

CONTACT INTERACTION AT THE COMPOSITES INTERFACES BETWEEN THE MICROCRYSTALLINE PARTICULATE AND THE MOLTEN MATRIX

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The peculiarities in structure formation of interfacial zones at the composite's boundaries between the molten Fe–C–B–P–Mo matrix and the filler's solid phases of W_2C and WC that have microcrystalline structure were investigated in this work. The structure of the interfaces was studied by methods of metallographic and automatized quantitative analyses. The interfaces of dissolution-and-diffusion type were observed between the matrix and the filler. A dissolution rate of the filler's microcrystalline phases of W_2C and WC was shown to decrease by ~ 1.7 – 1.8 times as against that of the crystalline phases of the same composition. This result was explained considering the dependence of an average shift of atoms from the equilibrium positions in the lattice on linear size of the phases. Since the average size of the microcrystalline phases is ~ 25 times smaller than that of the crystalline phases, the average shift of microcrystalline phase atoms from the equilibrium positions decreases by ~ 1.7 times. Correspondingly, the microcrystalline particulate dissolves in the molten matrix at the lower rate than crystalline one which prevents from formation of undesirable brittle compounds in the structure of composite's interfacial zones during infiltration.

Keywords: interfaces, microcrystalline phases, dissolution rate, size of phases, average shift of atoms.

Received 02.11.2018; Received in revised form 8.12.2018; Accepted 21.12.2018

1. Introduction

Over the past years, the composite materials find the wide application as coatings to protect and restore the quick-worn parts of the equipment [1]. These materials represent a heterogeneous system which is characterized by thermodynamic instability due to the presence of the developed internal interfaces. The instability results in the interface interaction of the components in the processes of production and performance of the composite coatings, which can lead to the formation of new undesirable phases at the interfaces, thus deteriorating the service characteristics. Therefore, strict control of the course of interfacial reactions occurring between the particulate and matrix is essential.

Among the particulate for macroheterogeneous composite materials, special attention is given to eutectic W–C alloy because of its attractive properties of high melting point, strength and hardness. The Fe–B–C–P–Mo alloy offers properties that makes it an attractive choice for a matrix. These properties include fluidity, retention at elevated temperatures, excellent wear, corrosion and oxidation resistance. However, the particulate/matrix interface is the most critical region in these composites since infiltration is carried out at high temperatures [2]. The exposure to molten matrix may severe degrade the particulate and result in extensive interfacial reactions [3]. To slow down the particulate/matrix reactions between the W–C filler and iron-base matrices, authors [4] applied spherical W–C particles obtained by a method of rotating electrode to produce the composites. The intensity of interfacial reactions was reported to decrease due to the reduction in the particulate surface contacting with molten matrix, with no attention being given to structural changes caused by an increase in a cooling rate of the particulate up to 10^3 – 10^4 K/s. Therefore, the aim of this work is to assess the influence of the cooling rate of the W–C particulate on their structure and the course of the interface interaction with the Fe–B–C–P–Mo matrix in the process of infiltration.

2. Experimental procedure

The macroheterogeneous composites were fabricated by infiltration of the W–C particulate by the eutectic Fe–1.8B–3C–1P–0.5Mo molten matrix alloy at 1180° C for 30 minutes. The used particulate, produced by the method of rotating electrode [4], had

spherical shape and was 0.5 to 2.0 mm in size. The cooling rate of the W–C particulate was $2 \cdot 10^3$ – 10^4 K/s. Optical microscopy and automatized method of quantitative analysis [5] were employed to investigate the specimens.

3. Results and discussion

Infiltration of the W–C particulate by the Fe–B–C–P–Mo matrix ensures the production of macroheterogeneous structure of the composite material (fig.1,a). All the specimens contain 50 to 60 vol. pct. of particulate embedded in the matrix. The microcrystalline W_2C and WC phases are observed in the particulate structure. With increasing cooling rate of the particulate from 10–20 to $2 \cdot 10^3$ – 10^4 K/s, the average size of the W_2C and WC phases decreases from 15 to 0.6 μm . The interfacial zones produced due to the dissolution and diffusion processes appear around the microcrystalline particulate. From graphical model of the interfacial zones built with applying automatized method can be concluded that their width decreases by ~ 1.7 – 1.8 times as compared with that around the crystalline particulate cooled at 10–20 K/s (fig. 1,b), which is indicative of the decrease in the dissolution rate of microcrystalline phases in the infiltrating matrix.

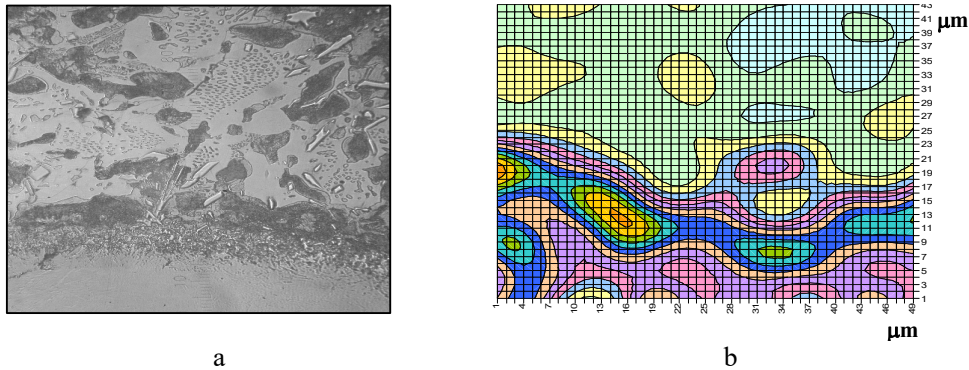


Fig. 1. Microstructure, x400 (a) and two-dimensional graphical model (b) of the interfacial zone between the microcrystalline W–C particulate and Fe–C–B–P–Mo matrix

The narrowing of the interfacial zone can be related to the differences in the dynamic characteristics of thermal expansion of the crystalline and the microcrystalline particulate exposed to the molten matrix. Therefore, the decrease in the average size of the microcrystalline phases by up to 25 times should be taken into consideration.

To explain experimental results, the classical concepts of statistical physics concerning a set of oscillators can be applied. We deal with a classical oscillator considering anharmonic terms of the formula for potential energy expressed by an average shift $\langle x \rangle$ of atoms from the equilibrium positions at temperature T .

Potential energy $U(x)$ of classical oscillator with anharmonic terms considered can be written as [6]

$$U(x) = cx^2 - gx^3, \quad (1)$$

where c – constant, g – coefficient that describes the asymmetry of mutual repulsion of the atoms.

The larger the average shift $\langle x \rangle$ of the particulate atoms from the equilibrium positions under the effect of molten matrix, the higher will be a dissolution rate of the phases exposed to melts. After applying classical Gibbs distribution and passing from discrete to continuous energy levels, the average shift of the atoms can be expressed as

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-\frac{U(x)}{kT}} dx}{\int_{-\infty}^{\infty} e^{-\frac{U(x)}{kT}} dx} \quad (2)$$

Under the integral of a denominator, the potential energy can be considered as harmonic, that is $U(x)=cx^2$, and then

$$\int_{-\infty}^{\infty} e^{-\frac{cx^2}{kT}} dx = \sqrt{\frac{\pi kT}{c}} \quad (3)$$

The integral of a numerator can be correspondingly expanded up to anharmonic term as follows [7]

$$\begin{aligned} \int_{-\infty}^{\infty} \exp\left(-\frac{cx^2}{kT}\right) \left(x + \frac{1}{kT} gx^4\right) dx &= \int_{-\infty}^{\infty} \exp\left(-\frac{cx^2}{kT}\right) x dx + \frac{g}{kT} \int_{-\infty}^{\infty} \exp\left(-\frac{cx^2}{kT}\right) x^4 dx = \\ &= \frac{1}{2} c^{-1} \Gamma(1) + \frac{g}{kT} \frac{1}{2} c^{-\frac{4+1}{2}} \Gamma\left(\frac{4+1}{2}\right) = \frac{3\pi^{1/2}}{4} \frac{g}{c^{3/2}} (kT)^{3/2}, \end{aligned} \quad (4)$$

where $\Gamma(x)$ – gamma function.

Finally, after dividing (4) by the denominator integral, we obtain

$$\langle x \rangle = \frac{3g}{4c^2} kT \quad (5)$$

We proceed on the assumption that the harmonic coefficient c does not practically change for the crystalline and the microcrystalline phases, but the coefficient g depends on their linear size. Then, we can estimate the interface interaction from the relationship between the force constants of dispersive law and the result long-range forces, i.e. we can evaluate the influence of the size of the phases on long-range forces superposition.

The dispersive law, i.e. the dependence of an oscillation frequency of the model mass-uniform spheres of the crystal lattice, can be written as [6]

$$\omega^2 = \frac{a}{M} \sum_p B_p (1 - \cos pka), \quad (6)$$

where ω – oscillation frequency, M – mass of the corresponding layer of the crystal lattice, B_p – force constant that considers the interaction of the layer in which the oscillation frequency is calculated with the atomic plane p located at a distance pa , a – lattice constant, k – wave vector.

If we multiply the right and the left sides of the equation (6) by $\cos rka$ (r – integer from the array to which p values belong) and integrate with respect to k in the first Brillouin zone, we obtain

$$M \int_{-\pi/a}^{\pi/a} \omega_k^2 \cos rka dk = 2 \sum_{p>0} B_p \int_{-\pi/a}^{\pi/a} (1 - \cos pka) \cos rka dk = -2\pi B_p / a \quad (7)$$

where ω_k – oscillation frequency of the wave vector k .

All the integrals in the sum over p are equal to zero, apart from that for which $p=r$. Then, the force constant B_p can be expressed in terms of Fourier cosine-transformation as a function of k and a . The coefficient g can be estimated by the force constant B_p that appears in the expression of dispersive law

$$B_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} \omega_k^2 \cos pkadk . \quad (8)$$

At that time, to a first approximation, the coefficient g is directly connected with the constant B_p that is proportional to a layer mass expressed by the second power of the linear size l of phases. If we consider the possibility of the similar structure of the next layers in two perpendicular directions to the previous layer, the integral dependence of lattice interlayer interaction can be expressed as linear size l raised to the sixth power. And, if we further estimate the value of the coefficient g that represents the asymmetry of atom mutual repulsion as the value re-calculated to the overall mass of the phase per an atom, the dependence can be expressed as

$$g \approx \text{const } l^{1/6}. \quad (9)$$

Considering the smaller size of the microcrystalline phase (by ~ 25 times on average) as against that of the crystalline phase, we obtain that g decreases by $\sim 25^{1/6} \approx 1.7$ times. Further, applying relationship (9) to expression (5), we may conclude that the average shift of the microcrystalline particulate atoms from the equilibrium positions decreases to the same extent. That is why, the average dissolution rate of the microcrystalline phases is also ~ 1.7 times lower than that of the crystalline phases which is in a good coincidence with experimental results. Thus, lesser stresses occur in the microcrystalline phases exposed to the molten matrix as compared with those in the crystalline phases which relates to the smaller average shifts of the atoms. As a result, the microcrystalline phases of the particulate dissolve in the molten matrix at the lower rate.

3. Conclusions

In summary, the structure formation of the composite's interfaces between the W–C microcrystalline particulate and the Fe–B–C–P–Mo matrix is controlled by dissolution and diffusion processes. The intensity of interfacial reactions decreases with the size of the microcrystalline phases diminishing. This result can be explained considering the relationship between the average shift of the particulate atoms from the equilibrium positions under the effect of molten matrix and the coefficient that depends on the linear size of the phases which can be estimated by the force constant of dispersive law.

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