111

«Journal of Kharkiv National University», №1041, 2013   *N.A. Azarenkov...*

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BIMONOCRYSTALL MATERIALS – IN SITU REFRACTORY MICROCOMPOSITES

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This article contains observation on the bimonocrystal materials received by using heavy gradient direct crystallization with a high content of the carbide phase. The effects of heat treatment on the microstructural changes and the growth of technological ductility were investigated. The dislocation structure of the phase boundaries, matrix and strengthening phases were studied. High-temperature mechanical testing was performed, mechanism of composition and mechanical microcomposites hardening was observed.
KEY WORDS: solidification, bimonocrystall carbide materials, implementation phase, dislocations, strengths

БИМОНОКРИСТАЛЛИЧЕСКИЕ МАТЕРИАЛЫ – ЕСТЕСТВЕННЫЕ ЖАРОПРОЧНЫЕ МИКРОКОМОЗИТЫ
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Рассматриваются бимонокристаллические материалы, полученные с помощью высокоградиентной направленной кристаллизации с высоким содержанием карбидной фазы. Исследовано влияние термической обработки на микроструктурные изменения и рост технологической пластичности. Изучена дислокационная структура фазовых границ, матричное и фазовое упрочнение. Выполнены высокотемпературные механические испытания, рассмотрен процесс композиционного и механического упрочнения.
КЛЮЧЕВЫЕ СЛОВА: кристаллизация, бимонокристаллические карбидные материалы, фаза внедрения, дислокации, прочность

БІМОНОКРИСТАЛИЧНІ МАТЕРІАЛИ – ПРИРОДНІ ЖАРОМІЦНІ МІКРОКОМПОЗИТИ
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Розглянуті бімонокристалічні матеріали отримані за допомогою високоградієнтної спрямованої кристалізації з високим вмістом карбідної фази. Досліджено вплив термічної обробки на мікроструктурні зміни і зростання технологічної пластичності. Вивчена дислокаційна структура фазових меж, матричне і фазове зміцнення. Виконані високотемпературні механічні випробування, розглянутий процес композиційного та механічного зміцнення**.**
КЛЮЧОВІ СЛОВА: кристалізація, бімонокристалічні карбідні матеріали, фаза впровадження, дислокації, міцність

One of the greatest challenges nowadays is creating construction materials based on refractory compounds and their alloys which would be capable of working in difficult conditions like high temperature, shock and radiation. There is high perspective in carbide and boride alloys researching, which are an important part of the heat- and wear-resistant materials (cermets in nuclear technology, the blades of gas turbine engines, high-speed steels). Gas temperature in modern aviation turbine is close enough to the melting point of the nickel alloys limiting their use in rockets and space technologiesdeveloped in Ukraine[1-4]. Requirements for high-temperature materials in nuclear reactors are increasing. It is clear that increasing working operating temperature due to the use of the refractory materials as the basis of construction materials is relevant [5, 6]. Most of the known high-temperature alloys (based on refractory metals and strengthened by the introduction phases) are formed by transition metals of IV- V(VI) A groups. The nature of hardening is mostly

Fig. 1 Formation of strong σ-bonds Me-x in refractory monocarbides and mononitrides due to the overlapping Px, Py, Pz - orbitals split p^6 shells Me^+, C^-, N^- [7].

determined by the amount and structure of reinforce phases and changes depending on the temperature. At temperatures above 1800 K the best solution is carbide hardening due to high stability of the carbide phase in comparison with the oxide and nitride phases. That is explained with the presence of the strong σ-bonds formed by overlapping orbitals of the P6 shells (Fig. 1) [7, 8]. The analysis of the phase diagrams of the Me'-Me''-X indicates that there are eutectics between the bcc refractory metal and refractory phase which is formed by the introduction of elements X and metal Me''. Therefore, these systems can be considered as quasi-binary. The main difficulty we faced using heat-resistant alloys is their low temperature brittleness. This is caused by several features that are typical for cast alloys. They are micro-heterogeneity of the supersaturated solid matrix dissolve, the presence of thermal stress, the release of a large number of eutectic carbides that has a detrimental effect on plastic morphology, embrittle influence of carbon. Intensively developing diffusion processes in these types of alloys define temperature range as 0.6-0.7 $T_{melting}$. A
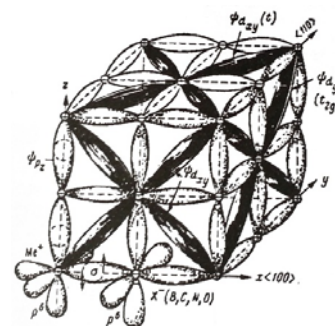
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«Journal of Kharkiv National University», №1041, 2013   N.A. Azarenkov...

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promising way to increase service characteristics of high-temperature alloys is to create optimal primary structure of the ingot and solidification management. It's clear that directional structure formation technology has high relevance. It allows us to create controlled regular structure in the quasi-eutectic alloy systems. However, available data is limited mainly by low-melting systems. "Practical composites" like NiTaC, CoTaC with exploitation area limited to 1500-1700 K are being developed. The main difficulties of creating high-temperature materials are active components and high melting point of refractory eutectic. Besides, difficult architectonic of the eutectics and their exceptional morphological diversity causes variety of contradictory eutectic structure scheme hypotheses, especially regular ones [5,9].

The main aimes reviewed in this work are the study of structure particulars of Me-Me'X microcomposites (Me – Mo, Nb, Ta; Me'- Zr; X-carbon) with high volume fraction of the reinforcing phase, investigation of bimonocrystal materials obtained with highgradient direct solidification, the effect of various types of heat treatment on the composite microstructure stability and strength properties of materials.

MATERIALS AND METHODS

Starting materials are: Mo - technical purity 99.8 wt%, Zr – 99.97 wt%, Ta, Nb - electron beam melting, C - spectral purity[11]. Volumetric fraction of the carbide phase in quasi-eutectic is: Mo -20-22%ZrC; Ta (Nb)- 28-30%$Ta_2(Nb_2)C$; Mo - 44-46% Mo_2C.

Microcomposites were prepared by the modified method of electron-beam zone recrystallization (vacuum < 10^{-4} Pa). Direct structure formation was produced by electron beam circular sweep. High static gradient G was supported during whole process. Zone refining of refractory metals presented during smelting process allowed the use of source materials of technical purity. Metallographic studies including stereometric analysis were completed on microscope MIM-8M. Drone-4M was used in X-ray diffraction analysis. The last were done in two parts. First part: identification of samples - qualitative analysis. Second part: determination of the relative content of the second phase - quantitative analysis. Dislocation structure was studied on thin foils using transmission microscopy (TEM) microscope JSM-200CK, acceleration voltage-200 kV [10,11]. Bursting test (Instron) performed in temperature range 300-2500K, stretch speed-10^{-2} s^{-1}.

RESULTS AND DISCUSSION

Tested systems of Me-carbide form faced-unfaced phases during solidification with sharply different fusion entropies. Therefore, it's necessary to create high static temperature gradient G on crystallization front during whole process to obtain spatially ordered homogeneous structures. (G = 400-650 K/cm, growth rate R = 10^{-5}…10^{-2} m/sec). It is found that in the process of complete phase growth the increase of temperature gradient G reduces the area of concentration supercooling, crystallization range, basic phase lead distance. This reduces the possibility of its dendrite, undirected branching (Fig. 2a,b). This confirms the referral criteria of structure formation G /R ≥ ΔT/D (ΔT – crystallization range, D – diffusion coefficient). In the process of solidification driven metallic phase decorates leading microrelief of carbide phase. Preferential growth direction (GD) is observed. GD ||<110>ZrC||<110>Mo, ||<112>Ta(Nb)||, <010>$Ta_2C(Nb_2C)$.

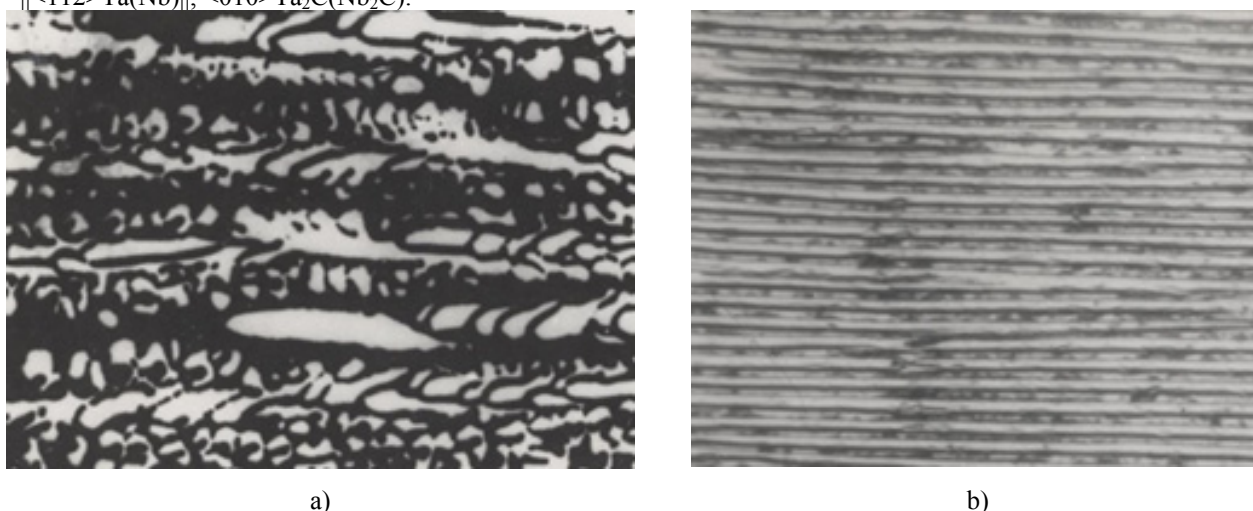a)   b)

Fig. 2 Influence of temperature gradient on microstructure in system Mo - Mo_2C
R=3.5 10^{-4} m/sec, a) dendrite structure G = 350 K/cm b) regular bimonocrystal structure G=550K/cm; longitudinal section; X 650; light areas – carbide phase

The legacy effect of oriented fuse microstructure by growing bi-crystal was discovered. Bimonocrystal materials were obtained after 1 – 2 zone passing. Structure had the appearance of threadlike carbide single crystals embedded in a single-crystal refractory matrix under equilibrium growth conditions. It was found that the dominant morphology of carbides was plate for Mo- Mo_2C, rod for Mo-ZrC, fibrous for Ta(Nb)-C.
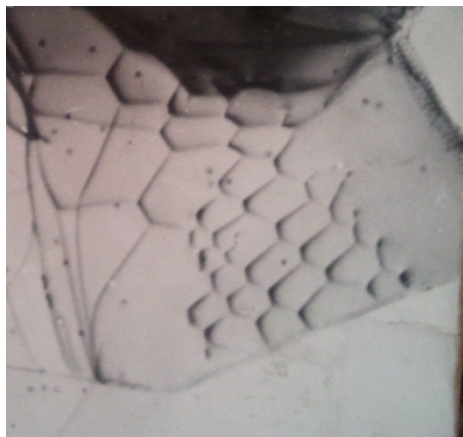
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Fig.3 Dislocation structure of microcomposite Ta-Ta$_2$C; R-10^{-4}m/sec; X 15 000

According to TEM researching carbide single crystals with a diameter of 0.6…0, 8 μm contain only stacking faults, other defects weren't detected. Defect concentration decreases during stationary growth. The dislocation density (ρ) of threadlike carbide crystal is ρ ∼ 10^{2}cm^{-2} while in metal matrix - ρ∼10^{8}cm^{-2}. It was found that in studied systems with condition of equal R and G for minimal phase inconsistency (Δd = 4.3% for Mo-ZrC), the dislocation density of the matrix phase : ρ<10^{2}cm^{-2}. In case of Δd = 11.7 % for Mo-Mo$_2$C, ρ = 5.9 10^8… 10^{9}cm^{-2}. Epitaxial dislocations grid extending to a depth of 25 - 45 nm was observed on a semi-coherent phase boundary surface (Fig. 3). It was determined that bimonocrystal materials had a local cleaning of metal matrix as a result of heat treatment after crystallization (T> 1500 K, τ = 3…5 hours). This is explained by the diffusion carbon transfer to the surface of the crystal base carbide. The latter plays the role of substrate in the decay of a supersaturated solid solution. (Fig. 4a,b). Dislocation density of the matrix phase is ρ ≤ 10^{7}cm^{-2}.
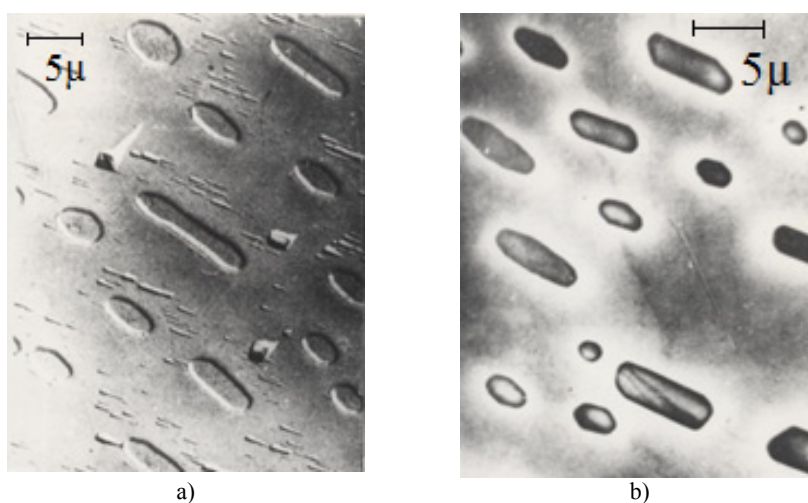
Fig. 4. Mo-ZrC system microstructure
a) initial composite, b) after annealing T= 1500 K, annealing time -3h.

As a result of after crystallization annealing the system of Mo-ZrC 10^{-4} weight % C was mostly cleaned from carbon. Observed treatment effect complies with the best results of complex refractory metals active crystals refining. That promotes technological ductility of carbide alloys [11].

The overall result established for the case of isothermal annealing of bicrystal materials is coarsening in areas of accelerated diffusion or defect areas. They are priority one phase expansion areas and places of similar plates consolidation where high density of dislocations is 10^9…10^{10}cm^{-2}. Bimonocrystal materials with regular structure are thermally stable up to 0.9 melting temerature. This is due to reduction of migration interphase boundary capability compared to large-general type grain boundaries. The deformation and hardening nature of microcomposite during explosive tests at 300 - 2500K were defined. It was found that the interaction between dislocation (moving in the matrix) and field of interfacial dislocations increase during deformation process. The field length was the same as the distance between the dislocations at phase interfaces 40…80 nm. In case of Mo-ZrC deformation in <110> direction was carried out in (110) plane. New slip plane in the matrix and carbide phases activate at temperatures higher than 0.7 T$_{melting}$. Different carbide crystallographic peculiarities of sliding along the (110) and (100) in <110> direction disappear. Slipping is carried out in one of the close-packed plane according to tension direction. Local stresses were created on carbide surface as a result of dislocation accumulation. These stresses exceed the theoretical shear strength of monocrystalcarbide. Most of the load is carried by extended threadlike carbide single crystals (l /d ∼ 1000, where l – length, d- carbide diameter). monocrystalscan withstand multiple fragmentation saving specific strength up to reaching the critical value: l/d critical = σ /2 τ (σ$_b$ -carbide strength,τ- matrix yield strength).

As we can see from Fig. 5 bimonocrystal materials strength is 2 – 4 times higher than the strength of known cast structure alloys within temperature range of 300-2500K[11].

The maximum strength values were observed in Mo-ZrC system and exceeded similar values of the best refractory materials such as W-(Zr,Ti,W)C with isotropic structure[12,13]. Microcomposite technological plasticity increased due to refractory matrix treatment. High strength was caused by typical mechanism of composite reinforcement. Deformation matrix hardening in combination with high recrystallization temperature (over 1800K) of bimonocrystal materials provides additional opportunity to improve the heat resistance of carbide heterophase materials. That kind of materials will surely find new application areas.
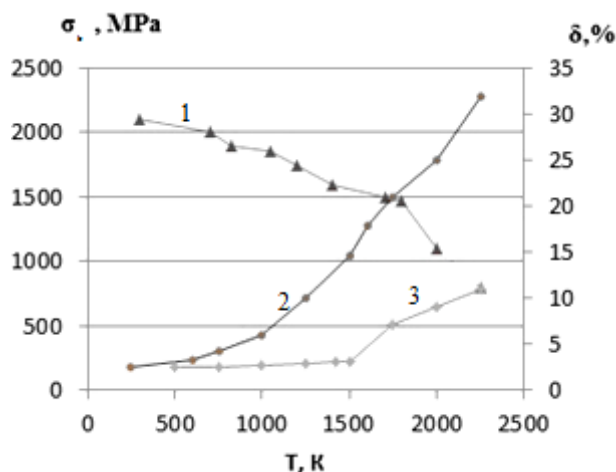
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Fig. 5. Temperature dependence: 1 - rupture strength(σ_b); 2 - plasticity (δ) after annealing; 3 - plasticity (δ) before annealing; Mo-ZrC system

CONCLUSIONS

In this work specific type of bimonocrystal material is considered in detail. Structure of this material takes form of threadlike carbide monocrystalswhich are embedded in the refractory metal matrix. Relationship between structural defects of bicrystal materials, dislocation density and structural stability was defined up to 0.9 melting temperature.

It was detected that the dislocation structure of interphase boundaries and the matrix is determined either by crystallization conditions or growth and relaxation processes. It was found that there is structure improvement during the after crystallization period coursed by movement of the phase boundaries into the matrix. Found conditions of material heat treatment leads to the matrix purification from carbon, embrittling carbides and eliminating pockets of local phase hardening.

It was possible to increase carbide materials technological ductility by 10-15%, while maintaining the highest level of specific strength. The behavior of materials with a large content of the carbide phase combined with high recrystallization temperatures was investigated. Such conditions provide additional opportunities to improve heat resistance and technological plasticity of carbide construction materials. Such materials will undoubtedly find new application areas as template stamps for high pressure equipment, wear-resistant coatings or materials for nuclear technology.

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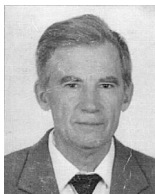
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