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SURFACE RELAXATION AS A POSSIBLE ORIGIN OF SURFACE MARTENSITE

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Abstract.— The origin of surface martensite has been investigated. It is shown that the surface transformation and the resulting martensites cannot be explained by composition changes near the surface but are most likely attributable to atom relaxations at the surface. The stress free strains in the vicinity of the surfaces associated with such atom relaxations are considered sufficient to produce mechanical instability of the β lattice to a $\{110\}\langle 1\bar{1}0 \rangle$ shear and thus leading to the formation of particular martensite variants.

Introduction.— In several recent investigations the extra maxima appearing in the electron diffraction patterns of B2 and DO₃ ordered β phase Hume-Rothery alloys have been shown to stem from a surface phase considered to be martensite (1-3). This has been followed by a more recent study (4) confirming through evidence of a surface phase transformation that the phase indeed is martensitic. The stability of the surface martensite has been shown to extend to a much higher temperature than the highest temperature at which the bulk martensite in the same alloy is stable (4). In addition, surface martensite has been shown to exist despite the fact that no bulk transformation is expected to occur in the same alloys even on cooling to the absolute zero (4).

The crystallographic details of the surface martensites have been established fairly well (1,3,4). The martensites have been shown to have 9R (or 18R) or 2H or intermediate structures depending on the surface orientation of the samples. Only selected variants of the same structure have been found to appear on a surface. The occurrence of such preferential variants has been shown to be determined by the availability, parallel to the surface, of the least distorted β /martensite interfaces of the corresponding variant/s (3).

The purpose of the present report is to examine whether changes in interplanar spacings in the vicinity of planar free surfaces (5,6) can account for a martensitic transformation and the observed martensitic variants at the surface.

Results and Discussion.— The concept that strains associated with the relaxed state of atoms in the vicinity of planar free surfaces can trigger a martensitic transformation is not new. In fact, Clapp (8) has already suggested such a possibility based on a theoretical analysis which led to the prediction that the most potent sites for the nucleation of a martensitic transformation would be available at the surface. Therefore, in this report we extend Clapp's analysis and attempt to investigate whether the variants that result from the growth of these primary nucleation centres on a given surface are the same as the observed surface martensite variants. Details of the calculations are given in an appendix.

Measured values of third order elastic constants from the works of Swartz et al. (9) and Guénin (10) were used in the present calculations and the analysis was carried out assuming that atoms at the surface and its vicinity relax outwards of the respective planes parallel to the surface. The effect of the strain due to this surface relaxation on the elastic constant, C' , corresponding to $\{110\}[\bar{1}\bar{1}0]$ shear was evaluated. The critical strain, ϵ_c , for which $C'(\epsilon) = 0$ in turn was cal-

culated for different $\{110\}[\bar{1}\bar{1}0]$ shear systems and for samples with different surface orientations. The values are summarized in table 1. It must be remarked that

Table 1 Critical strain %

System	Surface + (110)	(013)	(112)	(123)	(111)	(001)
011	6.95	3.53	4.11	3.76	4.93	3.53
101	6.15	3.86	4.11	4.66	4.93	3.53
110	3.53	15.19	8.18	7.81	4.93	24

no distinction can be made in the present calculations when the shear plane indices are interchanged with shear direction indices. Thus system $[110]$ for example could equally mean $(110)[\bar{1}\bar{1}0]$ shear and $(\bar{1}\bar{1}0)[110]$ shear. Keeping in mind this degeneracy we can still look for the most preferred martensite variants on a given surface as predicted from table 1. Such variants would correspond to the system for which the critical strain is the smallest. Despite the degeneracy in the predictions, we may attempt to look for a common behaviour which will explain the preference of particular variants on each surface according to table 1. It then follows that the most preferred variants/s should have a primary shear on $\{110\}<\bar{1}\bar{1}0>$ system/s that is/are nearly parallel to the sample surface. The observed martensitic variant/s on a given surface, as shown earlier (1,3) follow the same behaviour.

The above comparison between predicted and observed variants holds good for all surfaces with the exception of (001) surfaces. Samples having the latter surfaces do not exhibit any surface martensites even though the calculated critical strains are comparable in magnitude to similar strains estimated for other surfaces on which martensites are known to form. One reason for this behaviour may be that strains equal in amount to the critical value may still not be available on a (001) surface. Secondly, even if we concede that the transformation is triggered near the surface, growth of the nuclei would lead to variants having β /martensite interfaces that are inclined 45° to the sample surface. Considerable strains will then be built up during this growth process as opposed to the situation in all the other samples where the β /martensite interfaces are nearly parallel to the surface. One may thus envisage any strain build up as opposing further growth of the variant. In effect growth may be so limited and surface martensite thickness so small that they produce negligible diffraction effects which has been essentially used otherwise in recognising their presence.

One can also forward other comparisons to support the view that surface relaxation effects trigger the surface martensite transformation. The critical strain value which reflects the stability of the β phase may thus be compared against another parameter describing the stability of the β and martensite phases, viz., the temperature of surface martensite transformation. Table 2 shows this comparison

Table 2 Critical strains for surfaces and surface martensite transformation temperatures for β Cu-Zn and β Cu-Zn-Al alloys

Alloy	Critical strain %	Surface martensite transformation temperatures
Cu-19.3at%Zn-13at%Al	2.86 - 4.12	25 to 80°C
Cu-43.08at%Zn-2.46at%Al		
Cu-44.4at%Zn	4.38 - 5.24	- 30 to 25°C
Cu-48.2at%Zn		
Cu-48.3at%Zn	4.92-5.32	

for which pertinent data can be calculated or are available. As seen from this table a relatively less stable β phase predicted by a lower value of the critical strain is also consistent with the observed higher value for the transformation temperatures.

In conclusion it may be said that atom relaxations in the vicinity of planar free surfaces can be a possible origin of surface martensite.

Appendix.- Mechanical Instability due to surface relaxation as a function of orientation of the surface.

The free energy of a crystal as a function of homogeneous deformations is expressed as follows :

$$F - F_0 = \frac{1}{2} \sum C_{ij} \epsilon_i \epsilon_j + \frac{1}{6} \sum C_{ijk} \epsilon_i \epsilon_j \epsilon_k$$

This expansion limited to third order terms is sufficient in considering the influence of homogeneous deformation on the mechanical stability of the lattice (12). The second derivatives, F_{ij} , of the free energy with respect to the homogeneous deformation are the elastic constants of the lattice. When the lattice is subjected to a finite deformation, these derivatives are given by :

$$F_{ij} = \frac{1}{2} (C_{ij} = C_{ji}) + \frac{1}{6} \sum (C_{ijk} + C_{jik} + C_{ikj} + C_{jki} + C_{kij} + C_{kji}) \epsilon_k$$

where $[\epsilon_k]$ is the deformation tensor.

The deformed lattice is mechanically stable provided all the elements of the F_{ij} matrix have positive values. In general, however, the stability criteria are more complicated since the deformed lattice has lost elements of symmetry. Nevertheless, it has been shown for β phase alloys, which are of present interest, that the general criterion and the most critical one corresponds very nearly to $C_g^1 > 0$ (12,13). This is also the most critical criterion of the undeformed lattice, it is the elastic constant corresponding to a $\{110\}\langle 1\bar{1}0 \rangle$ shear. Consequently, simplified criteria for mechanical stability of the lattice are considered here in terms of the elastic constants corresponding to $\{110\}\langle 1\bar{1}0 \rangle$ shear as a function of surface relaxation. The procedure involves :

- evaluating the form of deformation for a given free surface
- estimating the elastic constants, F_{ij} , corresponding to various $\{110\}\langle 1\bar{1}0 \rangle$ shear systems and modified by the above deformation. Each expression for the elastic constants thus yields a maximum critical amplitude of deformation, ϵ_c , at the surface for which the elastic constant in question becomes zero.
- identifying the $\{110\}\langle 1\bar{1}0 \rangle$ system corresponding to the lowest ϵ_c which, a priori, will be the preferred system of shear in forming the surface martensite variant.

a) Deformation near the surface

The deformation in the vicinity of the free surface is assumed to be perpendicular to the surface and directed out of the crystal. If the reference axes is so chosen that the surface normal is a principal axis, then the deformation tensor consists only of the term $\epsilon_{11} = \epsilon$. To calculate F_{ij} it is necessary to express this tensor in terms of the crystal axes.

b) Calculation of elastic constants corresponding to shears of type $\{110\}\langle 1\bar{1}0 \rangle$.

In the case of $(110)[1\bar{1}0]$ or $(1\bar{1}0)[110]$ shear

$$[\epsilon_i] = \begin{vmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & 0 \end{vmatrix} = \pm \alpha \begin{vmatrix} 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

This deformation takes place in the vicinity of the surface in an already deformed lattice and changes the free energy F to

$$F' = F + \frac{\partial F}{\partial \epsilon_1} \epsilon_1 + \frac{\partial F}{\partial \epsilon_2} \epsilon_2 + \frac{1}{2} [F_{11} \epsilon_1^2 + F_{12} \epsilon_1 \epsilon_2 + F_{21} \epsilon_2 \epsilon_1 + F_{22} \epsilon_2^2]$$

The linear terms in the expression are non-zero terms, since F does not correspond to the minimum free energy.

The elastic constants are then expressed as

$$\frac{\partial^2 (F' - F)}{\partial \alpha^2} = 1/4 (F_{11} + F_{22} - 2F_{12}) = C'_{s,110}$$

If $F = F_0$ (undeformed lattice) this elastic constant is $C' = \frac{1}{2} (C_{11} - C_{12})$. The same calculation can be made for (101)[$\bar{1}$ 01] or ($\bar{1}$ 01)[101] systems represented in a shorter form a "101".

$$\frac{\partial^2 (F' - F)}{\partial \alpha^2} = 1/4 (F_{11} + F_{33} - 2F_{13}) = C'_{s,101}$$

Similarly for the system "011" :

$$\frac{\partial^2 (F' - F)}{\partial \alpha^2} = 1/4 (F_{22} + F_{33} - 2F_{23}) = C'_{s,011}$$

c) Calculation of the elastic constants C'_s

The deformation tensor having been defined with respect to the crystal axis, F_{ij} and the above derived elastic constants C'_s can now be calculated for the different shear systems.

$$C'_{s,110} = \frac{1}{2}(C_{11} - C_{12}) + 1/4\epsilon [(a_1^2 + a_2^2)(C_{111} - C_{112}) + 2a_3^2(C_{112} - C_{123})]$$

$$C'_{s,101} = \frac{1}{2}(C_{11} - C_{12}) + 1/4\epsilon [(a_1^2 + a_3^2)(C_{111} - C_{112}) + 2a_2^2(C_{112} - C_{123})]$$

$$C'_{s,011} = \frac{1}{2}(C_{11} - C_{12}) + 1/4\epsilon [(a_2^2 + a_3^2)(C_{111} - C_{112}) + 2a_1^2(C_{112} - C_{123})]$$

where a_1 , a_2 and a_3 are the direction cosines referred to the crystal axes of the normal to the surface and C_{111} , C_{112} and C_{123} are the third order elastic constants.

By putting $C'_{s,110}$, $C'_{s,101}$ and $C'_{s,011}$ zero, one obtains the critical value of deformation :

$$\epsilon_{c,110} = \frac{-2(C_{11} - C_{12})}{(a_1^2 + a_2^2)(C_{111} - C_{112}) + 2a_3^2(C_{111} - C_{123})}$$

$\epsilon_{c,101}$ and $\epsilon_{c,011}$ are similarly obtained by circular permutation.

The deformation $\epsilon_{c,110}$ is constant if $a_3 = \pm K$ where K is a constant since $a_1^2 + a_2^2 = 1 - a_3^2 = 1 - K^2$. Thus the critical deformation for the shear system "110" will be constant for all surfaces whose normals make the same angle, θ , with the [001] axis of the crystal. The ϵ_c values as a function of this angle θ are reported in fig. A1 for a Cu-Zn-Al alloy (14) where

$$C' = \frac{1}{2}(C_{11} - C_{12}) = 0.6 \times 10^{10} \text{ Pa}, \quad C_{111} = -133 \times 10^{10} \text{ Pa}$$

$$C_{112} = -65 \times 10^{10} \text{ Pa} \quad \text{and} \quad C_{123} = 660 \times 10^{10} \text{ Pa}$$

It is interesting to draw on a stereographic projection curves of constant ϵ_c for different surface orientations. Such a construction is shown in fig. A2 for the 110, 101 and 011 shear systems.

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