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Ordering in binary transition metal alloys

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ABSTRACT

We present the phenomenological thermodynamic modeling of binary alloys which demonstrate solubility of the components at high temperatures, and form intermediate phase near equiatomic composition at lower ones (the so-called sigma-phase). Besides, the regular solution miscibility gap takes place also. The nonequilibrium thermodynamic potential is written out as a sum of the free energy of regular solution and polynomial term of scalar order parameter φ, which describes the σ-phase ordering. There are four parameters in the model: the energy of regular solution mixing, the energy of σ-phase formation at zero temperature, and the widths of temperature and concentration intervals of σ-phase existence in the alloy with frozen-in random distribution of components. Up to now, both phase transitions which take place in a number of transition metals binary alloys (the σ-phase formation and miscibility in the regular solution) have been treated separately. In present work, the standard technique of phase diagram calculation allows us to analyze all possible phase diagrams which may arise in the alloy.

1. Introduction

Up to now, the most extended way of analytical description of binary alloys phase diagrams is based on following scheme [1]. First, one has to determine all possible phases in the system, and second, to write out the thermodynamic potentials $G_n(c, T)$ as a function of concentration c and temperature T for each phase numbered by index n. Then, the standard Gibbs procedure allows one to draw out the phase diagram. While modeling, thermodynamic potentials $G_n(c, T)$ are usually being fitted by polynomial spline—functions of concentration in combination with logarithmic terms which account for the mixing entropy. This requires experimental information concerning phase boundaries and enthalpy of mixing at different temperatures. This scheme is simple enough and allows one to use databases of universal form [2]. At the same time, it possesses some disadvantages. The first is a large amount of experimental information which is necessary for the database. One has to know all phases in the system and temperature and concentration ranges of their appearance. Also, to fit the thermodynamic potentials, several points on each phase boundary should be known. Thus, practically whole phase diagram should be known, and the scheme serves to fit the known data. The second one is using of so-called standard states—for some phases, one needs to know the thermodynamic potential at temperatures and concentrations, for which the phase does not exist in the experiment (i.e. is absolutely unstable). Thus, it is difficult to estimate correctly the metastable area of the phase existence.

Alternative way of thermodynamic modeling of binary phase diagrams arises from the phenomenological Landau theory of phase transitions [3]. The theory is based on the concept of order parameter, which corresponds to some symmetry of the system and changes sharply at the phase transition point. For binary system, the analytical calculation scheme looks as follows. First, one has to write out the nonequilibrium thermodynamic potential $G(c, T, \varphi)$ as a function of concentration, temperature and order parameter φ. The last is not obligatory single-component value, but here we suggest so for simplicity. Then, the potential should be minimized with respect to φ:

$$\frac{\partial G}{\partial \varphi} = 0 \tag{1}$$

Eq. (1) may have several solutions $\varphi_1(c, T)$, $\varphi_2(c, T)$, ... which represent several minima of $G(c, T, \varphi)$. These solutions correspond to possible phases in the system, and their temperature and concentration ranges of existence are being determined automatically as the ranges of existence of corresponding solutions. Then, the substitution

$$G_n(c, T) = G(c, T, \varphi_n(c, T)) \tag{2}$$

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gives equilibrium thermodynamic potentials for all phases, and one is able to draw out the phase diagram. The problem to construct the nonequilibrium potential looks difficult as compared with the traditional calculation scheme, but in some cases it may be solved successfully. The most natural way to write out the nonequilibrium potential is statistical modeling. For example, the use of Ising model allows to get the nonequilibrim potential of regular solution [4], its combination with the Potts model allows accounting melting and drawing out all binary diagrams with limited solubility of the components [5]. Phenomenological way of $G(c, T, \varphi)$ construction can be used also. In present work, we use it to model a binary alloy which demonstrates tendency to the phase separation and, simultaneously, forms intermediate phase near equiatomic composition (the so-called sigma-phase).

2. Nonequilibrim thermodynamic potential

Consider A–B binary alloy, which possesses mutual solubility of the components at high temperatures, demonstrate tendency to phase separation and forms intermediate sigma-phase at lower ones. While excluding the sigma-phase, the alloy behaves like a solid regular solution, so that the nonequilibrium thermodynamic potential consists of two terms

$$\begin{aligned} &G(c, T, \varphi) = G_{reg}(c, T) + G_{add}(c, T, \varphi), \\ &G_{reg}(c, T) = \varepsilon c(1-c) + T\{c\ln(c) + (1-c)\ln(1-c)\}, \\ &G_{add}(c, T, \varphi) = 12g\left(\frac{p(c,T)}{2}\varphi^2 - \frac{p(c,T)+1}{3}\varphi^3 + \frac{1}{4}\varphi^4\right). \end{aligned} \tag{3}$$

The first term is the free energy of regular solution, while the second describes first order phase transition between phases with order parameter $\varphi = 0$ and $\varphi = 1$. One can easily derive this inserting (3) into (1). Equilibrium free energies (2) for these phases are

$$G_{\varphi=0}(c, T) = G_{reg}(c, T), \qquad G_{\varphi=1} = G_{reg}(c, T) + 2g\left(p(c, T) - \frac{1}{2}\right). \tag{4}$$

These values are equal to each other when

$$p(c, T) = \frac{1}{2}. \tag{5}$$

This condition determines the line of the phase transition on the $c - T$ plane, when the spatial distribution of components is random and frozen. We will choose the $p(c, T)$ function by following considerations. Let us correspond the $\varphi = 0$ phase to the regular solution of the components, and $\varphi = 1$ one to the ordered sigma-phase. In that case, the order parameter should be interpreted as a volume part of sigma-phase in the system. If the spatial distribution of components is random and frozen, then the ordering should take place on some cupola-like curve at the $c - T$ plane. Therefore, the simplest approximation is

$$p(c, T) = \frac{1}{2} + [T - T_0 + k(c_0 - c)^2], \tag{6}$$

which provides the parabolic cupola. The point (c_0, T_0) is the cupola's maximum, and $2\sqrt{T_0/k}$ is its width at zero temperature. For sigma-phase, $c_0 = 0.5$, so that we got the model with four phenomenological parameters ε, g, k, T_0, which physical sense is as follows. Value $\varepsilon/2$ is the Kournakov temperature [6] of true solution; $2\sqrt{T_0/k}$ is the width of concentration range of the sigma-phase existence at zero temperature, if the spatial distribution of components is random and frozen; T_0 is the maximal temperature of the sigma-phase; $2gT_0$ is the energy difference between true solution and equiatomic sigma-phase at zero temperature. This completes the construction of nonequilibrium potential. Below, we used the temperature scale $T_0 = 1$ and fixed the width

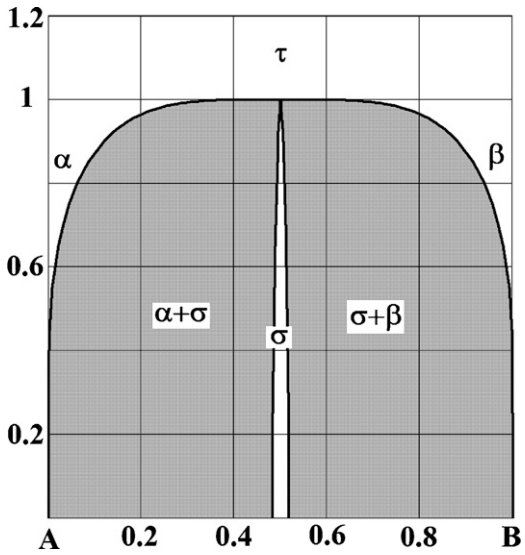

Fig. 1. The phase diagram with intermediate σ-phase and τ-phase above maximal temperature of its existence. Parameters of the model are $\varepsilon = 2$, $g = 0.125$.

$2\sqrt{T_0/k} = 0.4$, so that $k = 25$. Varying the two rest parameters, ε and g, we calculated all possible types of binary phase diagrams with intermediate sigma-phase. The results are presented in the next section.

3. Phase diagrams

To calculate the phase diagram, one needs chemical potentials of the A and B components in each phase. Those may be obtained

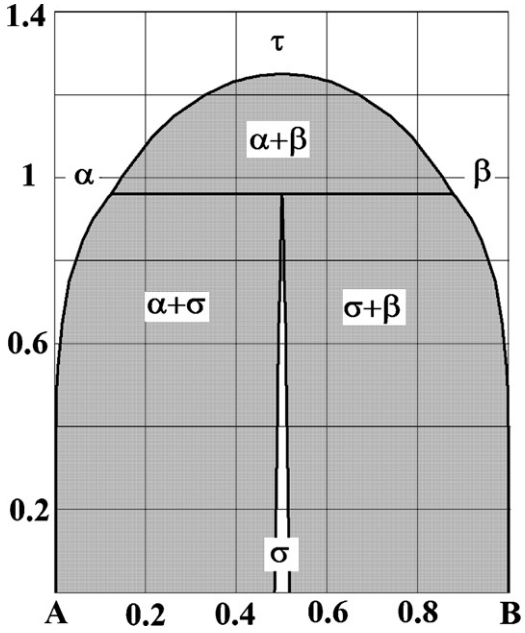

Fig. 2. The temperature range of σ-phase is limited from above by triple α–σ–β equilibrium and true solution miscibility gap. Parameters of the model are $\varepsilon = 2.5$, $g = 0.5$.