

Thermodynamics of the Displacive Mechanism of α_1 Transformation in a β' Copper-Zinc Alloy

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Thermodynamics of the displacive mechanism of plate-shaped phase α_1 was analyzed in β' Cu-Zn alloys. It was proposed that the displacive transformation of the α_1 plate took place in the solute-depleted region formed in the parent phase during the incubation period. The thermodynamic analysis indicated that the driving force of α_1 transformation, ΔG , increased with the reduction of x_d , the solute concentration of the depleted region. And, ΔG could overcome the transformation barrier with solute depletion to a certain degree. In addition, x_d was higher than the equilibrium concentration in the phase diagram. Therefore, the shear formation of α_1 plate in the solute-depleted region was thermodynamically supported.

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Keywords: β' copper-zinc alloy, α_1 plate, thermodynamics, shear transformation, solute-depleted region

I. Introduction

Garwood⁽¹⁾ first found the surface relief phenomenon accompanying the formation of plate-shaped phase α_1 in β' Cu-Zn alloys. Garwood⁽²⁾ and Cornelis and Wayman⁽³⁾ revealed that the $\beta' \rightarrow \alpha_1$ crystallography had typical features similar to the martensitic transformation. The formation of α_1 plates exhibited a dual nature, i.e., displacive and diffusional characteristics⁽⁴⁾⁽⁵⁾. The mechanism of the α_1 transformation is closely related to diffusion of solute atoms.

Ghilarducci and Ahlers⁽⁶⁾ observed a relaxation internal friction peak near 473 K in a Cu-Zn-Al alloy, and considered that this Debye peak be associated with solute atoms. Shen *et al.*⁽⁷⁾ and Kang *et al.*⁽⁸⁾⁽⁹⁾ further pointed out that internal friction peaks are induced by diffusion and segregation of solute atoms in ordered β' matrix before α_1 plate formation. Additionally, the concentration distribution of solute atoms during the incubation period possesses a large fluctuation comparing with that in the quenched sample⁽⁷⁾⁻⁽⁹⁾. Therefore, it is suggested that the solute-depleted region appear during the incubation period. Takezawa and Sato⁽¹⁰⁾ implied that the formation of solute-depleted regions be created by stress-induced diffusion around defects.

At the early stage of α_1 growth, the change of the solute composition near the interface of the α_1 plate and matrix is strongly emphasized. Wu *et al.*⁽¹¹⁾⁽¹²⁾ observed the composition difference between α_1 plate and the parent phase at a stage when the α_1 plate fully inherited both

order and APD structures of the parent matrix. Yang *et al.*⁽⁹⁾ and Tadaki and Shimizu⁽¹³⁾ observed that the solute composition of the α_1 plate is higher than the equilibrium concentration of the phase boundary in the phase diagram. And, the solute content in the matrix region adjacent to the interfaces is lower than the average of the matrix. This fact can be explained only by assuming a diffusion process involved in the transformation. The above results are well consistent with the other studies⁽¹⁴⁾⁻⁽¹⁷⁾.

The diffusion of solute atoms during growth of the α_1 plate may be caused by the stress field around pre-existing defects⁽¹⁰⁾⁽¹¹⁾. Schmitz *et al.*⁽¹⁸⁾ suggested that elastic anisotropy may play an important role in promoting solute diffusion at defects. As a result, solute depletion may continue to appear at the tip of the α_1 plate, where the stress field may provide an effective driving force⁽¹⁸⁾. Wu *et al.*⁽¹¹⁾ provided a direct experimental confirmation that there appears the solute-depletion region near dislocations adjacent to α_1 plate. Meng *et al.*⁽¹⁹⁾ observed nucleation of the α_1 plate in discontinuous stress field at the α_1 plate tip. Yang *et al.*⁽²⁰⁾ also confirmed the existence of the shear stress field accompanying the α_1 growth. Thus, the combined effect of solute depletion and increasing elastic anisotropy leads to the formation of the solute-depleted region for α_1 shear growth.

As for the formation of the α_1 plate, three experimental conclusions may be drawn 1) the solute-depleted region may appear during incubation period and at the stage of α_1 growth; 2) the α_1 plate inherited the ordering and antiphase domain structures of the parent phase; 3) the α_1 plate had different solute composition with the matrix. Therefore, the displacive mechanism of α_1 transformation was proposed⁽⁶⁾⁻⁽²²⁾. The solute depleted region appeared in the parent phase during the incubation period and then, α_1 plate transformation took

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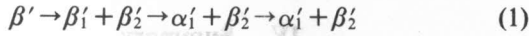
place in this region by martensite-like mechanism. The α_1 plate is not martensite of a diffusionless reaction, because the composition of α_1 is different from that of the original matrix⁽¹³⁾. The transformation of the α_1 plate is a diffusion-controlled shear process.

Hsu and Zhou⁽²³⁾⁽²⁴⁾ proposed a thermodynamic model for α_1 shear formation. The formation of the α_1 plate was considered to be a diffusionless transformation, the same as that of martensite. And, the composition of the α_1 plate is the same as that of the parent matrix. The thermodynamics analysis denied the α_1 shear mechanism because the driving force is positive during the temperature range of α_1 formation.

The purpose of the present paper is to present a thermodynamic analysis to shear model of the α_1 formation in the solute-depleted region in a β' Cu-Zn alloy.

II. Thermodynamic Model

The model for the shear mechanism of α_1 transformation in the solute-depleted region can be expressed as



where β' is the parent matrix with x_0 . β'_1 and β'_2 are the solute-depleted and solute-enriched region with x_d and x_e respectively. α'_1 is the embryo of the α_1 plate both with x_d . x represents the atomic fraction of solute zinc.

The solute atom has tendency of diffusion and segregation towards crystal defects of the parent matrix, such as grain boundaries and dislocations⁽²⁵⁾. The energy change during incubation period, ΔG_1 is

$$\Delta G_1 = \Delta G_s + \Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} \quad (2)$$

where ΔG_s is energy change of defects themselves and $\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2}$ is the Gibbs free energy change attending $\beta' \rightarrow \beta'_1 + \beta'_2$ respectively. ΔG_s is the nonchemical driving force for the formation of solute-depleted regions whereas $\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2}$ is the energy barrier.

The critical condition for the formation of the solute-depleted regions is

$$\Delta G_1 = 0 \quad (3)$$

$\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2}$ can be expressed as

$$\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} = n[G^{\beta'}(x_d) - G^{\beta'}(x_0)] + [G^{\beta'}(x_e) - G^{\beta'}(x_0)] \quad (4)$$

where n and N are the volume fraction of the solute-depleted and solute-enriched region respectively. $G^{\beta'}(x)$ is the Gibbs free energy of β' matrix with composition x .

It is obtained that

$$N(x_e - x_0) = n(x_0 - x_d) \quad (5)$$

Substituting eq. (5) into (4) and dividing by n , in a limited case, $\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2}$ is

$$\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} = G^{\beta'}(x_d) - G^{\beta'}(x_0) + (x_0 - x_d) \frac{dG^{\beta'}}{dx} \quad (6)$$

$G^{\beta'}(x)$ can be expressed as⁽²³⁾

$$G^{\beta'} = G^{\beta} + G^{\beta \rightarrow \beta'} \quad (7)$$

where

$$G^{\beta} = (1 - x_{Zn})G_{Cu} + x_{Zn}G_{Zn} + E^{\beta}(1 - x_{Zn})x_{Zn} + RT[(1 - x_{Zn}) \ln(1 - x_{Zn}) + x_{Zn} \ln x_{Zn}] \quad (8)$$

$$G^{\beta \rightarrow \beta'} = -18425\eta^2 - RT[2(1 - x_{Zn}) \ln(1 - x_{Zn}) + 2x_{Zn} \ln x_{Zn} - (\eta + 1 - x_{Zn}) \ln(\eta + 1 - x_{Zn}) - (x_{Zn} - \eta) \ln(x_{Zn} - \eta) - (x_{Zn} + \eta) \ln(x_{Zn} + \eta) - (1 - \eta - x_{Zn}) \ln(1 - \eta - x_{Zn})] \quad (9)$$

where R and T are the gas constant and absolute temperature respectively. E^{β} (-43014 J/mol) is the interaction parameter in β ⁽²³⁾. η is the order parameter and defined as⁽²³⁾

$$(\eta/0.32)^2 + (T/700)^5 = 1 \quad (10)$$

From eqs. (6) to (10), $\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2}$ is obtained as

$$\begin{aligned} \Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} = & -43014(x_0 - x_d)^2 \\ & + RT\{0.66 \ln[(1 - x_d)/(1 - x_0)] \\ & + 0.66x_d \ln[x_d(1 - x_0)/x_0(1 - x_d)] \\ & + (1 + \eta - x_d) \ln[(1 + \eta - x_0)/(1 + \eta - x_d)] \\ & + (x_d - \eta) \ln[(x_0 - \eta)/(x_d - \eta)] \\ & + (x_d + \eta) \ln[(x_0 + \eta)/(x_d + \eta)] \\ & + (1 - \eta - x_d) \ln[(1 - \eta - x_0)/(1 - \eta - x_d)]\} \\ & / 1.34 \quad (11) \end{aligned}$$

The α_1 plate nucleates in the solute-depleted region by shear mechanism. The free energy change attending this process, ΔG_2 is

$$\Delta G_2 = \Delta G^{\beta'_1 \rightarrow \alpha'_1} + \Delta G^{\alpha'_1 \rightarrow \alpha_1} \quad (12)$$

where $\Delta G^{\beta'_1 \rightarrow \alpha'_1}$ and $\Delta G^{\alpha'_1 \rightarrow \alpha_1}$ are the free energy change attending $\beta'_1 \rightarrow \alpha'_1$ and $\alpha'_1 \rightarrow \alpha_1$ respectively. $\Delta G^{\beta'_1 \rightarrow \alpha'_1}$ is chemical driving force for the α_1 nucleation whereas $\Delta G^{\alpha'_1 \rightarrow \alpha_1}$ is the energy barrier.

From Ref. (23), it is obtained

$$\begin{aligned} \Delta G^{\beta'_1 \rightarrow \alpha'_1} = & 8738\eta^2 - 7232.4 + 20874.32x_d - 13967x_d^2 \\ & + (3.14348 - 3.94061x_d) \\ & \times T - 8.17 \times 10^{-4}x_d T^2 \quad (13) \end{aligned}$$

From eqs. (11) and (13), the total driving force for the α_1 transformation, ΔG is

$$\Delta G = \Delta G_s + \Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} = -\Delta G^{\beta' \rightarrow \beta'_1 + \beta'_2} + \Delta G^{\beta'_1 \rightarrow \alpha'_1} \quad (14)$$

III. Results and Discussion

Figure 1 shows ΔG at various solute depletion concentrations (x_d) in a Cu-42 at%Zn alloy ($x_0 = 0.42$) in terms of eq. (14). The temperature range of the α_1 formation is 473 ~ 673 K⁽¹⁹⁾. It can be seen that ΔG is positive when $x_d = x_0 = 0.42$. It is indicated that the shear mechanism of the α_1 plate the same as martensite is thermodynamically impossible. However, with depleting of solute atoms, i.e., $x_d < x_0$, ΔG will gradually change to

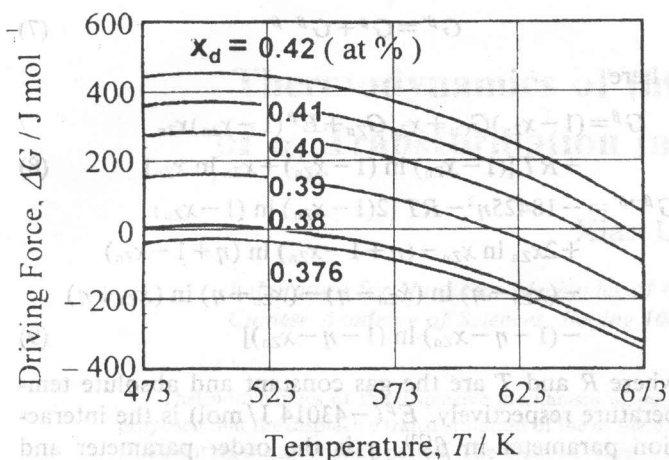


Fig. 1 ΔG vs T in a Cu-42 at% Zn alloy.

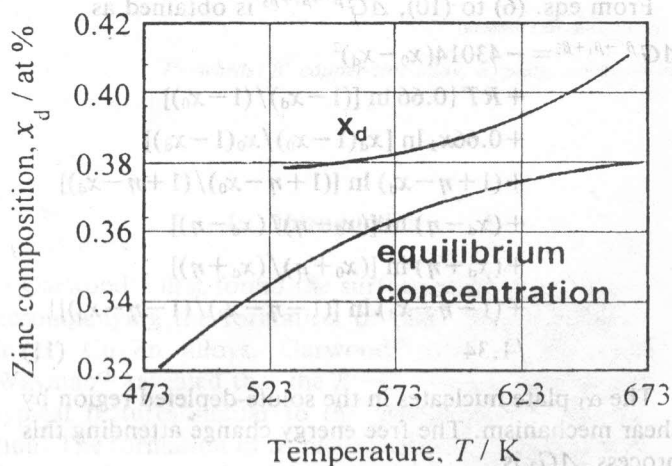


Fig. 2 x_d vs T in a Cu-42 at% Zn alloy.

negative from the high to low temperature. And, ΔG will become wholly negative with solute depletion to a certain degree. *i.e.*, $x_d=0.376$. Kang *et al.*⁽⁸⁾⁽⁹⁾ obtained by ATEM/EDAX that the zinc compositions of the depleted region is about 0.38 at pct at 543 K in the Cu-42 at% Zn alloy. From Fig. 1, it is seen that ΔG is negative. Therefore, the transformation of the α_1 plate may take place thermodynamically by shear mechanism in the solute-depleted region.

The transformation resistance of α_1 plate is lower than that of martensite⁽⁸⁾⁽¹²⁾⁽¹⁶⁾⁽²²⁾. The nonchemical energy for the martensite transformation with a 9R structure is 10.4 J/mol⁽²⁶⁾. Letting $\Delta G = -10.4$ J/mol, the initial concentration of the α_1 plate can be obtained as a function of the reaction temperature, as shown in Fig. 2. The equilibrium zinc concentration of the phase boundary in the phase diagram is also listed. It may be seen that the lower the transformation temperature, the higher the depletion degree. And, the solute concentration of the depleted region is higher than the equilibrium one of the phase boundary in the phase diagram. This means that the α_1 plate has a partially supersaturated composition, consistent with experimental results⁽⁸⁾⁻⁽¹⁴⁾.

Hsu and Zhou⁽²³⁾ also proposed a thermodynamic model of α_1 shear formation. The mechanism is $\beta'(x_0) \rightarrow \alpha_1(x_0)$. This means that β' and α_1 possess the same composition and that α_1 and martensite possess the same shear mechanism. The calculation results showed that the shear formation of α_1 plate is thermodynamically impossible due to the positive driving force. In fact, both α_1 plate and martensite are products of shear transformation. However, it is the solute-depleted region where α_1 plate transforms by martensitic-type displacive mode. As a result, the concentration of the α_1 plate is different from that of the matrix. The α_1 plate only has a partial supersaturation of solute composition, as compared with the parent phase. Different from the martensitic transformation, the formation of the α_1 plate consists of continuous coupling of diffusion and shear. In other words, the formation of the α_1 plate belongs to a diffusion-controlled shear process.

The present thermodynamic consideration is in agreement with the thermodynamic treatment for bainite transformation in Fe-C and Fe-C-X alloys⁽²⁷⁾.

IV. Summary

The shear mechanism of the α_1 formation in the solute-depleted region is thermodynamically analyzed in a β' Cu-Zn alloy. The model is: $\beta' \rightarrow \beta'_1 + \beta'_2 \rightarrow \alpha_1 + \beta'_2$ (β' , β'_1 , β'_2 , and α_1 : the parent phase, the solute-depleted region, solute-enriched region, the embryo of the α_1 plate). The transformation mechanism consists of two steps. The solute-depleted region appears first in the matrix, followed by martensitic-type transformation of α_1 plate. The shear and depletion take place simultaneously. Thermodynamic calculations show that the driving force of the α_1 formation increases with the reduction of zinc concentration of the depleted region and may become negative corresponding to a certain degree of solute depletion within the whole reaction temperature range. As a result, the shear formation of the α_1 plate can be thermodynamically realized.

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Regarding a second phase as elastic inhomogeneities, distributed stresses in a matrix containing rigid spheroidal inhomogeneities are evaluated analytically using the Eshelby method and the Mori-Tanaka theory. The average stresses in the inhomogeneities and surrounding matrix are graphically indicated when the external stresses applied to the composite are axisymmetric. The effects of elastic modulus, shape and volume fraction of the second phase on the variations of the average stresses in the composite are discussed. The results obtained are used to understand the stress states in composites and give us design principles of composites with desirable mechanical properties.

Keywords: composite, elastic deformation, stress distribution, stress state, inhomogeneous, ellipsoidal inhomogeneity, Mori-Tanaka theory, matrix design method, Mori-Tanaka theory, matrix design

Introduction

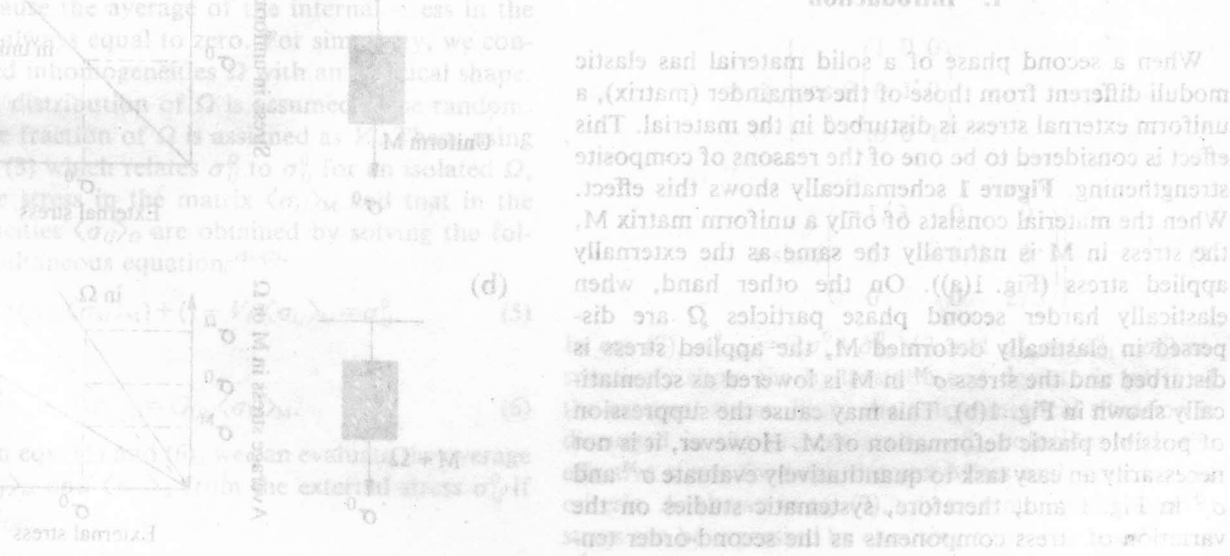


Fig. 1 Schematic diagram showing the stress distribution of an applied external stress to (a) a uniform matrix M, (b) a composite containing rigid spheroidal second phase particles Q embedded in M.

The Eshelby method in micromechanics has shown that the distributed stress in an ellipsoidal inhomogeneity embedded in an infinitely extended matrix becomes uniformly distributed. Using the Mori-Tanaka method for average stress together with Eshelby's theory, the average stresses in the inhomogeneities can be evaluated including elastic interactions between inhomogeneities. Adopting these methods, we will discuss and graphically show the effects of elastic modulus, shape and volume fraction of the second phase on the stress states in a composite under external stresses. Different from simplified experiments, in laboratory, matrix stresses may be loaded to actual composites in real applications. This case is also included in the present analysis as will be seen. The results obtained are useful to find the stress

When an isolated inhomogeneity Q is embedded in the matrix M, the Eshelby method⁽¹⁾ has shown that the external stress σ_0 in Q caused by the application of a uniform external stress σ_0 to M + Q become uniform. The