O. V. Sukhova^{*}, Yu. V. Syrovatko

Oles Honchar Dnipro National University, Dnipro, Ukraine *e-mail: sukhovaya@ukr.net

FORMATION OF Cu- AND AI-BASED COMPOSITES REINFORCED WITH AI-Co-Cu AND AI-Co-Ni QUASICRYSTALLINE PARTICLES

The formation of dissolution-and-diffusion interfaces between Al–Co–Cu or Al–Co–Ni quasicrystalline fillers and copper- or aluminum-based molten binders during the infiltration of the composites was studied in this work. When contacting with copper-based melt, filler crystal phases dissolve almost completely, but when contacting with aluminum-based melt – only partially. Quasicrystalline phase practically does not dissolve and remains in the structure of interfacial zones. The higher dissolution rate of the quasicrystalline phase as compared to that of crystal one is explained with taking into account the formalism of the theory of high anisotropic crystals. The expressions for free energy and heat capacity of quasicrystal and crystal phases are suggested on the basis of the Debye model. The slower dissolution of the quasicrystalline phase is connected with the distribution of excess energy among the larger quantity of freedom degrees. This approach is shown to allow controlling composite structure through the intensity of interfacial reactions between the matrix and the reinforcement.

Keywords: quasicrystals, infiltration, metal matrix composites, interfacial reactions, dissolution, theory of high anisotropic crystals, excess heat capacity.

1. Introduction

Liquid metal infiltration of quasicrystalline reinforcing filler particles shows promise as a way to produce metal matrix composites [1-3]. Despite the good results obtained with this technique, some difficulties remain related with complete or partial dissolution of filler phases, with detrimental consequences for the performance characteristics [4–8]. In order to overcome these problems, special attention is to be paid to reducing the interface reactions between the molten metal and the quasicrystalline reinforcement which could lead to composite strength degradation. High properties of the metal matrix composites are attributed to strong matrix/reinforcement interfacial bonding. Because the matrix/particle interfaces result from dissolution processes during infiltration, further enhancements may be expected by preserving the quasicrystalline phase in the structure. The optimization of the structure- property relationship for the composites can be done through the theoretical analysis of the interfacial reactions between the reinforcing particles and the matrix. Therefore, in this paper we analyze the effect of the structure of crystalline and quasicrystalline filler phases on the kinetics of their dissolution in the molten metal for the purpose of controlling interfacial reactions during the infiltration of composites.

2. Experimental procedure

Cu- or Al-based composites reinforced with quasicrystalline Al–Co–Cu or Al–Co–Ni particles were produced by infiltration without applying pressure [7, 8]. For fabricating composites, JI62, BOU 10-2 or AMr30 alloys were selected as matrix materials, and the Al₆₅Co₂₀Cu₁₅ or Al₇₂Co₁₈Ni₁₀ alloys as reinforcement.

The instruments used in the microstructural characterization of the investigated composite materials were optical microscopes (OM) *Neophot* and *GX-51*, quantitative analyzer *Epiquant*, scanning electron microscope (SEM) *P3MA 102-02*. The alloys were also studied by powder X-ray diffraction (XRD) with using Cu K_{α} radiation.

[©] O. V. Sukhova, Yu. V. Syrovatko, 2017

The local phase compositions were determined in SEM by energy dispersive X-ray (EDX) analysis. The usual scattering of the measurements was about ± 0.2 at. pct.

3. Results and discussion

Infiltration technique leads to the formation of flawless interfacial zones between reinforcing particles and the matrix resulting from specific dissolution and diffusion processes [7, 8]. The morphology and spatial distribution of the quasicrystalline D-phase depend on the composite material. In the J62 or EpOU 10-2 matrix composites crystalline phases of particles dissolve almost completely and the quasicrystalline phase is dispersed with different degree of uniformity in the metal matrix. This degree depends on interphase reactions and increases for the **БрОЦ** 10-2 matrix composite material. In the AMr30 matrix composite the crystalline phases encircle reinforcing Al-Co-Cu or Al-Co-Ni particles due to the partial dissolution of crystalline phases that are located, mainly, close to the interface. To explain the higher dissolution rate of the crystal phases as compared with that of the quasicrystalline phase, the formalism of the theory of high anisotropic crystals can be applied. The crystal and quasicrystal phases can be considered as layered structures. Therefore, interaction between the layers, oscillations inside the layers, oscillations of one layer relative to another, and oscillations of layer bends are to be taken into account. With crystal phases, the bonds between the layers can be ignored. Correspondingly, the frequency dispersion can be found as follows

$$\omega_3^2 = \gamma^2 \chi^4 \tag{1}$$

where γ is the group velocity, χ is the stiffness coefficient, and ω_3 is the frequency dispersion of acoustical spectrum branch. The free energy of crystal phases interacting with copper-based melts

$$F = 4T \int_{0}^{\infty} \ln\left(1 - e^{-\frac{\hbar\gamma\chi^{2}}{T}}\right) 2\pi\chi d\chi = \frac{4\pi T^{2}}{\hbar\gamma} \int_{0}^{\infty} \ln\left(1 - e^{-z}\right) dz, \qquad (2)$$

where $z = \frac{\hbar \gamma \chi^2}{T}$.

As far as high temperatures $T \gg \hbar \omega_3$ are considered, we apply the Debye formalism. In so doing, we change the upper integral limit for a finite quantity

$$\frac{\theta}{T} = \frac{\hbar\omega_D}{T} \approx \frac{\hbar\gamma\chi_{\max}^2}{T} = x \,.$$

As a result, we obtain the expression for the free energy

$$F = \frac{4\pi T^2}{\hbar\gamma} \int_0^x \ln(1 - e^{-z}) dz = \frac{4\pi T^2}{\hbar\gamma} z \ln(1 - e^{-z}) \Big|_0^x - \frac{4\pi T^2}{\hbar\gamma} \int_0^x \frac{z dz}{e^z - 1}, \quad (3)$$

where $x = \frac{\hbar\omega_{3 \max}}{T} = \frac{\hbar\gamma\chi_{\max}^2}{T}$.

From this,

38

$$F = \frac{2V}{\pi^2} \chi_{\max}^2 \ln \frac{\hbar \gamma \chi_{\max}^2}{eT}.$$
 (4)

For crystal phases from expression (4) we calculate entropy $S = -\frac{\partial F}{\partial T}$, internal energy E = F + TS, and heat capacity

$$C_V = \frac{2V}{\pi^2} \chi^2_{\text{max}} = const \,. \tag{5}$$

Expression (5) does not depend on temperature which complies with the Dulong-Petit law. This expression is true for a geometric mean frequency $\boldsymbol{\varpi}$ of atom vibrations

$$\boldsymbol{\varpi} = \boldsymbol{\varpi}_0 e^{\frac{\lambda V_0 P}{N_c}} \tag{6}$$

where N is the quantity of atoms in a cell, λ is the thermal expansion coefficient of crystals, V_0 is the volume, and P is the pressure.

The averaged vibration frequency of atoms does not depend on the thermal expansion coefficient of crystals that is linear-dependent on heat capacity

$$\lambda/C = \frac{1}{\Theta V_0(P)} \frac{d\Theta}{dP}$$
(7)

It follows from the above equations that the higher the heat capacity of the phases, the quicker they dissolve in the melts.

With quasicrystalline phase dissolving much slower, the bonds between the layers are preserved. Correspondingly, the frequency dispersion can be found as follows

$$\omega_3^2 = u_z^2 k_z^2 + \gamma^2 \chi^4, \qquad (8)$$

where u_z is the acoustic wave velocity and k_z is the wave vector.

The free energy of the quasicrystalline phase interacting with a copper-based melt can be determined from

$$F = \frac{8VT}{(2\pi)^3} \int_{0}^{k_{z_{\text{max}}}} dk_z \int_{0}^{\chi^2_{\text{max}}} \ln\left(1 - \exp\left(-\frac{\hbar}{T}\sqrt{u_z^2 k_z^2 + \gamma^2 \chi^4}\right)\right) 2\pi \chi d\chi$$
(9)

where V is the volume and $\frac{V}{(2\pi)^3}$ is the quantity of modes.

From here, the inner integral

$$F = \frac{4\pi T}{\gamma \hbar} \int_{0}^{x} \ln(1 - e^{-z}) dz = \frac{4\pi T}{\gamma \hbar} \left[x \ln(1 - e^{-x}) - \int_{0}^{x} \frac{z dz}{e^{z} - 1} \right].$$
(10)

where $z = \frac{\hbar}{T}\sqrt{a + \gamma^2\chi^4}$, *a* is a parameter $\sim u_z^2 k_z^2$, $x = \frac{\hbar}{T}\sqrt{a + \gamma^2\chi_{max}^4}$ is the integral limit. After the additional substitution of $x = \frac{\hbar}{T}\sqrt{u^2 k_z^2 + b}$ and $y = \frac{\hbar}{T}\sqrt{u^2 k_{zmax}^2 + b}$ with the parameter $b = \gamma^2\chi_{max}^4$, we obtain the following expression for the free energy

$$F = \frac{4VL^2}{8\pi^2 \gamma u} \left[T \ln \hbar L - T \ln T - \frac{3}{2}T + \frac{1}{6}\hbar L - \frac{1}{24}\frac{\hbar^2 L^2}{T} + \frac{1}{80}\frac{\hbar^3 L^3}{T^2} \right], \quad (11)$$

where $L = \sqrt{\left(u^2 k_{z \max}^2 + \gamma^2 \chi_{\max}^4\right)}$.

From here

$$C_{V} = \frac{\partial E}{\partial T} = \frac{VL^{2}}{2\pi^{2}\gamma u} \left[1 + \frac{1}{12} \frac{\hbar^{2}L^{2}}{T^{2}} - \frac{3}{40} \frac{\hbar^{3}L^{3}}{T^{3}} \right].$$
 (12)

Since the expression $\hbar L = \hbar \sqrt{u^2 k_{z \max}^2 + \gamma^2 \chi_{\max}^4}$ has a meaning that is similar to Debye temperature, expression (12) can be written as

$$C_{V} = 3R \left[1 + \frac{1}{12} \frac{\Theta^{2}}{T^{2}} - \frac{3}{40} \frac{\Theta^{3}}{T^{3}} \right]$$
(13)

Hence, the heat capacity of the quasicrystalline phase is temperature dependent. Its values deviate from the Dulong-Petit law and exceed those of the heat capacity of the crystal phases. But the quasicrystalline phase has more degrees of freedom. According to energy equipartition law, the heat capacity depends on the quantity of freedom degrees. So, it can be concluded that the excess energy of the quasicrystalline phase distributes among the larger quantity of freedom degrees. Respectively, the heat capacity and geometrically averaged frequency of atom vibrations decrease. As a result, this phase dissolves in the copper-based melts slower than crystal ones.

In the case of wetting quasicrystalline phases by aluminum-based molten binder, the bonds between the atom layers are preserved and the frequency of atom vibrations is expressed by equation (8). The free energy and heat capacity of the crystal and quasicrystal phases are circumscribed by expressions (11) and (13) respectively. However, the Debye temperature Θ from expression (13) is different for these phases. The Debye temperature Θ_1 corresponds to the case when copper-based melt wets the quasicrystalline phase, the temperature Θ_2 – when aluminum-based melt wets the quasicrystalline phase, and the temperature Θ_3 – when aluminum-based melt wets the crystalline phase. These temperatures are related as follows: $\Theta_2 > \Theta_3 > \Theta_1$. Hence, the heat capacity of the phases after interaction with aluminum-based melt shall be higher than that after interaction with copper-based melt. Nevertheless, the dissolution in aluminum-based melt slows down because of the larger quantity of freedom degrees of the quasicrystalline phase, with heat capacity per a freedom degree decreasing.

4. Conclusions

For Cu- or Al-based composites reinforced with quasicrystalline Al–Co–Cu or Al– Co–Ni particles, the slower dissolution of quasicrystalline decagonal D-phase during the infiltration as compared with that of crystalline phases can be explained with using the theory of high anisotropic crystals. The quasicrystalline phase is characterized by the linear excess heat capacity that distributes among the larger quantity of freedom degrees. As a result, the geometrically averaged frequency of surface atom vibrations decreases which leads to reducing the interfacial reactions between the molten metal and the quasicrystals.

With Debye temperature increasing, the excess heat capacity of the quasicrystalline phase influences to a bigger extent. This feature combined with dispersion distribution in three directions allows controlling the dissolution processes during infiltration and enhancing the performance characteristics of the composites interfaces.

References

1. Lee, S. M. Metal matrix composites reinforced by gas-atomised Al–Cu–Fe powders [Text] / S. M. Lee, J. H. Jung, E. Fleury, W. T. Kim, D. H. Kim // Materials Science and Engineering. – 2000. – V. 294 – 296. – P. 99 – 103.

2. **Zhenyuan, L.** Microstructure and mechanical properties of Al–7%Si matrix composites reinforced by $Al_{63}Cu_{25}Fe_{12}$ icosahedral quasicrystal particles [Text] / L. Zhenyuan, G. Haoran, Q. Haiou // Applied Mechanics and Materials. – 2011. – V. 55–57. – P. 1022-1027.

3. **Kenzari, S.** Influence of oxidation of i-AlCuFeB particles on the formation of Al-based composites prepared by solid state sintering [Text] / S. Kenzari, P. Weisbecker, G. Geandier etc. // Philosophical Magazine. – 2006. – V. 86, No. 3 – 5. – P. 287 – 292.

4. **Kenzari, S.** Formation and properties of Al composites reinforced by quaisicrystalline AlCuFe particles [Text] / S. Kenzari, P. Weisbecker, M. Curulla etc. // Philosophical Magazine. – 2008. – V. 88, No. 5. – P. 755 – 766.

5. Laplanche, G. Microstructures and mechanical properties of Al-base composite materials reinforced by Al–Cu–Fe particles [Text] / G. Laplanche, A. Joulain, J. Bonneville etc. // Journal of Alloys and Compounds. – 2010. – V. 493. – P. 453 – 460.

6. **Carreno-Morelli, E.** Processing and characterization of aluminium-based MMCs produced by gas pressure infiltration [Text] / E. Carreno-Morelli, T. Cutard, R. Schaller, C. Bonjour // Materials Science and Engineering. – 1998. – V. A251. – P. 48 – 57.

7. Sukhova, O. V. Metal matrix composites reinforced with Al–Co–Cu particles [Text] / O. V. Sukhova, Yu. V. Syrovatko // Visnik Dnipropetrovs'kogo Universitetu. Seria Fizika, radioelektronika. – 2016. – Issue 23, V. 24. – P. 53 – 58.

8. **Syrovatko, Yu. V.** Strukturoobrazovanie kompozitsionnykh materialov, uprochnyennykh kvazikristallami [Text] / Yu. V. Syrovatko, O. V. Sukhova // Visnik Dnipropetrovs'kogo Universitetu. Seria Raketno-kosmichna tekhnika. – 2013. – Issue 4, V. 21. – P. 113 – 121.

Received 15.10.2017