https://doi.org/10.46813/2024-149-170

UDC 669.018:621.039

STRUCTURE AND PROPERTIES OF REFRACTORY BIMONOCRYSTAL MICROCOMPOSITES

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The features of high-gradient crystallization of refractory quasi-binary alloys have been studied. The processes of phase nucleation and their joint influence on the evolution of the formation of spatially ordered microstructures are considered. The possibility of regulating the volumetric ratio of phases by crystallization of alloys of non-eutectic composition has been revealed. The results of expanding the area of compositional growth and the possibility of creating a regular quasi-eutectic microstructure without primary carbides are explained. The mechanism of post-crystallization heat treatment has been determined, leading to the purification of the matrix from interstitial impurities and embrittling carbides, the creation of perfect bi-monocrystalline materials that are thermally stable up to pre-melting temperatures with a high level of ductility and heat resistance.

INTRODUCTION

The creation of high-tech technologies is inextricably linked with the progress of materials science, the main task of which is the development and creation of materials with a high degree of thermodynamic and phase stability up to pre-launch temperatures. Most materials of practical and scientific interest are heterophasic [1]. The traditionally established method for improving the manufacturability of refractory metal alloys and expanding the areas of their practical application is maximum purification from interstitial elements and optimal alloying [2, 3].

The operating temperatures of most refractory alloys are 0.4…0.5 the melting temperature of the base, which indicates far from exhaustive possibilities for their wide application. An increase in the tensile strength of alloys based on molybdenum, tantalum, niobium in the temperature range above 0.5 T_{melt} by 5…10 kg/mm^2 is equivalent to an increase in the operating temperature of these materials by 400…500 K, for tungsten alloys above 600 K.

There is a search for an optimal solution to the problem of compatibility of maximum heat resistance and technological processing. For some heat-resistant alloys based on VA-VIA metals, it is necessary to use limited alloying, lowering the homologous temperature, ensuring ductility. The problem arises of ensuring high-temperature stability of materials at hot pressing temperatures and secondary plastic deformation operations (forging, rolling, etc.) [4].

Analysis of the state diagrams of quasi-binary alloys, refractory metal–interstitial phase, interstitial phase, shows that, other things being equal, the volume fractions of strengthening phases in quasi-binary eutectics increase in the sequence – oxides, nitrides, carbides, borides. The concentration of interstitial phases is related to the dissociation energy ΔH of the Me-X compound by the following relationship:

$$Cx \approx \exp(-\frac{\Delta H_{Me-x}}{RT}). \quad (1)$$

As energy increases, solubility decreases and heat resistance increases. Carbides are characterized by high values of Young's modulus $E \approx (2.8 \cdot 10^5)$ ... $(6.5 \cdot 10^5)$ MPa , while for most transition metals $E \approx 1.4 \cdot 10^5$ MPa [4, 5].

Refractory carbides are more stable than oxides, which determine the effectiveness of carbide high-temperature hardening. The service temperature of eutectic composites Co-TaC, Ni-TaC with filamentary carbides, developed for gas turbine engines, is significantly higher than that of known nickel alloys with traditional strengthening methods. Refractory metals – the basis of modern structural materials – increase the homological operating temperature. However, insufficient study of refractory-based composites is associated with their activity and high temperatures. At the same time, high melting temperatures make it possible to realize temperature gradients at the boundary of the solid and liquid phases during directed crystallization that are much greater than during the crystallization of low-melting eutectics. The role of the most important structure formation parameter G has been practically not studied. Limited data on the dislocation structure of high-temperature composites, diffusion parameters necessary for the development of the theory of eutectic crystallization, and practical applications [5].

A study of the state diagrams Me'-Me"-X shows that there are eutectics between the bcc refractory metal Me' or a solid solution based on it and the refractory phase formed by the interstitial element x and the metal Me", that is, these systems can be considered as pseudo-binary [6]. Prospective studies of boride carbide alloys, which are an important component of a wide range of heat- and wear-resistant materials (cermets for nuclear installations, blades of gas turbine engines), emitter materials [7]. Carbide-forming refractory metals included in reactor materials reduce the creep rate and radiation swelling.

It is known that radiation damage to materials is compensated at the atomic level, while macroscopic

effects of structure degradation (coagulation of phases, swelling, creep, embrittlement) arise due to microstructural changes – structural defects, precipitation of second phases, the formation of dislocation loops, which is determined by the nature of their bonds with the matrix component of the alloy, the state of the interphase boundary. The latter determines the distribution and concentration of stress, being the source of destruction or stability of the structural material [8, 9].

Further increase in the structural stability, physical and physical-mechanical properties of composite materials and coatings based on them is possible by studying the internal physical processes occurring both in the matrix, strengthening phases, and at interphase boundaries directly during the solidification process and in the post-crystallization period. Extended interphase boundaries in euthentic composites, reaching $\sim 10^4 \text{cm}^2/\text{cm}^3$, different morphology and dispersion of the structure with the same volume fraction of reinforcing phases, and relaxation processes determine the specificity of their behavior, which for refractory systems have practically not been studied [10].

Known methods of melting and heat treatment of materials on a refractory basis (induction, plasma-arc, zone melting) do not allow strictly controlling the solidification conditions, regulating the shape of the crystallization front at the liquid-solid interface – the main parameter of directional structure formation, obtaining a spatially ordered arrangement of phases in the volume compositions. The enormous role of the developed technique for high-gradient directional crystallization of refractory alloy systems, considered in this work, is obvious.

The purpose of this work is to study the internal physical processes occurring in quasi-eutectic alloys based on molybdenum, niobium and tantalum with carbon and zirconium in the process of high-gradient crystallization. Determination of the evolution of the structural-phase state under various conditions of heat treatment, defectiveness of the structure, the possibility of regulating the volumetric ratio of phases in composites by crystallization of alloys of non-eutectic composition, determination of the area of compositional growth, creation of a perfect bi-monocrystalline structure of refractory alloys with increased performance characteristics.

MATERIAL, TECHNICAL OF THE EXPERIMENT

The starting materials used were Ta, Nb, Mo of technical purity, zirconium iodide, and carbon of spectral purity. Alloys of quasi-eutectic composition Me′-Me″X, where Me′ – Mo, Ta, Nb; Me″ – Zg; X – interstitial element, were subjected to melting in vacuum $p < 10^{-4}$ Torr. A modified method of electron beam zone recrystallization was used by creating a high static temperature gradient at the boundary of the solid and liquid phases due to forced cooling of the processed ingot by a refrigerator located at the phase boundary at a certain distance from the molten zone. As a result of regulating the temperature gradient G at the phase boundary, the shape of the crystallization front (FC) and the crystallization rate $R = 10^{-2} \ldots 10^{-1}$ m/h changed. Metallographic and electron microscopy JSM-200CK analyzes were carried out at an accelerating voltage of 200 kV. Phase identification was carried out by microdiffraction; micro-X-ray spectral analysis (Camebax) of samples was used; microhardness was determined using a PMT-3 device. Structural-phase analysis of samples with a diameter of 10…25 mm was carried out on alloy ingots cut by the electric spark method, followed by electropolishing to remove the surface distorted layer.

RESULTS, DISCUSSION

For refractory metal-interstitial phase systems, there is data on phase equilibria, which is important for assessing their structural state, but the processes of their directional crystallization, the stability of the phases formed during this process, and diffusion processes have not been sufficiently studied. The complex architecture of carbide eutectics and their morphological diversity are the reason for the emergence of various schemes for the formation of eutectic structures, especially regular ones. It was found that during the solidification of Mo(Nb, Ta, Zr)-C alloys, the nucleation of a colony (grain) is initiated by the base phase (carbide), characterized by a higher entropy of melting and a greater tendency to form flat-edged growth forms. Subsequently, a crystal of the interstitial phase grows from the nucleus, from which the growth of a bicrystal begins (Figs. 1, 2). In Fig. 1 the primary Ta_2C crystal has a facet corresponding to the β Ta_2C crystal lattice.

Fig. 1. Primary crystal Ta_2C, x15000

Rod- or plate-shaped branches are formed on the edges of the base crystal; the space between the branches is supersaturated with the second component of the metal phase. It has been established that the driven metal phase, as it were, decorates the surface of the base crystal. Subsequently, the perfection of the bicrystal structure is determined by the structure of the constituent phases and the entire microcomposite (MCM) as a whole (see Fig. 2).

It was found that interstitial impurities $\sim 10^{-1}$ wt.% lead to the formation of cellular-dendritic structures. Under conditions of high-gradient (G=350...600 K/cm) crystallization in vacuum $\sim 10^{-4}$ Pa leads to purification of the alloy from oxygen and nitrogen to 10^{-3} wt.%, carbon $\sim 10^{-3}$ wt.%, the content of metal impurities is less than $\sim 10^{-3}$ wt.% [11].

Fig. 2. Branching of primary crystals ZrC, x20000

It has been shown that for the formation of regular, spatially ordered structures in the case of complex alloys, a flat crystallization front is formed if

$$\frac{G}{R} > \frac{\Delta T_{A,B} + \Delta T_i}{D}, \quad (2)$$

where $\Delta T_{A,B}$ is the crystallization interval, determined by the composition and increasing with its deviation from the eutectic concentration; ΔTi is the difference in solidus and liquidus temperatures along the monovariant Thalweg, index *i* corresponds to impurities or alloying elements in the case. It has been determined that in the case of unidirectional high-gradient crystallization, the redistribution of atoms can occur only in a supercooled layer of liquid (below TE) with a width $d_{tran} = \frac{\Delta Ts}{G}$, where ΔTs – supercooling, $d_{stran} \sim 10^{-2} \dots 10^{-3}$ cm. The latter explains the deviation of the value n = 0.3…0.4 found in the studied alloys from the theoretical value n = 0.5 depending on the dispersion

$$\lambda = AR^{-n}. \quad (3)$$

Different tendency of the studied alloys to directional growth of phases was discovered. The lowest propensity is for molybdenum-based alloys (distribution coefficient $K_{C\to Mo}$ = 0.08), the highest in Ta(Nb)-C systems, where $K_{C\to Nb}$ = 0.54, $K_{C\to Ta}$ = 0.57. At the same time, the range of crystallization rates ensuring the formation of regular bimonocrystalline structures in Ta(Nb)C alloys is much wider $R = (0.27 \dots 9.8) \cdot 10^{-5}$ m/s than in Mo-C alloys and Mo-ZrC $R \leq (1.66 \dots 2.2) \cdot 10^{-5}$ m/s, which is qualitatively consistent with the stability criterion

$$\frac{G}{R} > \frac{\Delta T}{D}, \quad (4)$$

where D is the diffusion coefficient.

The results obtained are explained by the difference in the entropy of melting. The quasi-binary Mo-ZrC system is characterized by a large difference in thermophysical parameters. The entropy of melting of the molybdenum phase is

$$S_{melt(Mo)} = 12.65 \frac{J}{mol*deg}, S_{melt(ZnC)} = 54.62 \frac{J}{mol*deg}.$$

It was discovered that an increase in the G gradient at the interphase boundary (from 350 to 600 K/cm) prevents two-phase instability and leads to the creation of regular structures.

Predominant growth directions (HP) and phase conjugation planes have been determined

$$\text{HP} \parallel < 112 >_{Mo} \parallel < 110 >_{Mo_2C}$$
$$\text{and ПР} \parallel (120)_{Mo} \parallel (123)_{Mo}.$$

This is observed at G > 400 K/cm. With increasing temperature gradient G, the orientation changes

$$< 111 >_{Mo} \parallel < 110 >_{Mo_2C}$$
$$\text{and ПР} \parallel (101)_{Mo} \parallel (0001)_{Mo}.$$

In the Mo-ZrC system, a bimonocrystalline structure is formed $G > 450$ K/cm:

$$\text{HP} \parallel < 110 >_{Mo} < 110 >_{ZnC}$$
$$\text{and ПР} \parallel (110)_{Mo} \parallel (110)_{ZnC}.$$

The existence of an unambiguous orientational relationship between phases in regular MCM is the result of a good degree of atomic matching of mating planes at the phase interface. The latter determines the dimensional and thermal stability of the structure of microcomposites up to pre-melting temperatures.

The result of controlled high-gradient crystallization of alloys is the formation of perfect bi-monocrystalline microcomposites – whisker-like crystals of submicron-sized carbides embedded in a refractory metal matrix, which are practically defect-free (Fig. 3). The dislocation density of thread-like carbide single crystals is 10^2 cm^{-2}. The value is $l/d \leq 1000$, where *l*, *d* are the length and diameter of carbide single crystals, respectively.

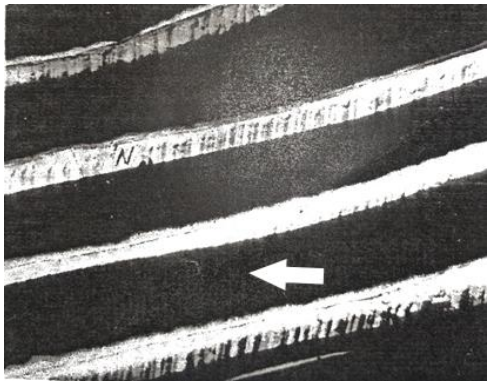

Fig. 3. Bimonocrystalline microcomposite. System Nb-Nb_2C. Arrow indicates Nb_2C, longitudinal section, x1500

The results of tensile mechanical tests show fragmentation of the fibers, but the destruction of the MCM does not occur due to strain hardening of the matrix. The presence of a semi-coherent interphase boundary and extended sections of the plastic matrix layer allows deformation processes to develop freely in the composite, similar to [12]. In this case, the layer is easily deformed, absorbing the energy released when the crack propagates. MCM exhibits a high level of strength and ductility (Fig. 4).

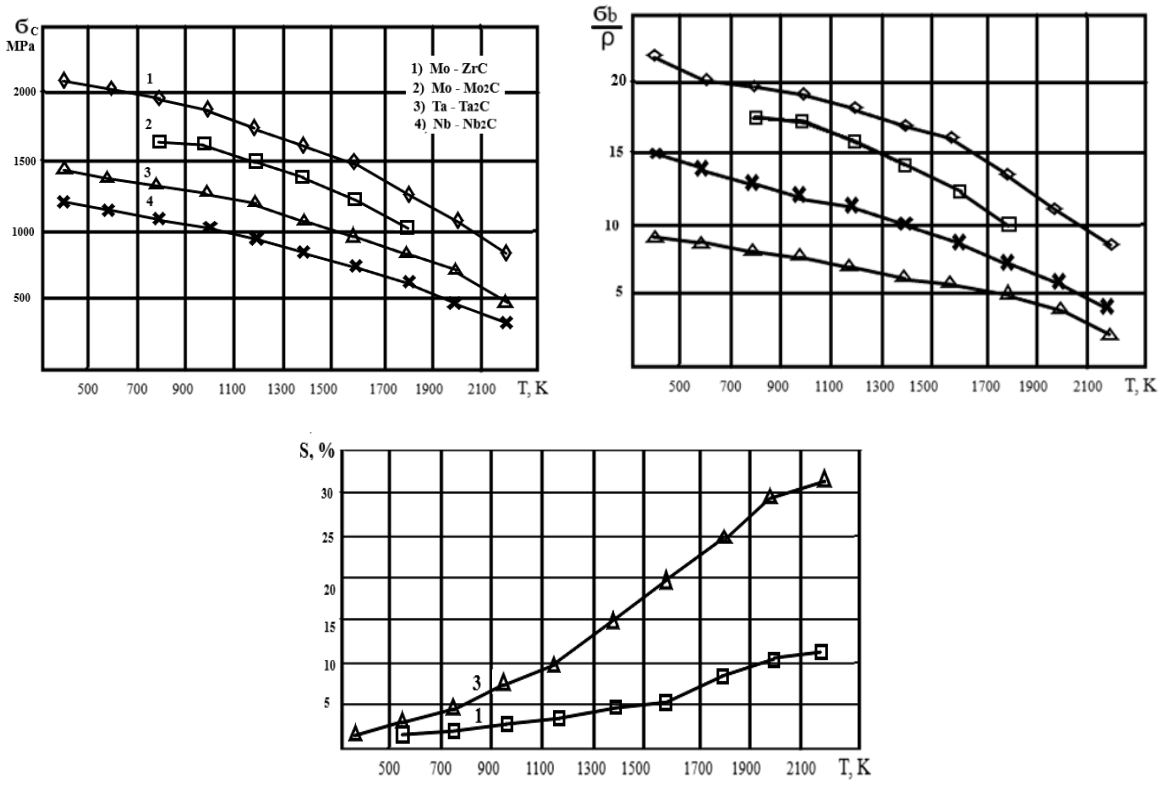

Fig. 4. Temperature dependence of strength σ_b, σ_b/ρ, and plasticity δ

Maximum values $\sigma_{b(Mb\text{-}ZnC)}$ = 2300…2400 MPa (T_{sp}>300 K) and more than 1000 MPa (T_{sp}–2000 K) plasticity $\delta > 30\%$, which exceeds the strength characteristics of the most high-strength alloys of type W+(Ti, Zr, W)C [13].

The observed significant increase in the technological plasticity of MCM is explained by the influence of high-temperature heat treatment (1500 K, 10 h) in the post-crystallization period due to the diffusion "pumping" of carbon located in the metal matrix to the surface of the carbide and its cleaning. This process occurs at distances of several microns, which corresponds to the dispersion of MCM. The effect of cleaning the matrix from embrittling carbides was discovered due to the presence of effective carbide formers in the alloys. The latter is thermodynamically explainable by comparing the heats of formation of various carbides [10].

The possibility of maintaining the compositional (quasi-eutectic) microstructure when changing the carbon concentration within the following limits is considered (Fig. 5, 6): Mo-C – 16…20 at.% (C_E~17 at. %), Nb-C – 10…14 at.% (C_E = 10.5 at. %), Ta-C – 9.5…15 at.% (C_E=12 at.%), , Mo-ZrC – 1.3…1.95 mas.% (C_E=1.45 at.%), that is, in the field of quasi-eutectic compositions.

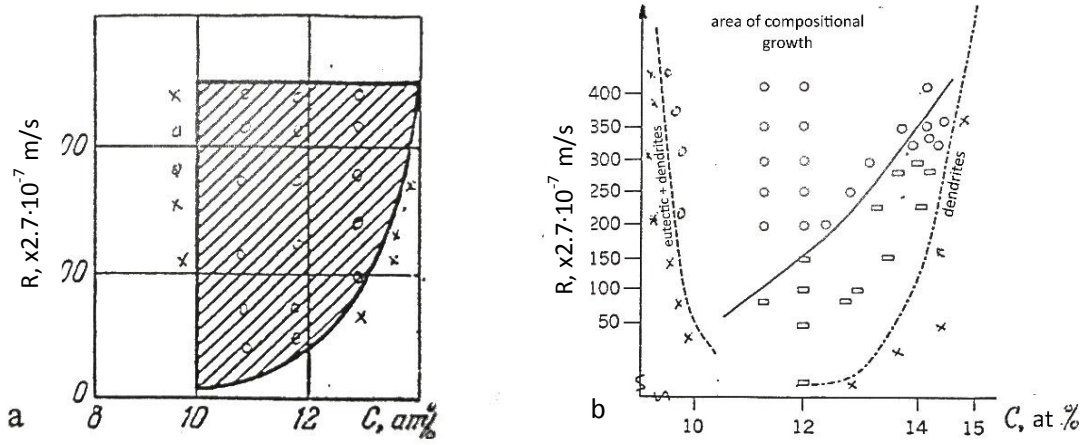

Fig. 5. Changing the size of the quasi-euthentic microstructure area:
a – Nb-Nb_2C alloys (shaded area); b – Ta-Ta_2C system (o – rods, □ – plates, x – dendrites), depending on the crystallization rate and carbon content

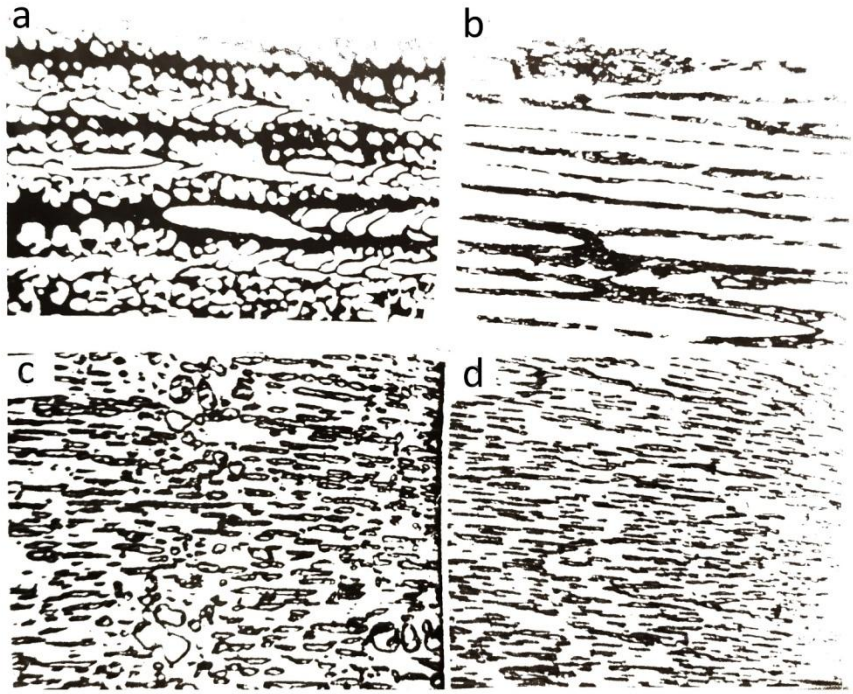

Fig. 6. Influence of composition and crystallization conditions on the microstructure of composites: eutectic-dendritic (a, b) structure (Mo-15 at.%C, R =1.66·10^{-5} m/s, G=300 K/cm (a); G=500 K/cm (b), longitudinal section, x650) and quasi-eutectic (c, d) structure (Nb-13.1%C, R =4.05·10^{-5} m/s (c), R = 8.32·10^{-5} m/s (c, d), longitudinal section, x600)

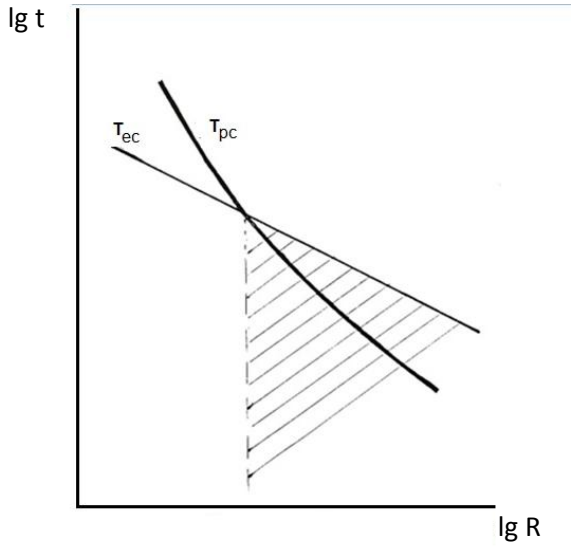

Fig. 7. Rate dependence of temperatures on the PC of quasi-eutectics (T_{ec}) and primary crystals (T_{pc}). A quasi-eutectic structure is formed in the shaded area

It has been determined that with an increase in the crystallization rate, the boundary of the compositional growth region (CGR) in hypereutectic alloys expands (see Fig. 5). According to A. Bochvar's model of competing growth, the formed microstructure at a fixed supercooling is determined by the ratio of the growth rates of the quasi-eutectic R_e and the dendrites of the excess phase R_g. At $R_e < R_g$ a mixed eutectic-dendritic structure is formed, and at $R_e > R_g$ a quasi-eutectic structure is formed. It has been determined that the boundaries of the quasi-eutectic compositional growth region correspond to the relation $\Delta T_{ec} = \Delta T_{pc}$, where ΔT_{ec} and $_{\Delta Tpc}$ are supercooling at the quasi-eutectic growth front and the top of the dendrites. The dependence of the temperature at the crystallization front on the crystallization rate is presented in Fig. 7.

The experimentally discovered asymmetry of the region of compositional growth of metal-carbide systems makes it possible to explain the appearance of "rims" of the uncut metal phase near the carbide phase during the solidification process. The latter phenomenon is characteristic of eutectic systems formed by transition metals with interstitial phases [13].

CONCLUSIONS

The features of nucleation and evolution of the compositional structure under conditions of high-gradient zone recrystallization have been studied. The relationship between the perfection of the structure of the carbide phase leading crystallization, the driven metal phase decorating its surface, and the entire microcomposition (MCM) as a whole has been clarified. It has been determined that a high static temperature gradient and directional heat removal determine the preferential branching of the base crystal and the creation of a bimonocrystalline structure. It has been established that the single-crystallinity of phases can be judged by their regular, ordered arrangement in the volume of the ingot. The Nb(Ta)-C systems have the greatest propensity for directional structure formation, the Mo-Mo_2C, Mo-ZrC systems have the minimum, which is explained by the thermophysical parameters of the components of the composite material (CM). It has been discovered that it is possible to regulate the volume ratio of phases in MCM by crystallizing alloys of non-eutectic composition under certain conditions.

The region of compositional growth (CGR), its asymmetry, and the region of alloy compositions, the solidification of which gives an oriented quasi-eutectic microstructure without primary crystals, have been experimentally determined. At the same time, the regularity of the structure is maintained despite random fluctuations in composition and crystallization rate, which do not remove the alloys from the region of compositional growth. Heat treatment of composites causes the refractory matrix to be purified by diffusion transfer of carbon to the surface of the carbide phase. As a result of the growth of the base carbide phase, its volume fraction increases. The presence of active deoxidizers in the matrix allows you to control the oxygen content in the melt. Tensile tests of MCM, which have thermal and dimensional stability up to pre-melting temperatures, have shown high strength and technological ductility (more than 20…30%), which expands the scope of their application in critical parts of power equipment.

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Article received 02.12.2023

СТРУКТУРА ТА ВЛАСТИВОСТІ ТУГОПЛАВКИХ БІМОНОКРИСТАЛІЧНИХ МІКРОКОМПОЗИТІВ

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Вивчено особливості високоградієнтної кристалізації тугоплавких квазібінарних сплавів. Розглянуто процеси зародження фаз, їх еволюцію, спільний вплив на формування просторово-упорядкованих мікроструктур. Виявлено можливість регулювання об'ємного співвідношення фаз шляхом кристалізації сплавів неевтентичного складу. Пояснено результати розширення області композиційного росту, можливості створення регулярної квазіевтентичної мікроструктури без первинних карбідів. Визначено механізм посткристалізаційної термообробки, що призводить до очищення матриці від домішок впровадження та крихких фаз, створення досконалих, термічно стабільних структур до передплавильних температур бімонокристалічних матеріалів з високим рівнем пластичності, жароміцності та фізичних властивостей.