

tion has explicitly non-stationary character, growth periods are replaced by stabilization time and even decrease as the reaction cell in the process of synthesis undergoes a number of transformations. Exothermic regions replace the areas with endothermic decay.

The obtained samples of sintered material were tested for hardness. By the results of the experiments and the character of point arrangement the dependences

(Fig. 4) of alloy hardness and rate of combustion front propagation on quantitative content of titanium carbide in the batch are plotted.

At increase of titanium carbide content in the batch the alloy hardness grows and combustion front rate decreases by nonlinear law and the character of dependences changes practically at one and the same value of titanium carbide mass in the batch (4...12 wt. % termite).

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CHANGE IN STABILITY OF SOLID SOLUTION AT RADIATION INFLUENCE

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Stability of solid solution at radiation influence has been investigated. Expressions for diffusion streams of binary alloy components, which specify the existence of temperature interval in which the phenomenon of ascending diffusion of elements is observed, were received. Vacancy characters of diffusion, configuration entropy, and potential energy of atomic bonds were considered at derivation. The ascending diffusion testifies to stability infringement of homogeneous solid solution – stratification. Influence of radiation is connected with increase in concentration of vacancies which changes the energy of atomic bonds and, simultaneously, accelerates diffusion processes. The condition of alloy stability with regard to stratification at radiating influence was obtained.

Radiation of metallic systems with charged particles or neutrons may result in some cases in significant changes of material structural-phase state. Radiation changes temperature of existence of one or another phase, results in change of stability of solid solutions (element segregation, phase dissolution etc.), causes occurrence of new exotic phases [1].

Accumulation of excess vacancies in the volume causing the occurrence of macroscopic elastic tensile stresses is typical for radiation influence. All principle experimentally observed laws of radiative swelling of fine metals were explained by bounded solubility of the excess vacancies in metal matrix [2–4]. From this point of view the solution of the problem of changing temperature of solid solution stability field at radiation is of interest. It is necessary to determine in what way the increased concentrations of vacancies may influence the layering of initially homogeneous solid solution.

1. Diffusive constituent of element streams

Let us consider binary alloy with concentrations of elements n_a and n_b . Let atoms of alloy components be transferred by vacancy mechanism. Diffusive constituents of atom streams are determined by the expressions

$$J_a = \frac{D_a}{n_0} [-n_v \cdot \text{grad}(n_a) + n_a \cdot \text{grad}(n_v)],$$

$$J_b = \frac{D_b}{n_0} [-n_v \cdot \text{grad}(n_b) + n_b \cdot \text{grad}(n_v)]. \quad (1)$$

Here J_a, J_b are the diffusion flows of elements of alloy a and b respectively, D_a, D_b are the coefficients of element diffusion, n_v, n_0 are the concentrations of vacancies and sites of crystal lattice respectively. Equations (1) are obtained by standard method of three planes provided the independence of diffusion process for some elements of alloy.

Taking the simplifying assumption on smallness of vacancy concentration gradient we obtain:

$$\begin{aligned} J_a &= -\frac{n_v}{n_0} D_a \cdot \text{grad}(n_a), \\ J_b &= -\frac{n_v}{n_0} D_b \cdot \text{grad}(n_b). \end{aligned} \quad (2)$$

Then the directed flows of elements caused by gradients of thermodynamic characteristics should be taken into account.

2. Atomic bond energy

Radiation influence results in the fact that thickness of metallic material is influenced by elastic tensile stresses and contains considerable concentrations of excess vacancies. Therefore, the whole range of structural-phase conversions in alloys at radiation should be described within the model of material being at high negative pressures.

The complexity of description of metallic systems in the form of concentrated solid solutions is connected with the problem of determining activity of this or that element in alloy. This complexity may be avoided, however. For this purpose it is sufficient to find the method of calculation of alloy internal energy depending on composition, pressure and concentration of excess vacancies.

To a first approximation a rather simple model in which binding energies of each atom only with nearest neighbors are taken into account at calculation of internal energy may be accepted. Vacancy in metal corresponds to disappearance of those binds which occurred for the atom abandoned crystal lattice site.

Then the description of conditions of layering in the initially homogeneous alloy ab of stoichiometric composition is considered as an example. The obtained results are easily generalized to any homogeneous in initial state metallic system. At the first stage concentrations of atomic bonds of different type (aa , bb , ab) should be calculated

$$n = z \cdot \frac{n_0}{2}; n_{aa} = n \cdot \frac{n_a^2}{n_0^2}; n_{bb} = n \cdot \frac{n_b^2}{n_0^2}; n_{ab} = n \cdot \frac{2 \cdot n_a \cdot n_b}{n_0^2}.$$

Here n is the general concentration of atomic bonds, n_0 is the concentration of crystal lattice site, z is the coordination number.

Let ε_{aa} , ε_{bb} , ε_{ab} be average energies of proper atomic bonds. Then a part of Gibbs energy ΔG_1 determined by density of atomic bond energy may be expressed in the form

$$\Delta G_1 = n[\varepsilon_{aa} \gamma_a^2 + \varepsilon_{bb} \gamma_b^2 + 2\varepsilon_{ab} \gamma_a \gamma_b]; \gamma_a = \frac{n_a}{n_0}; \gamma_b = \frac{n_b}{n_0}.$$

Fraction $\Delta\mu_{xa}$ put into chemical potential of atoms of the type a and connected with atomic bond energy is determined by the expression

$$\Delta\mu_{xa} = \frac{z}{n_0} [(\varepsilon_{aa} + \varepsilon_{bb} - 2\varepsilon_{ab})n_a + (\varepsilon_{ab} - \varepsilon_{bb})n_0].$$

Denoting $\Delta\varepsilon = \varepsilon_{aa} + \varepsilon_{bb} - 2\varepsilon_{ab}$, atomic bond energy contribution may be written down into the value of chemical potential of atoms of the type a :

$$\Delta\mu_{xa} = \frac{z \Delta\varepsilon}{n_0} n_a. \quad (3)$$

If there are excess vacancies with concentration n_v in metallic system then a total number of dangling bonds in the accepted model turns out to be equal to zn_v . Here a possible existence of divacancies is not taken into account. Vacancy formation is accompanied by two processes. Firstly, the value of total concentration of crystal lattice site n_0 (swelling) decreases and, secondly, the atomic bonds existing before disappear. The first reason of changing sum energy of atomic bonds was not taken into account at the first stage. To determine the contribution of split bonds it is necessary to know the type of bonds which were split at vacancy formation. In general case the answer to the raised question is rather difficult. However, it may be assumed that probabilities of split of one or another bond at quasi-equilibrium state obey to Boltzmann distribution. Then probabilities of the fact that bonds of this or that type turn out to be split are determined by the expressions

$$\begin{aligned} \omega_{aa} &= \beta \frac{n_v}{n_0} \exp\left(-\frac{\varepsilon_{aa}}{kT}\right); \quad \omega_{bb} = \beta \frac{n_v}{n_0} \exp\left(-\frac{\varepsilon_{bb}}{kT}\right); \\ \omega_{ab} &= \beta \frac{n_v}{n_0} \exp\left(-\frac{\varepsilon_{ab}}{kT}\right). \end{aligned}$$

Normalization condition has the form

$$z n_v = n_{aa} \omega_{aa} + n_{bb} \omega_{bb} + n_{ab} \omega_{ab}.$$

Normalization factor β equals to

$$\beta = 2 n_0^2 \left[n_a^2 \cdot \exp\left(-\frac{\varepsilon_{aa}}{kT}\right) + n_b^2 \times \right. \\ \left. \times \exp\left(-\frac{\varepsilon_{bb}}{kT}\right) + 2 n_a n_b \cdot \exp\left(-\frac{\varepsilon_{ab}}{kT}\right) \right]^{-1}.$$

Change of chemical potential of atoms of the type a connected with atomic bond energy is determined by the expression

$$\begin{aligned} \Delta\mu_{xa} &= \frac{z n_a}{n_0} \left(\Delta\varepsilon - \frac{\beta n_v}{n_0} \cdot \Delta\varepsilon' \right), \\ \Delta\varepsilon' &= \varepsilon_{aa} \exp\left(-\frac{\varepsilon_{aa}}{kT}\right) + \\ &+ \varepsilon_{bb} \exp\left(-\frac{\varepsilon_{bb}}{kT}\right) - 2\varepsilon_{ab} \exp\left(-\frac{\varepsilon_{ab}}{kT}\right). \end{aligned} \quad (4)$$

The obtained expression (4) in comparison with (3) takes into account the influence of excess vacancies on atom chemical potential.

3. Accounting interdiffusion

Resultant expressions for independent diffusion flows of binary alloy elements have the form:

$$\begin{aligned} J_a &= -\frac{n_v}{n_0} D_a' \left[1 - \frac{z n_a}{n_0 kT} \left(\Delta\varepsilon - \frac{\beta n_v \Delta\varepsilon'}{n_0} \right) \right] \cdot \text{grad } n_a, \\ J_b &= -\frac{n_v}{n_0} D_b' \left[1 - \frac{z n_b}{n_0 kT} \left(\Delta\varepsilon - \frac{\beta n_v \Delta\varepsilon'}{n_0} \right) \right] \cdot \text{grad } n_b. \end{aligned} \quad (5)$$

Flows of components of binary alloy are dependent. At simultaneous motion of different type atoms the Kirkendall effect takes place. The experimentally observed Kirkendall effect consists in flow of crystal as the whole. Such flow rate is determined by the expression

$$V = \frac{1}{n_0} (J_a + J_b).$$

At transition to the reference system moving with rate V relative to the laboratory one the flows of components are equal and directed to the opposite sides:

$$J'_a = -J'_b = \frac{n_b}{n_0} J_a - \frac{n_a}{n_0} J_b. \quad (6)$$

Substituting expressions for flows (5) into (6) we obtain

$$J'_a = -\frac{n_v}{n_0} \left[(D'_a + D'_b) - \tilde{D} \frac{z}{kT} \left(\Delta\varepsilon - \frac{\beta n_v}{n_0} \Delta\varepsilon' \right) \right] \cdot \text{grad } \eta_b,$$

$$\tilde{D} = \frac{D_a n_b + D_b n_a}{n_0}, \quad D'_a = D_{0a} \exp\left(-\frac{E_{ma} + \sigma \Omega_a}{kT}\right).$$

Here D'_a, D'_b are the coefficients of alloy component diffusion subject to the influence of elastic stresses, E_{ma}, E_{mb} are the energies of component migration, Ω_a, Ω_b are the atomic volumes, σ is the value of elastic stresses.

Fulfilling the condition

$$\Delta\varepsilon - \frac{\beta n_v}{n_0} \Delta\varepsilon' \geq \frac{D'_a + D'_b}{z \tilde{D}} \cdot kT = \xi \cdot kT, \quad (7)$$

the process of ascending diffusion of atoms of the type a occurs. It means that fluctuation of atom a concentration does not disappear but starts growing and finally turns into extraction of atoms of the type a . The similar arguments are valid for atoms of the type b . Condition (7) means the excess of energy directed to implementation of layering over the thermal motion energy.

Condition of instability (7) which should be analyzed in each concrete case has the form in expanded form

$$\Delta\varepsilon - 2n_v n_0 \times$$

$$\frac{\varepsilon_{aa} \cdot \exp\left(-\frac{\varepsilon_{aa}}{kT}\right) + \varepsilon_{bb} \cdot \exp\left(-\frac{\varepsilon_{bb}}{kT}\right) - 2\varepsilon_{ab} \cdot \exp\left(-\frac{\varepsilon_{ab}}{kT}\right)}{n_a^2 \cdot \exp\left(-\frac{\varepsilon_{aa}}{kT}\right) + n_b^2 \cdot \exp\left(-\frac{\varepsilon_{bb}}{kT}\right) + 2n_a n_b \cdot \exp\left(-\frac{\varepsilon_{ab}}{kT}\right)} \geq$$

$$\geq \xi \cdot kT. \quad (8)$$

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4. Discussion of the results

Condition (8) seems to be rather complicated for analysis. Though, it may be used at estimation calculations directed to explanation of existing experimental results.

To illustrate the efficiency of the approach to the description of solid solution decomposition proposed in this work let us examine the hypothetic alloy for which $\varepsilon_{aa} = \varepsilon_{bb}$ and $\Delta\varepsilon = 2\varepsilon_{aa} - \varepsilon_{ab}$. Expanding the exponent into series

$$\exp\left(\frac{\varepsilon_{aa} - \varepsilon_{ab}}{kT}\right) \approx 1 + \frac{\Delta\varepsilon}{2kT},$$

and introducing notations $x = \frac{\Delta\varepsilon}{2kT}$, let us transform the equation (8) in the form

$$\varphi(x) = (\gamma_a \gamma_b + \gamma_v) \varepsilon_{ab} \cdot x^2 + \Delta\varepsilon(1 - 2\gamma_v - 2\gamma_a \gamma_b \xi) \cdot x - \Delta\varepsilon \xi \geq 0,$$

where $\gamma_a = \frac{n_a}{n_0}$, $\gamma_b = \frac{n_b}{n_0}$, $\gamma_v = \frac{n_v}{n_0}$.

The diagram of dependence $\varphi(x)$ is presented qualitatively in the Figure.

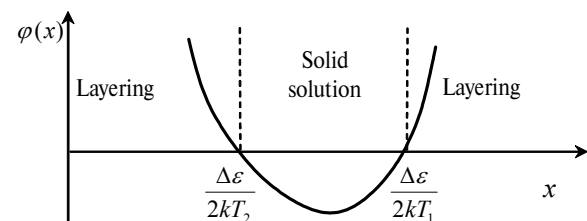


Figure. Graphic expression of solid solution stability field

In general case the whole interval of changing x (and therefore, T) is divided into three areas. Layering in initially homogeneous solid solution is observed in the field limited by critical temperatures $T_1 \leq T_{sp} \leq T_2$. Values of critical temperatures are searched as solutions of quadratic equation $\varphi(x_{sp}) = 0$. Critical temperatures change at change of concentration of excess vacancies created by radiation. The given example shows that the developed phenomenological approach is suitable for explanation of the experimentally observed results of solid solution layering and influence of increased concentrations of excess vacancies on this layering. To analyze the layering of concrete alloys it is necessary to use the condition (8).

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