pairs in a long range ordered matrix. Otherwise the neglect of interaction between pairs means a simplification that introduces errors.

4) The pair energy can be calculated as a sum of pairwise chemical interaction energies between neighboring atoms in the fcc lattice. Only nearest neighbour interaction energies will be considered, since in the fcc lattice the nn atom distance is considerably shorter than higher order neighbour distances. Since the nn interatomic distance in fcc and in bcc is practically the same, it is assumed that the nn interaction energies are equal for both lattices. This assumption is also supported experimentally (3). A consequence is that the orthorhombic martensite lattice that is observed can be replaced by an fcc lattice, since the difference in structure affects only atoms that are further away than nn whose interaction energy is being neglected.

The probability of having an atom A=Cu, Zn or Al on site J=I to IV is p_A^J. For perfect long range order (T=OK) in the used alloy

$$p_{Cu}^{I}=p_{Cu}^{II}=1,\ p_{Cu}^{III}=4C_{Cu}-2,\ p_{Cu}^{IV}=0,\quad p_{Al}^{I}=p_{Al}^{II}=0,\ p_{Al}^{III}=0,\ p_{Al}^{IV}=4C_{Al}.$$

On transformation to the fcc lattice, sites I to IV transform to 1 to 4 and $p_A^1=p_A^2=p_A^I$, $p_A^3=p_A^{III}$ and $p_A^4=p_A^{IV}$. All nn pairs sites in the β phase (I-III, I-IV, II-III, II-IV) remain nn pairs in fcc.

Once the equilibrium concentration of the pairs which were nn in β is attained in one martensite variant it remains in equilibrium after transformation to a different variant. Hence nearest neighbour disordered pairs do not contribute to a change in energy after shearing, and cannot be responsible for the rubber-like behaviour. It will be sufficient to consider III-IV disordered pairs.

The chemical interaction energy between atom A and B is defined as $m_{AB}=-2M_{AB}+M_{AA}+M_{BB}$, where M_{AA}, M_{AB} and M_{BB} are the pair interaction energies between A-A, A-B and B-B pairs in the martensite lattice. The formation energy E_F^M of a disordered A-B pair can be evaluated by counting the difference in total bond energies between atoms when the two A-B atoms are interchanged in their position on 3 and 4, without changing the occupation of the surrounding atoms. The formation energy E_F^M depends on whether A-B pairs are nn or nnn neighbour in fcc. They become nn neighbour in fcc during the transformation from β, if the pair axis is normal to the Bain axis, denoted by N and nnn if they are parallel to the Bain axis, denoted by P. The formation energies E_F^M for the 3-4 disordered pairs of Cu-Zn, Cu-Al and Al-Zn have been calculated and are listed:

$$E_F^M\ (\mathrm{Cu\ Zn},\ N) = 6\ C_{Al}\ (m_{Cu\ Al} - m_{Cu\ Zn}) + 6\ (2C_{Cu} - 1)\ m_{Cu\ Zn}$$

$$E_F^M\ (\mathrm{Cu\ Al},\ N) = 3\ (2C_{Cu} - 2C_{Al} - 1)\ (m_{CuZn} + m_{CuAl}) + 12\ C_{Al}\ m_{CuAl}$$

$$E_F^M\ (\mathrm{Al\ Zn},\ N) = 3(2C_{Cu} - 1)\ (m_{CuAl} - m_{CuZn})$$

The formation energy for pairs parallel to the Bain axes are

$$E_F^M\ (A\ B, P) = \frac{4}{3}\ E_F^M\ (A\ B,\ N).$$

Using $m_{CuZn} = w_{CuZn}^{(1)} = 955k$ (4), $m_{CuAl} = 1345\ k \pm 25k$, $m_{AlZn} \approx 0$ (2) where $w_{AB}^{(1)}$ are the measured nearest neighbour chemical interaction energies in the β phase, and k the Boltzmann constant multiplied by 1K, the following numerical values for E_F^M are obtained for the alloy Cu-12 at % Zn- 18 at % Al: E_F^M (Cu Zn, N)= 2713k, E_F^M (Cu Al,N)= 3273k, E_F^M (Al Zn,N)= 468k. Supposing that the pair concentration in equilibrium is proportional to exp - E_F^M/kT, the CuZn and CuAl disordered pairs are present in so small quantities compared to Al Zn that their contribution can be neglected. In thermal equilibrium the energy contribution from the Al-Zn disordered pairs then is

$$E_{th} = \frac{1}{3}\ n_o\ E_F^M\ (P)\ \exp - \frac{E_F^M\ (P)}{kT} + \frac{2}{3}\ n_o\ E_F^M\ (N)\ \exp - \frac{E_F^M\ (N)}{kT}$$

Here n_o is the number of available pair sites, one third of which are parallel to the Bain axes and 2/3 are normal. In the simplest approximation n_o is given by the product of the occupation probabilities in the long range ordered lattice, $n_o = \frac{1}{4}\ p_{Zn}^{III}\ p_{Al}^{IV} = 3.6\ 10^{-2}$. The new martensite variant has the Bain axis normal to the original martensite, consequently a P type disordered pair changes to an N pair and one N pair changes to P. The energy contribution of the stress induced variant then is

$$E_\sigma = \frac{1}{3}\ n_o\ E_P^M\ (N)\ \exp - \frac{E_{F(P)}^M}{kT} + \frac{1}{3}\ |E_F^M\ (N) + E_F^M\ (p)|\exp - \frac{E_{F(N)}^M}{kT}$$

Using $E_F^M\ (P) = \frac{4}{3}\ E_F^M\ (N)$, the difference $E_\sigma - E_{th}$ can be written as:

$$E_\sigma - E_{th} = \frac{1}{9}\ n_o\ E_F^M\ (N)\ \exp - \frac{E_F^M\ (N)}{kT}\ (1 - \exp - \frac{E_F^M\ (N)}{3kT}\ )$$

For Cu-12% Zn - 18% Al at T= 300k,

$E_{th} = 3.29k$ and $E_\sigma - E_{th} = 0.16k = 1.33$J/mole.

Thus the difference is only 5% of the total contribution in thermal equilibrium. A plot of $E_\sigma - E_{th}$ versus E_F^M (N) shows that $E_\sigma - E_{th}$ has a broad maximum around E_F^M (N) = 500k ($E_\sigma - E_{th} = 0.18k$), and decreases to 0.14k at E_F^M (N) = 300k and 800k. The numerical value of E_F^M (N) therefore does not sensitively influence E_σ-E_{th} in this range.

The calculated energy difference is now compared with the experimental results of ref. 1. There it has been found that the resolved critical shear stress to induce the new variant is $\tau_+^{(1)} = 8\mathrm{MN/m^2}$ for the first cycle and $\tau_+^{(2)} = 4\ \mathrm{MN/m^2}$ for the second and subsequent cycles. The stress at which the variant disappears again on unloading is $\tau_- = 0$ for all cycles. The amount of shear is a= 0.32 ± 0.01. The stress hysteresis is due to energy dissipation during the movement of the interface. The higher

τ_+ for the first cycle may be caused by the rearrangements of existing lattice defects at the interface. The hysteresis stress $\tau_+ - \tau_- = 4MN/m^2$ for the subsequent cycles agrees well with the corresponding stress to induce martensite from the β phase (5); this observation is consistent with the supposition that the transformation occurs via the β phase, which is present as a thin layer at the interface between the martensite variants (1): The critical stress then consists of a friction part which can be assumed to be independent of the direction of the moving interface, $\tau_{fr} = (\tau_+^{(2)} - \tau_-^{(2)})/2$ and a component $\tau_E = \tau_+^{(2)} - \tau_{fr}$, which is a measure of the driving force. The energy difference between the variants then is $\Delta E = \tau_E . a$. For $\tau_E = 2MN/m^2$ and a= 0.32, $\Delta E = 0.64 J/cm^3 = 4.9 J/mole$. This value is higher by a factor of 3.5 than the theoretically deduced difference of $E_\sigma - E_{th} = 1.3 J/mole$. Considering however the approximation made and the smallness of the effect, an agreement within a factor 3.5 is quite satisfactory. It is difficult to evaluate the quality of the appoximations, but it seems that the restriction to nearest neighbour interactions is a possible source for the discrepancy. Although the contribution from next and next nearest neighbours in the fcc lattice can be included by using an effective nn interaction energy, the higher than second neighbour interactions are different for an fcc lattice and the actually observed more complex 3R orthorhombic martensite. It had been shown experimentally that at least in binary CuZn the energy between both structures indeed differs (6). Therefore restriction to first neighbours in an fcc lattice is a simplification, which introduces a certain error. In view of these facts it is concluded that rubber like behaviour in CuZnAl can well be explained by the contribution of the short range disorder in a long range ordered martensite matrix.

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