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THERMODYNAMIC METHOD OF CALCULATING THE EFFECT OF ALLOYING ADDITIVES ON INTERPHASE INTERACTION IN COMPOSITE MATERIALS

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16. Abstract
The effect of alloying additives to the matrix of a composite on the high-temperature solubility rate of a single-component fiber was analyzed thermodynamically. With an example of binary Ni alloys, with Group IV-VI transition metals reinforced with W-fibers, agreement between the calculated and experimental data was demonstrated.

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THERMODYNAMIC METHOD OF CALCULATING THE EFFECT OF ALLOYING ADDITIVES ON INTERPHASE INTERACTION IN COMPOSITE MATERIALS

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Carried out herein is the thermodynamic analysis of the effect of alloying additives, introduced into the matrix of a composite material, on the rate of high-temperature solubility of single-component fibers in the matrix. It is proposed that the effect of the alloying additives be evaluated using the coefficient of effect $K_f^{(i)}$, and an expression is obtained for calculating this coefficient. The sign and absolute magnitude of $K_f^{(i)}$ make is possible to compare the effect of various alloying elements on the rate of interphase interaction in the compounds. The results of the experiments are found to be in agreement with the results of the calculations. /121*

A composite material in the thermodynamic plane is a heterogeneous system, consisting of two or more phases, which have a varying physical nature and structure, for which the presence of a network of internal interfaces, concentration gradients and internal stresses is characteristic. All of this leads, in the general case, to thermodynamic instability of the compound, a clear-cut manifestation of which is the interphase interaction of the components, both in the course of the technological cycle and in the operational process. The interphase interaction is accompanied by the formation of diffusion zones at the interface, which, in many cases, lead to undesirable phenomena — embrittlement of the material, reduction in its strength, and so on.

It is common knowledge that alloying of a matrix may substantially reduce the rate of dissolution of the fibers. It is clear that the effect of the alloying additives may alse be inverse, i.e., it may lead to intensification of the interphase

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*Numbers in the margin indicate pagination in the foreign text.

interaction. This depends on the nature of the matrix, the fibers and the alloying elements. The selection of the alloying additives should be directed, and the bases for such a selection may be thermodynamic criteria, the utilization of which makes it possible to predict the effect of alloying on the rate of the interphase interaction, and to select, from an entire spectrum of alloying variants, those which will direct the process of diffusion interaction in the required direction, and will make it possible to locate the rational areas for experimental search.

We will examine a composite material, reinforced with fibers, consisting of a single-component substance (we will designate this substance by the letter f). The matrix of the composite material is a solid solution based on component 1, in which small concentrations N_f of the substance f and N_ι of the alloying additive ι are dissolved.

We will assume that, with high-temperature interphase interaction, only dissolution of the fiber in the matrix is observed, while the components of the matrix alloy in the fiber are not dissolved.

Our task is to select the quantitative thermodynamic criterion /122 which could be used, without carrying out special experiments, to indicate *a priori* that the introduction of some alloying additive or another will accelerate or slow the dissolution of the fiber in the matrix.

The driving force of the process of dissolution of the fiber in the matrix is the difference in the chemical potentials of the substance of which the fiber consists, both in the matrix and in the fiber itself. The higher this difference, the more intensely the dissolution takes place. Thus, the dissolution of the fiber will be intensified by those alloying additives which reduce its chemical potential in the matrix alloy, and the rate of dissolution will be decreased by the components which increase its chemical potential in the matrix.

We will examine to what the difference in chemical potentials of the substance f is equal in the binary solution 1-f and in the ternary solution 1-f-ι, which contains the very same atomic share of the component f as the binary solution. In this case, we will assume that $N_f \ll 1$ and $N_\iota \ll 1$, and that both solutions are regular.

The magnitude of the chemical potential $\mu_f^{(b)}$ of the substance f in the regular binary solution 1-f may be expressed by the relationship [1]

$$\mu_f^{(b)} = \mu_f^{(0)} + RT \ln N_f + \Omega_{1f}(1-N_f)^2 \qquad (1)$$

Here, $\mu_f^{(0)}$ is the chemical potential of the pure substance f; R is the universal gas constant; T is the absolute temperature; Ω_{1f} is the parameter of interaction of the components in the regular binary solution 1-f, which does not depend on the temperature and concentration.

The expression for the chemical potential $\mu_f^{(T)}$ of the substance f in the three-component regular solution has the form [1]

$$\mu_f^{(T)} = \mu_f^{(0)} + RT \ln N_f + \Omega_{1f}(1-N_f)^2 + \Omega_{1\iota} N_\iota^2 - (\Omega_{1f} + \Omega_{1\iota} - \Omega_{\iota f}) N_\iota (1-N_f) \qquad (2)$$

where $\Omega_{1\iota}$ and $\Omega_{\iota f}$ are the parameters of interaction of the components in the regular binary solutions 1-ι and ι-f, respectively.

If $N_\iota \ll 1$ and the magnitude N_f in the two- and three-component solutions is identical, then, subtracting (1) from (2), we obtain

$$\mu_f^{(T)} - \mu_f^{(b)} = \Omega_{1\iota} N_\iota^2 - (\Omega_{1f} + \Omega_{1\iota} - \Omega_{\iota f}) N_\iota - (\Omega_{1f} + \Omega_{1\iota} - \Omega_{\iota f}) N_\iota N_f \qquad (3)$$

The difference in the chemical potentials $\mu_f^{(T)} - \mu_f^{(\iota)}$ may also be expressed through the activity of the components

$$\mu_f^{(T)} - \mu_f^{(\iota)} = (\mu_f^{(0)} + RT \ln a_f^{(T)}) - (\mu_f^{(0)} + RT \ln a_f^{(b)}) = RT(\ln a_f^{(T)} - \ln a_f^{(b)}) \qquad (4)$$

Here, $a_f^{(T)}$ and $a_f^{(b)}$ are the activities of the substance f in the ternary and binary solutions.

As is common knowledge, the activity of the component f is associated with its concentration N_f and the coefficient of activity β_f by the relationship

$$a_f = \beta_f N_f \tag{5}$$

In the general case, β_f is a function of the concentrations of the substance f and the alloying additives, but if these concentrations are small, then, in accordance with [2], the magnitude of β_f for the examined ternary solution may be represented in the form

$$\beta_f = \gamma_f \beta_f^{(\iota)} \tag{6}$$

where γ_f is the coefficient of activity of the substance f in the binary solution 1-f; $\beta_f^{(\iota)}$ is the coefficient of activity of the substance f in the ternary solution 1-f-ι, brought about by the effect of only the alloying additive ι (in other words, it is the /123 coefficient of activity of the substance f in the ternary alloy 1-f-ι, if the binary solution 1-f, with the very same concentration of the component f as in the ternary alloy 1-f-ι, is selected as the standard state).

Thus, the activities of the substance f in the binary and ternay solutions may be expressed by the relationships

$$a_f^{(b)} = \gamma_f N_f \tag{7}$$

$$a_f^{(T)} = \beta_f^{(T)} N_f \tag{8}$$

By substituting (7) and (8) into (4), with regard for (6), we obtain

$$\mu_f^{(T)} - \mu_f^{(b)} = RT(\ln \beta_f^{(T)} - \ln \gamma_f) = RT \ln \frac{\beta_f^{(T)}}{\gamma_f} = RT \ln \beta_f^{(\iota)} \tag{9}$$

From comparison of (3) and (9), it follows that

$$\ln \beta_f^{(\iota)} = [\Omega_{1\iota} N_\iota^2 - (\Omega_{1f} + \Omega_{1\iota} - \Omega_{\iota f})(1 - N_f) N_\iota]/RT \tag{10}$$

Disregarding the terms of the second order of triviality, and taking into account the fact that $N_f \ll 1$, one may obtain the following approximate relationship from (10):

$$\ln \beta_f^{(\iota)} \approx \frac{\Omega_{\iota f}-(\Omega_{1\iota}+\Omega_{1f})}{RT} N_\iota - \frac{K_f^{(\iota)}}{T} N_\iota \qquad (11)$$

Here

$$K_f^{(\iota)} = \frac{\Omega_{\iota f}-(\Omega_{1\iota}+\Omega_{1f})}{R} \qquad (12)$$

The coefficient $K_f^{(\iota)}$, which does not depend on the concentration and temperature, will be called the coefficient of effect of the alloying additive on the activity of the substance f in the matrix (or, in abbreviated form, the coefficient of effect).

As follows from (11), the logarithm of the coefficient of activity $\beta_f^{(\iota)}$, in the first approximation, is proportional to the magnitude $K_f^{(\iota)}$ and the concentration of the alloying additive N_ι.

This result is in accordance with the law of I. M. Sechenov [3], obtained for solutions of gases and liquids.

As is common knowledge [4], the parameter of interaction Ω_{1j} in the binary system 1-j is associated with the relative partial heat of dissolution $\Delta\overline{H}_{j-1}$ of the element j in the solvent 1 by the relationship

$$\Delta H_{j-1} \approx \Omega_{1j}(1-N_j)^2 \qquad (13)$$

When $N_j \ll 1$, the approximation $\Delta\overline{H}_{j-1} \approx \Omega_{1j}$ is correct, and, for diluted solutions, expression (12) may be written in the form

$$K_f^{(\iota)} \approx \frac{\Delta H_{f-\iota}-(\Delta H_{f-1}+\Delta H_{\iota-1})}{R} \qquad (14)$$

Here, $\Delta\overline{H}_{f-\iota}$, $\Delta\overline{H}_{f-1}$ and $\Delta\overline{H}_{\iota-1}$ are the relative partial enthalpy of dissolution of the substance of the fiber ι in the alloying metal ι, the substance f in the solvent 1, and the alloying additive ι in the solvent 1, respectively.

If $K_f^{(\iota)}>0$, then $\beta_f^{(\iota)}>1$, and, consequently, the alloying additive will increase the activity (and, hence, the chemical potential) of the substance f in the matrix, i.e., it will increase the stability of the fiber—matrix system. The greater the absolute magnitude of $K_f^{(\iota)}$, the more strongly pronounced the effect of the alloying element will be.

If $K_f^{(\iota)}<0$, then $\beta_f^{(\iota)}<1$, and the introduction of the alloying additive ι will evoke more intense dissolution of the fiber in the three-component matrix 1-f-ι, as compared with the two-component /124 matrix 1-f. The greater the modulus $K_f^{(\iota)}$, the more intensely the interphase interaction will take place.

Thus, the sign and magnitude of the coefficient of effect may serve as the criterion which can be used to compare the effect of the alloying additives on the rate of dissolution of the fibers in the matrix. By virtue of the approximate nature of the assumption that actual alloys obey the laws of regular solutions, an accurate quantitative calculation is, in the majority of cases, impossible; however, even approximately calculated values of $K_f^{(\iota)}$ may give the experimenter very important information on the rational direction of the studies. Information on the effect of alloying additives on the solubility of a substance f may be obtained from the diagrams of state of the ternary systems 1-f-ι as well; however, first, the necessary sections of the diagrams are absent for a number of practically important systems, and second, it is impossible to draw information on the effect of alloying additives on the rate of occurrence of the processes of dissolution of the fibers in the matrix directly from the diagrams of state, whereas the utilization of the criterion $K_f^{(\iota)}$ makes it possible to obtain such information and to construct "effect series" of the alloying additives, in which these additives are placed in order of increase or diminution of their effect on the rate of dissolution of the fibers.

The physical sense of the criterion $K_f^{(\iota)}$ may be ascertained if one makes use of the quasichemical interpretation of regular solutions. As is common knowledge [4], the parameter of interaction Ω_{ij} of the components i and j of a regular binary solution may be represented in the form of a function of the bonding energy of the various pairs of atoms

$$\Omega_{ij} = Zn_0 \left[E_{ij} - \frac{1}{2} (E_{ii} + E_{jj}) \right] \tag{15}$$

where Z is the coordination number; n_0 is the number of atoms in the Γ-atom of the solution; E_{ij}, E_{ii} and E_{jj} are the bonding energy between the atoms i-j, i-i and j-j, respectively.

Substitution of (15) into (12) leads to the relationship

$$K_f = \frac{Zn_0}{R} [(E_{\iota f} + E_{11}) - (E_{1\iota} + E_{1f})] \tag{16}$$

Thus, if the sum of the bonding energies of the solvent—solvent (E_{11}) and the alloying additive—fiber ($E_{\iota f}$) atoms will be greater than the sum of the bonding energies of the solvent—alloying additive ($E_{1\iota}$) and solvent—fiber (E_{1f}) atoms, then the alloying will lead to an increase in the thermodynamic stability of the compound, insofar as $K_f^{(\iota)}$ will be positive. In the opposite case, the introduction of an alloying element will evoke a reduction in the stability of the compound material, insofar as $K_f^{(\iota)}$ will be negative.

As is evident from formula (12), the magnitude of $K_f^{(\iota)}$ may be calculated if the parameters of interaction of the binary systems 1-f, 1-ι and ι-f are known.

These parameters are usually determined by experimental means. However, such an approach is very time-consuming, and does not provide perceptible advantages, as compared with direct experimental study of the effect of alloying additives on the kinetics of dissolution of fibers in the matrix.

If one calculates $K_f^{(\iota)}$ according to formula (14), then the values of the relative partial heats of dissolution may be calculated by means of development of the diagrams of state of the corresponding binary solutions. However, unfortunately, not all types of diagrams make is possible to obtain the necessary data for carrying out the indicated calculations. In recent years, thanks to the work done by L. Kaufman and Kh. Bernstain [1], it has become possible to /125 calculate the parameters of interaction for a broad sphere of binary systems. Utilizing the idea of "competition of phases" of various structures, the authors of [1], on the basis of data obtained during the study of the phase transitions at high pressures, carried out the estimated calculation of the difference in enthalpy for the majority of transition metals in the three crystalline modifications: face-centered cubic lattice, body-centered cubic lattice and close-packed hexagonal.

The utilization of these data made it possible to represent the parameters of interactions, which determine the behavior of regular binary solutions of transition metals of periods V and VI, in the form of functions of the group number of the elements in the Mendeleev table, their enthalpy of volatilization, atomic volumes and the difference in the phase enthalpy in various crystalline modifications.

We calculated the parameters of interaction according to the method of Kaufman and Bernstain for binary systems formed by transition metals of periods IV-VI. The obtained values of the parameters of interaction were utilized for substitution into formula (12).

Given in the table are the calculated values of the coefficients of effect of alloying additives $K_f^{(i)}$ for the compounds Ni—W, Co—W, Nb—W, Ti—W and Ti—Mo. Examined as alloying additives are Ti, V, Cr, Fe, Co, Ni, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir and Pt. We will compare the results of the calculation with the available experimental data on the effect of alloying additives on the rate of dissolution of tungsten fibers in a nickel matrix.

It follows from analysis of the results of the calculation that alloying of nickel with elements of period IV, which stand to the left of nickel in the Mendeleev table (Ti, V, Cr, Mn, Fe, Co),

COEFFICIENTS OF EFFECT OF ALLOYING ADDITIVES

Compound Ni—W		Compound Co—W		Compound Cr—W		Compound Nb—W		Compound Ti—W		Compound Ti—Mo	
Alloying Element	Coeff. of effect K_f', deg.	Alloying Element	Coeff. of effect K_f', deg.	Alloying Element	Coeff. of effect K_f', deg.	Alloying Element	Coeff. of effect K_f', deg.	Alloying Element	Coeff. of effect K_f', deg.	Alloying Element	Coeff. of effect K_f', deg.
Zr	38800	Zr	40300	V	−400	Pd	17800	Pd	13500	Co	11800
Hf	38300	Hf	30800	Ni	−500	Fe	16900	Co	10000	Pd	8700
Al	23500	V	22000	Fe	−600	Ni	16800	Rh	9300	—	—
V	23400	Ti	20300	Co	−600	Al	15700	Pt	8500	Rh	7100
Ti	20300	Nb	19400	Zr	−700	Os	15300	Ni	7600	Ir	5500
Nb	19800	Ta	18500	Hf	−1400	Ru	15200	Ir	6800	Pt	5500
Ta	18800	Cr	9000	Ti	−2100	Rh	14900	Al	3500	Ni	4400
Cr	9500	Mo	4100	Rh	−3000	Co	14600	Zr	2200	Zr	1600
Mo	4500	Fe	−100	Pt	−3200	Ir	13900	Hf	900	—	—
Mn	700	Ni	−200	Ru	−4700	Zr	3500	V	−4600	Hf	800
Fe	300	Pd	−400	Ir	−4800	Hf	2800	Cr	−4800	Re	−1400
Co	200	Rh	−2800	Os	−5200	Re	2700	Ru	−4900	Ru	−1700
Pd	−400	Pt	−3600	Nb	−5300	Ti	2100	Os	−5100	Os	−1800
Rh	−2600	Ru	−3800	Mo	−5500	Cr	−600	Ni	−5200	V	−2200
Ru	−3400	Ir	−4200	Ta	−6500	V	−800	Re	−5300	Ta	−2700
Pt	−3500	Os	−4700	Re	−6700			Ta	−5500	Nb	−2900
Os	−4000	Re	−7200					Mo	−7000	Cr	−3600
Ir	−4100										
Re	−6900										

should promote an increase in the stability of the Ni—W compound, and, the further to the left the element stands, the greater the effect it has on the stability of the system.

Of the number of examined transition metals of periods V and VI, the alloying elements, which stand to the left of tungsten (Zr, /126 Hf, Nb, Ta), should promote an increase in the thermal stability of the Ni—W compound. The solid solution based on nickel with elements of periods V and VI, located to the right of tungsten (Ru, Rh, Pd, Re, Os, Ir, Pt), should form less stable compounds with tungsten fibers than the compounds with a matrix of pure nickel.

It was shown in study [5] that the introduction of chromium into nickel-tungsten alloys leads to a substantial decrease in the rate of dissolution of the tungsten fibers. With an increase in the chromium concentration, the rate of interphase interaction falls. In compounds, with a matrix composition corresponding to maximallysaturated ternary nickel alloys, the diffusion zones were not detected after 100 hours of annealing at 1100 and 1200° C. This makes it possible to draw a conclusion on the stability of the interphase boundary in such composites.

From study [6], it is known that alloys of nickel with titanium dissolve tungsten fibers much more slowly than pure nickel, and the rate of dissolution of tungsten filaments in alloys containing more than 38% Ti is so low that the diffusion zone is not detected, even after impregnation of the fibers with a liquid matrix.

It has also been established experimentally [7] that matrices of nickel alloys with iron dissolve tungsten fibers more slowly than pure nickel.

It is shown in [8] that the utilization of Nichrome, with small additives of aluminum and titanium (alloy EI 435), as a matrix considerably reduced the rate of dissolution of tungsten fittings, as compared with a matrix of pure nickel.

It is also common knowledge [9] that Mn additives promote an increase in the structural stability of a nickel—tungsten compound.

Thus, the available experimental data are in qualitiative agreement with the results of theoretical analysis.

Conclusions

The effect of alloying additives, introduced into the matrix of a composition material, on the rate of dissolution of fibers in it may be evaluated quantitatively using the thermodynamic coefficients proposed in the article, which can be calculated according to the parameters of interaction of the corresponding regular binary solutions. The sign and absolute magnitude of these coefficients make it possible to compare the effect of various alloying elements on the rate of interphase interaction in the compounds. Using an example of alloying of nickel, reinforced with tungsten fibers, the qualitative agreement of the results of the calculation with the experimental data is shown.

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