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THE RUBBER EFFECT IN Cu-Zn-Al MARTENSITE

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1. Introduction

Rubber like behaviour has been observed in several noble metal alloy martensites, as In-Tl (1,2), Au - Cd(3,4,5) Cu - Au - Zn(6), Cu-Al-Ni(7) and Cu-Al-Zn(8). Crystals of these alloys when deformed plastically in the martensitic state regain their original shape after the stresses are released. Only if the sample remains too long in the stressed state can the rubber effect disappear with the martensite remaining deformed after unloading. This behaviour indicates that thermally activated time dependent processes are important. In most of the alloys mentioned the martensite is twinned and stresses lead to the displacement of the twin interfaces, which return to their original position after unloading. In the Cu - Zn - Al alloy (8) the rubber effect is observed in untwinned single crystalline martensite. Only during stressing new plates appear within the original martensite. On releasing the stresses these newly formed plates disappear again. The stressing-unloading cycle can be repeated without a change in the rubber-like behaviour.

Why do the interfaces go back to their original positions in the twinned martensite or disappear completely in the Cu - Zn - Al alloy? Two explanations have been offered: Birnbaum and Read (4) suggested that in the martensite order faults between split super-dislocations exist, which on twinning go over to high energy defects that change the volume free energy of the twinned martensite, thus providing a force that drives the interface back to its original position when the external stress disappears. Rubber like behaviour can also be expected if twinning requires in addition to the macroscopic twin shear a reshuffling of the atoms to the correct position which is time dependent (5,6). Lieberman et al (5) used this model to explain the rubber effect in Au - Cd twinned martensites, which have the more complex Ölander structure that is absent in most other martensites.

The initial report of a rubber-effect in Cu - Zn - Al alloys (8) has left a great number of questions unanswered. In this paper therefore further experiments are described which serve to clarify the crystallography of the transformation. In a later paper a model will be presented which attempts to explain the rubber like behaviour in these alloys.

2. Experimental techniques and results

Cu - Zn - Al martensitic single crystals were prepared in the same way as described in ref. 8. The composition of the alloy used is 70 at % Cu - 12 at % Zn - 18 at % Al, having an M_s temperature of 50°C. A martensitic single crystal was induced by stressing the β phase single crystal in tension above M_s, and was retained by cooling the stressed sample to room temperature (8). The martensitic single crystals were then compressed at room temperature. Broad bands appeared

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extending across the whole cross section of the sample similar to the behaviour observed for binary Cu-Zn(9). The interface between the bands and the original single crystalline material is planar.

In a first step the crystallography of the new phase was determined. By transmission electron microscopy (TEM) it has been shown that the stress induced martensite has the same 3R structure as that obtained after cooling below M_S. The orientation of the martensite lattice was analysed by the X-ray Laue method. Due to the more complex martensitic 3R structure, the Laue patterns are more difficult to interpret. Therefore the relationship between Laue patterns and the lattice orientation had to be established first.

The martensite lattice generally is described by an orthorhombic axes system (10). $[00\bar{1}]_o$ is parallel to the normal of the close packed planes, which are packed in an ABCBCACAB sequence (neglecting long range order). $[010]_o$ is parallel to the close packed direction in the compact plane, corresponding to $\langle 111\rangle_{fcc}$ in an fcc lattice. $[100]_o$ is normal to $[010]_o$ and $[00\bar{1}]_o$, and corresponds to a $\langle 112\rangle_{fcc}$ in the face centered lattice.

The only Laue patterns that could easily be recognized were those containing the $(001)_o$ reflection. In order to index the other patterns, samples of given orientation were also studied by TEM, and the results were compared. In this way the relationship between Laue patterns and crystal orientation could be established unequivocally.

When the single crystals were compressed, plates with planar interfaces were induced. By keeping the stress applied for 24 h at room temperature, the new structure stabilized and did not disappear anymore on unloading. X-ray analysis by the Laue method showed that the structure of the plates is identical to that of the initial martensite, i.e. by compression a new variant of the martensite structure is formed. This result was further substanciated by TEM studies. In addition, X-ray diffraction patterns taken immediately after stressing and after stabilization did not differ.

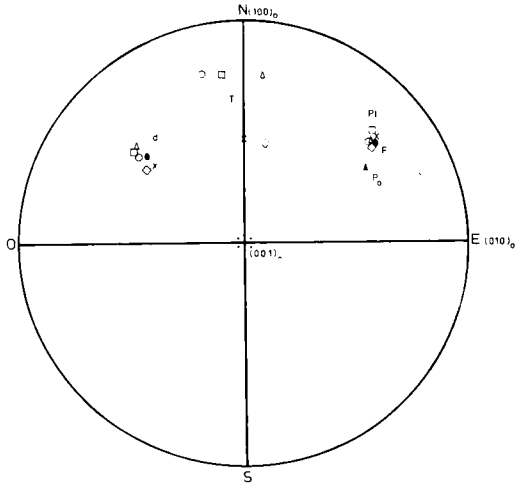

Fig.1: Experimentally determined interface orientation P at Pl, shear direction d and compression axis T for several single crystals denoted by different symbols, with respect to the orthorhombic axis system. Filled symbols at P, Po and d are calculated values.

The orientation relationship with the new variant, the interface orientation with plane normal P and the direction of the corresponding shear d were determined with respect to the orthorhombic axes system of the parent martensite. The results are collected in figure 1. Data from different single crystals are denoted by different symbols. In figure 1 is also shown the orientation of the single crystal compression axis, denoted by T. The filled circles at P, Po and d are calculated orientations. The amount of the shear was determined from the shape change of the new variant and was found to be $a = 0.32 \pm 0.01$.

The stress which is necessary to induce the new variant was also measured as a function of transformation strain during the loading and the unloading part of the cycle. For this reason samples of 35 mm length and 3 mm diameter were cut from the original martensitic single crystals. The stress-strain curves during a compression cycle

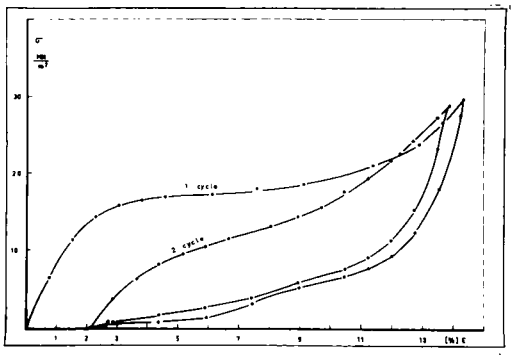

Fig. 2: Stress σ versus ε for the first and second compression cycle.

were determined at room temperature after the martensitic single crystal had been aged at room-temperature for 30 days. In figure 2 is shown the stress (load divided by initial cross section) versus strain (elongation divided by initial length). The Schmid factor for the shear system of this sample is μ=0.49. On loading the crystal is first deformed elastically. (In figure 2 the initial slope is distorted by machine effects.) The critical resolved stress for the first cycle is $\tau_+^{(1)} \approx 8 MN/m^2$. After most of the sample is transformed the stress starts to rise more steeply with strain than before. On unloading the stress remains lower and reaches zero when practically all material has retransformed. During the second cycle the critical stress remains lower than during the first cycle ($\tau_+(2) \approx 4 MN/m^2$) whereas the unloading curve changes less. During the next 12 cycles the hysteresis curve remains largely unchanged. More detailed studies on the influence of various pretreatments are in progress. The following additional experiments have also been performed: a) When the martensite crystal is deformed at liquid air, the rubber effect does not age out, even if the sample remains stressed for 7 days. This behaviour is in agreement with the supposition that thermally activated processes are responsible for aging, which are frozen in at 78 K. b) If the martensite sample is cooled below 0°C right after the transformation from the β phase, the rubber effect is absent and the crystal remains deformed after unloading. This has been verified by using also a sample with M_S=+10°C. When this sample subsequently was heated to 90°C for 30 min. in the martensitic state by applying stresses which prevented the retransformation to β, on subsequent cooling to 0°C the sample showed rubber like behaviour. Some precursory processes in the martensite have to occur in order that the rubber effect is formed. c) A twin variant that has been induced by compression and aged, retransforms to the original martensite on stressing in tension but after unloading the former variant appears again. d) In a further experiment a martensitic single crystal was induced from the β phase by a compression instead of tension. After aging and tensioning rubber like behaviour is observed. Summing up, it can be stated that thermally activated processes stabilize the martensite, independently of whether it is obtained from the β phase or induced as new variant in a martensite matrix. When new variants are formed by stresses in the stabilized martensite, they are less stable and disappear again on relieving the stress.

3. Discussion

The phase that is induced by deforming the martensite is a variant of the same martensitic structure as the original single crystal, and therefore the interfaces are those between two martensite variants. The unit lattice cell of the martensite structure is symmetric with respect to the $(010)_o$ plane, but neither $(100)_o$ nor $(001)_o$ are symmetry planes. Therefore it is expected that a martensite lattice can be transformed into two crystallographically equivalent variants. This has indeed been observed when both variants are equally favoured by the applied stress, (i.e. when the orientation of the sample axis lies on the great circle through $[001]_o$ and $[100]_o$, not shown in figure 1 in order to keep the drawing transparent). Figure 1 indicates that variants of only one set of equivalent pairs are induced.

The analysis of the results will be based on a recently published model for the martensitic transformation (11) which permits to describe the atom movements during the transformation. In this model the transformation from the

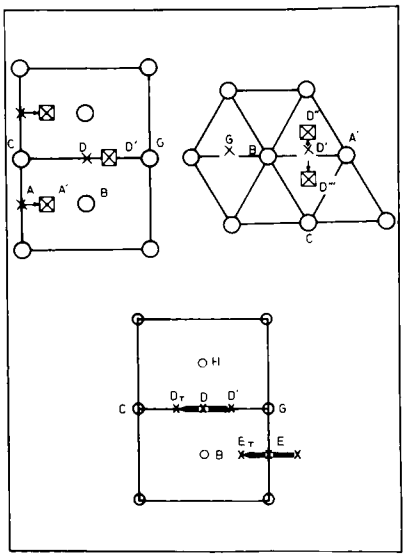

Fig. 3 a) (upper left): Movement of atoms during primary shear on $(110)_\beta$. X move to $\boxed{X}$ on the plane above the plane of the circled atoms. b) (upper right): from movements on the close packed plane from X to $\boxed{X}$ (i.e.D↳D'' or D''') to obtain correct stacking. c) (below): Atom movement D'→D↦D_T on the martensite plane which corresponds to the plane of a) in β.

β phase to the martensite is decomposed into a primary shear on the $\langle 110\rangle_\beta\langle 1\bar{1}0\rangle_\beta$ shear system of the β phase of amount $\gamma_1 = 0.25$. In a hard sphere model the shear is associated with a contraction of 3.17% normal to the plane. In figure 3a is shown the atom movement of a $(110)_\beta$ plane (A→A', D→D') with respect to the plane below. After this shear the inclined plane BCA' becomes a close packed plane whose stacking however is not yet correct. Atoms lying on the close packed plane above BA'C of figure 3b have positions corresponding to D', intermediate between the possible positions D'' or D''' of a close packed stacking sequence. In order to remedy this the atoms have to move from D' to D'' or D''', associated with a dilatation of 5.13% normal to the compact plane. The condition that an undistorted habit plane exists determines the average fraction of shears of the compact planes in D'→D'' and D'→D'''. For the presently studied alloys the average secondary shear is close to zero ($\gamma_2 = 0.02$), which means that two shears from D' to D'' are compensated by one shear to D''', since $|D''' - D'| = 2\,|D'' - D'|$, leading to an ABCBCACAB structure. For $\gamma_2 = 0$ the secondary shear can be considered as a shuffle of atoms with average shear zero. On this basis the transformation from one martensitic variant to the new one can easily be visualized. To simplify the discussion it is assumed that the amount of secondary shear $\gamma_2 = 0$, and that the small dilatation of the secondary shear plane can be neglected. It can be shown that these simplifications do not change appreciably the results. The transformation from one variant to the other can then be decomposed into the following steps: 1) a reshuffling without shape change (D'', D'''→D' of figure 3b), 2) a primary shear on the plane CGB, corresponding to the movement of D' to D_T on the plane above CGB, as shown in figure 3c and 3) a reshuffling on the newly formed compact plane, in order to complete the transformation. The lattice spacings of figure 3c are those of an intermediate martensite phase and differ slightly from those of the β phase of figure 3a. After the shear D'→D_T two compact planes exist, on which the shuffle can occur: The planes B D_TC and H D_TC. In the first case the new reshuffling direction has a component normal to the primary plane that is parallel to the corresponding direction D'→D'' or D'→D''', in the second case they are antiparallel. Therefore the total shuffle normal to the primary plane during the shear is smaller for BD_TC than for HD_TC. The shuffling distances of the atoms during the shear are considerably smaller than for other atom movements that lead to a different arrangement. Therefore in this model an identical variant is formed by the interface movement normal to the primary plane.

The orientation of the shear plane BCG (figure 3c) can easily be determined with respect to the original orthorhombic axes system. In figure 1 it is plotted as a filled circle at P_o. Similarly, the shear direction D'→D_T is shown at d, denoted by a filled circle. Whereas d shows good agreement between the experimental results and the theory, the direction P_o clearly lies outside the measured range. This discrepancy is not due to the approximations made (i.e. $\gamma_2 = 0$, no distortion normal to the secondary shear plane). Apparently some additional factors have to be taken into account which cause a deviation of the shear plane from the low indexed orthorhombic primary plane. Such a deviation can be well accounted for if it is supposed that both marten-

site variants are separated by a thin layer of a bcc β phase structure, as was originally suggested by Wasilewski (12). In the presence of the β phase the additional condition that the interface between the martensite and the β phase be undistorted, has to be satisfied. Let us consider therefore the orientation of two martensite variants that are in contact with the β phase. The orientation relationship, the habit plane orientation between martensite and β, and the martensite shear direction with respect to the β phase have been calculated. A set of four martensite variants have their habit planes close to a $(110)_\beta$ plane of the β phase, two of them with the martensite shear direction nearly opposite to that of the other two. Hence two different combinations of a variant pair with opposite shear directions are possible. The interface that is formed when both variants get in touch macroscopically lies symmetrically between the individual habit planes, and the shear direction of one variant with respect to the other is given by the difference between the martensite shear directions. This follows from the symmetry between both variants. The results for one pair combination is shown as filled circles at P and d in figure 1. The d is the same as that calculated earlier for a shear on the primary plane. The orientation differs from P_o, but agrees well with the experimental results. The second combination of variants leads to a different interface orientation that has not been observed and therefore is not plotted. The latter pair would need the larger shuffle during shear and this may be the reason why it is not found experimentally.

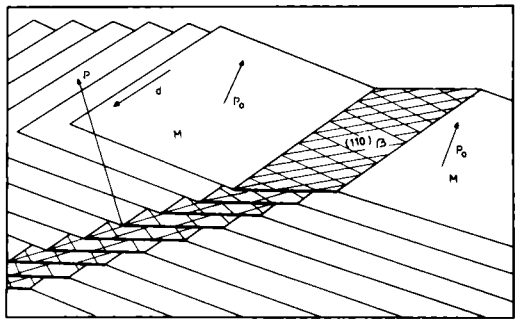

Fig. 4: Schematic drawings of the interface zone of β structure between the martensite variants M. Shown are the $(110)_\beta$ planes and martensite P_o planes, corresponding to those of Fig. 3a and c. The shear direction is denoted by d, and the interface orientation by P.

From the present discussion emerges a picture for the interface structure that is sketched schematically in figure 4. In this figure are drawn the primary planes (the same as in figure 3c) for the martensite variants separated by a layer of β phase consisting of $(110)_\beta$ planes and having the normal P which deviates by ≈ 7° from P_o, due to the different spacings of the primary plane in the martensite and in β. The direction of the martensite shear is parallel to d, which is normal to P and P_o (figure 1). Interface movement occurs now by a shear in d on the primary plane of one variant associated with a displacement of the β phase layers by the transformation of martensite into β at the front and retransformation to martensite at the back of the layer. This transformation is coupled to a small shuffling of atoms with respect to their positions on the primary plane. Since, as discussed earlier the displacement during reshuffling is considerably smaller than the distance between primary planes, the reshuffling does not lead to atom displacements across primary planes. Therefore it is concluded that the formation of the new variant by the displacement of the interface zone leads to a structure identical to the original one, without the creation of additional faults, which would change the free energy of one variant with respect to the other, even when the layer between the variants has a β phase structure.

The rubber-like behaviour remains to be discussed now. A change in free energy during the formation of the new variant can be accomplished either by the production of defects at the moving interface or by the transformation of existing defects into higher energy configurations. To the former belongs the shuffling model for the Au-Cd transformation (5), to the latter the behaviour of split superdislocations (4). On the basis of the present analysis it is unlikely that in Cu - Zn - Al the moving interface creates defects, since the amount

of reshuffling is too small. Therefore existing defects must be the reason for the rubber effect. However, since both variants are completely equivalent with respect to the β phase, any defect that existed in the β phase prior to the transformation must have the same energy in both variants, unless a restructuration in the martensite occurs. This requirement indeed is met experimentally since it had been observed that a martensite crystal did not show rubber like behaviour, when it was not aged after transformation from the β phase. Existing defects are on the one hand dislocations and antiphase domain boundaries. It is unlikely that they are responsable for the rubber effect in annealed crystals, where the dislocation density and domain area are small. It had been shown elsewhere (13) that domain boundaries produce small changes in M_s only if they are present in extremely high densities. Other types of defects which are more likely candidates are disordered atom pairs which exist in equilibrium in a long range ordered matrix, and which are known to contribute to M_s temperature (14).

In a separate paper it will be shown that the rubber effect indeed can be explained quantitatively by the contribution of disordered pairs.

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