

A THERMODYNAMIC INVESTIGATION ON SPINODAL DECOMPOSITION BOUNDARY IN Cu-Ti ALLOYS^①

Wei Yinghui, Wang Xiaotian

Institute of Materials Science and Engineering

Xi'an Jiaotong University, Xi'an 710049

ABSTRACT Metastable miscibility gap and spinodal decomposition boundary in Cu-Ti alloys have been established by thermodynamic calculation, in which a developed regular solution model and limited thermodynamic experimental data have been used. It was found that the coherent strain energy has less influence on spinodal decomposition in Cu-Ti alloys, and chemical spinodal decomposition boundary and coherent one are roughly overlapping. The calculated results are in coincidence with other experimental data.

Key words Cu-Ti alloy spinodal decomposition thermodynamics

1 INTRODUCTION

Aged hardening Cu-Ti alloy is a kind of promising electric functional material (for example: IC lead frame materials) due to its high conductivity and strength. There is some investigation on the way of strengthening by spinodal decomposition and ordering in the course of phase separation in Cu-Ti alloys so far^[1]. But there exists considerable controversy in the literature on phase separation, especially on the sequence of ordering and spinodal decomposition. It is a simple and direct way of predicting phase separation path by thermodynamics. Unfortunately, there are few available thermodynamic experimental data for determining metastable miscibility gap, which is an important region for one to understand the phase transformation essence in Cu-Ti alloys. The objective of this investigation is to establish metastable miscibility gap and spinodal decomposition boundary by means of setting up a reasonable thermodynamic model and using limited experimental data.

2 DERIVING AN EXPRESSION FOR ΔG

The general condition for equilibrium of an

isothermal system at constant pressure is given by a minimum value for

$$G = H - TS \quad (1)$$

where G is the Gibbs energy, H the enthalpy and S the entropy. If a total amount of 1 mole of components A and B is mixed, the increase in Gibbs energy of the system is given by

$$\Delta G = \Delta H - T \Delta S \quad (2)$$

where ΔH is the molar enthalpy of mixing and ΔS the molar entropy of mixing. For the case of ideal mixing, $\Delta H = 0$ and ΔS is given by the term of Gibbs so that:

$$\Delta S = -R \left[(1-X) \ln(1-X) + X \ln X \right] \quad (3)$$

where X is the atomic fraction of component B.

Practically in all cases there is, however, a non zero heat of mixing and an entropy of mixing not equalling the Gibbs term. This can be taken into account by putting

$$\begin{aligned} \Delta G &= \Delta G^{id.} + \Delta G^{ex.} \\ \Delta S &= \Delta S^{id.} + \Delta S^{ex.} \end{aligned} \quad (4)$$

and

$$\Delta G^{id.} = RT \left[(1-X) \ln(1-X) + X \ln X \right] \quad (5)$$

With (2) it is easily seen that

$$\Delta G^{ex.} = \Delta H - T \Delta S^{ex.} \quad (6)$$

① Supported by the National Natural Science Foundation of China

Received Oct. 4, 1995; accepted Jan. 17, 1996

This expression has to be zero for $X = 1$ or $X = 0$, whereas on the basis of thermodynamics for these same values the first derivative of ΔG^{ex} with respect to composition must be a finite value. These conditions are fulfilled if ΔG^{ex} is taken as a power series of X which is divisible by $X(1-X)$, thus

$$\Delta G^{ex} = X(1-X)f(X) \quad (7)$$

From the calculations concerning binary mixtures of liquids it turns out that generally experimental values for ΔG^{ex} can be represented with reasonable precision if three terms of the power series are taken into account. Supposing that this might also be the case for the copper titanium system, $f(X)$ must be written as follows:

$$f(X) = A_0 + A_1X + A_2X^2 \quad (8)$$

Moreover, as one is considering a certain temperature range it is advisable to take a temperature influence into account. Therefore, supposing H_i and S_i to be constants, then

$$A_i = R(H_i - TS_i) \quad (9)$$

where R is gas constant

With the aid of the above equations the following expression for ΔG can be expressed as:

$$\Delta G = RX(1-X)[H_0 - TS_0 + X(H_1 - TS_1) + X^2(H_2 - TS_2)] + RT[(1-X)\ln(1-X) + X\ln X] \quad (10)$$

In order to determine the constants of equation (10), six independent equations are necessary. Using the properties of the top of the solid miscibility gap, namely that the second and the third derivative of the Gibbs energy with respect to composition must be zero, thus two equations result, namely

$$\left. \begin{aligned} \Delta G''|_{X=X_0} &= 0 \\ \Delta G'''|_{X=X_0} &= 0 \end{aligned} \right\} \quad (11)$$

$$\left. \begin{aligned} \Delta G'' &= 0 = -2(H_0 - TS_0) + (2 - 6X)(H_1 - TS_1) + (6X - 12X^2)(H_2 - TS_2) + T/[X(1-X)] \\ \Delta G''' &= -6(H_1 - TS_1) + (6 - 24X)(H_2 - TS_2) + (2X - 1)T/[X^2(1-X)^2] \end{aligned} \right\} \quad (12)$$

Furthermore, the variation of partial molar Gibbs energy of component i in solid solution

may be expressed as:

$$\Delta \mu_i = \mu_i - \mu_i^0 \quad (13)$$

where μ_i is partial molar Gibbs energy of component i in the mixture and μ_i^0 the molar Gibbs energy of the pure component i and that

$$\Delta \mu_{Cu} = \Delta G - X(\partial \Delta G / \partial X) \quad (14a)$$

$$\Delta \mu_{Ti} = \Delta G - (1-X) \cdot (\partial \Delta G / \partial X) \quad (14b)$$

The equilibrium conditions for the two equilibrium phase *viz*

$$\left. \begin{aligned} \Delta \mu_{Cu}|_{X_1} &= \Delta \mu_{Cu}|_{X_2} \\ \Delta \mu_{Ti}|_{X_1} &= \Delta \mu_{Ti}|_{X_2} \end{aligned} \right\} \quad (15)$$

provide two other equations, namely:

$$\begin{aligned} &T[\ln(1-X_1) - \ln(1-X_2)] + \\ &[(X_1^2 - X_2^2)(H_0 - TS_0)] + \\ &[X_1^2(2X_1 - 1) - X_2^2(2X_2 - 1)] \cdot \\ &[H_1 - TS_1] + [X_1^3(3X_1 - 2) - \\ &X_2^3(3X_2 - 2)] \cdot [H_2 - TS_2] \\ &= 0 \end{aligned} \quad (16)$$

and

$$\begin{aligned} &T[\ln X_1 - \ln X_2] + \\ &[(1-X_1)^2 - (1-X_2)^2] \cdot \\ &[H_0 - TS_0] + \\ &[2X_1(1-X_1)^2 - 2X_2(1-X_2)^2] \cdot \\ &[H_1 - TS_1] + \\ &[3X_1^2(1-X_1)^2 - 3X_2^2(1-X_2)^2] \cdot \\ &[H_2 - TS_2] = 0 \end{aligned} \quad (17)$$

3 CALCULATION OF THE METASTABLE MISCIBILITY GAP AND SPINODAL DECOMPOSITION BOUNDARY

If introducing available experimental data directly into equations (12), (16) and (17), a comparative error will be led to. By mathematic imitating for experimental data available in References[2] and [3], one may obtain the values of T and x for the top of the solubility gap, namely $T = 1101.78$ K and $x = 4.775\%$ (in atom). Moreover two sets of values obtained from the two phase boundary, namely, $T = 898$ K, $X_1 = 0.02179$, $X_2 = 0.0737$ and $T = 1053$ K, $X_1 = 0.035$, $X_2 = 0.06783$ as given in Reference [2]. By introducing three sets of values mentioned above into equations (12), (16) and

(17) respectively, the following six values for the constants are derived:

$$H_0 = -1.0778 \times 10^5 \quad S_0 = 3.578$$

$$H_1 = -1.479 \times 10^5 \quad S_1 = -17.007$$

$$H_2 = 4.693 \times 10^4 \quad S_2 = 105.93$$

This gives for equation (10), then

$$\Delta G = RX(1-X) \left[-1.0778 \times 10^5 - 3.578T + X(-1.479 \times 10^5 + 17.007T) + X^2(4.693 \times 10^4 - 105.93T) \right] + RT \left[X \ln X + (1-X) \ln(1-X) \right] \quad (18)$$

Let equation (18) be equal to zero, metastable miscibility gap can be obtained as shown in Figure 1, in which chemical spinodal decomposition boundary is also exhibited by determining the variation of solute content with temperature according to equation (12). Some inflexion values of spinodal at various temperature are listed in Table 1.

Fig. 1 Metastable miscibility gap and chemical spinodal decomposition boundary calculated in Cu-Ti alloys

1 —miscibility gap;
2 —chemical spinodal decomposition;
□ —given by Ref. [2]

4 DISCUSSION

In the past, most alloy systems were thermodynamically treated according to the regular solution model. Excess Gibbs mixing energy is given by

$$\Delta G^{ex} = X(1-X)\Omega \quad (20)$$

where Ω being a constant, which is unchanging with solute content and temperature

It is proved that this model is suitable for a few alloy systems. In most cases, Ω is a function of temperature and solute content. In Cu-Ti alloy system, a complex phase transformation process appears due to continuous (or homogeneous) transformation (early stage spinodal decomposition and ordering) and heterogeneous transformation (later stage nucleation and growth), so it is reasonable to treat Ω as a function of temperature and content.

Comparing metastable miscibility gap calculated in the paper with available Cu-Ti alloy phase diagram, it is found that the former locates below titanium equilibrium solubility curve in copper, and the highest temperature of miscibility gap is below eutectic temperature of the Cu-Ti alloys.

Table 1 Inflexion values of spinodal at various temperature

T/K	$T/^{\circ}C$	X_1	X_2
300	27	4.755×10^{-3}	6.748×10^{-2}
400	127	7.000×10^{-3}	6.580×10^{-2}
500	227	9.738×10^{-3}	6.371×10^{-2}
600	327	1.325×10^{-2}	6.100×10^{-2}
700	427	1.800×10^{-2}	5.729×10^{-2}
800	527	2.550×10^{-2}	5.123×10^{-2}

Inflexion values of spinodal at room temperature, obtained by using discriminant $\Delta G'' \leq 0$, are 0.476% and 6.75% (in atom), respectively. It is shown that all Cu-Ti alloys in which titanium content is below the maximum of Ti solubility limit in copper can be separated by spinodal decomposition at certain temperature. This has been proved by a lot of investigations^[1, 2, 4, 5, 6] (See Table 2) There are a series of Ti content and temperature, investigated by some researchers, at which alloys of relevant content are instable to spinodal decomposition. This is in good coincidence with calculated spinodal boundary.

Cahn first considered the influence of coherency internal stresses, which is a decisive

Table 2 Some experiment results on the scope of content and temperature of spinodal decomposition occurring in Cu-Ti alloys

Content / % (in atom)	Temperature / K	Source
2. 07, 4. 05, 6. 77	673~ 823	[2]
1. 32, 5. 24	673~ 773	[4]
3. 7	673~ 723	[5]
3. 29	573~ 773	[6]

factor for the morphology of modulation, on modulated structure in elastically anisotropic materials. Thus, Spinodal boundary determined above using $\Delta G' \leq 0$ is only a chemical spinodal boundary in which a coherent stress was not considered. According to Cahn's theory, discriminant of coherent spinodal is $\Delta G'' + 2\eta^2 YV_m \leq 0$, where $2\eta^2 YV_m$ is the factor of influence of coherent stress on spinodal decomposition, and $\eta = d(\ln a)/dx$, Y the elastic module, V_m the molar volume. If let $\eta = 0.0124 \text{ mol}^{-1}$, (In fact, η is a variation value with solute content. Here is an average one), $Y = 1.148 \times 10^{11} \text{ N} \cdot \text{m}^{-2}$ [7], $V_m = 7.14 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, one may obtain $2\eta^2 YV_m \approx 252 \text{ J}$, which is smaller than $\Delta G''$ so as to be neglected. It is shown that there is less influence of coherent stresses on spinodal decomposition, and chemical spinodal boundary and coherent one are overlapping in Cu-Ti alloys.

It is emphasized that spinodal decomposition is a continuous transformation process, and modulated wavelength is growing continuously at certain temperature even during rapid quenching. The modulated structure is coarsening seriously when aging at higher temperature in short time (a few second). Thereafter, a cellular transformation which belongs to nucleation and growth occurs. Because transformation temperature between spinodal and nucleation growth is difficult to determine due to the content fluctua-

tion in alloy of definite content, temperature at which spinodal occurs is an approximate value. So far, the highest temperature obtained by experiment in Cu-Ti alloys is 823 K [2], which is in good keeping with the calculated results in this paper.

5 CONCLUSIONS

(1) The change of Gibbs energy of solid solution in Cu-Ti alloys may be expressed as follows:

$$\Delta G = RX(1-X) \left[-1.0778 \times 10^5 - 3.578T + X(-1.479 \times 10^5 + 17.007T) + X^2(4.693 \times 10^4 - 105.93T) \right] + RT \left[X \ln X + (1-X) \ln(1-X) \right]$$

(2) Cu-Ti alloys in which titanium content is below the solubility limit of copper are decomposed by spinodal model at the specific scope of temperature.

(3) Coherent strain has less influence on spinodal decomposition of Cu-Ti alloys. Chemical spinodal boundary and coherent one are roughly overlapping.

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(Edited by Lai Haihui)