Physical and chemical properties of composite (Mo$_{1-x}$Nb$_x$)Si$_2$

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Abstract. In this study, the effect of NbSi$_2$ in the range from 10 to 90 wt% was investigated on the properties of composites (Mo$_{1-x}$Nb$_x$)Si$_2$ obtained by hot pressing a solid-phase mixture of molybdenum and niobium disilicides at a temperature of 1700°C. Graphs of the dependence of density, bending strength, electrical resistivity, CLTE and microhardness of the content of NbSi$_2$ were obtained. It was found, that with an increasing level of NbSi$_2$ in the content, the flexural strength drops to 130 MPa. The electrical resistivity depending on the content of niobium silicide is extreme with a maximum for the composition (Mo$_{0.5}$Nb$_{0.5}$)Si$_2$. In the concentration range of NbSi$_2$ 20-100 wt.% CLTE and microhardness of the composite within the error does not change.

1. Introduction
In the modern world ceramics is widely used in all areas of industry. Ceramics has a number of positive qualities: high strength, oxidation resistance, ability to work at high temperatures [1]. Composites with the addition of silicides are used to create heat-loaded products that can be used in aviation, energy and other industries. Molybdenum disilicide is of great interest as a potentially useful high temperature material with low electrical resistivity (21.5 $\mu\Omega\cdot$cm) [2]. To date, the main application it has found in the manufacture of high-temperature heating elements operating in the air atmosphere up to 1800°C [3], molybdenum disilicide is used to create glow plugs for diesel cars, rocket nozzles, also thin layers of silicides are used in microelectronic devices as contacts and compounds [4,5]. In work [6] was shown that the coating of molybdenum disilicide increases the hardness of the niobium alloy and contributes to its resistance to oxidation. In the future, such coatings can increase the survivability of turbine blades in jet engines, and therefore increase their life. In the study [6], it was shown that when coating the niobium alloy, niobium and molybdenum disilicides are formed. We have suggested that the coating on niobium composite (Mo,Nb)Si$_2$ will increase the resistance of such coating due to better adhesion. However, initially it was required to study the physical and chemical properties (Mo,Nb)Si$_2$ ceramics. Previous studies in this area have shown that at higher temperatures, niobium penetrates the crystalline structure of molybdenum disilicide, forming other brittle intermediate compounds such as (Mo,Nb)$_3$Si$_3$ at the interface [6].
2. Experimental part

Commercial high-purity MoSi$_2$ powder (99.5%) was used as the starting material, that was obtained magnesium-thermal synthesis of (OOO "Plasmoce", Moscow). Powders were characterized using SEM (LEO Supra 50 VP, with a system of microanalysis INCA Energy + Oxford, Germany), XRD (XRD-6000 of the firm "Shimadzu", Japan) and particle size analysis (Fritch, Analysette 22, Germany). The distribution of powder particles size was determined using laser particle size analyzer. It was found that the distribution curve is characterized by three broad peaks with average values at 3, 10 (the dominant faction) and 40 µm in the range 0.5 – 60 µm. SEM powder analysis showed a diverse of forms (polygonal) of powder particles, agglomerates of smaller particles are observed between large crystals.

Solid-phase mixtures of MoSi$_2$ and NbSi$_2$ powder were prepared to produce a composite (Mo$_{1-x}$Nb$_x$)Si$_2$ (0≤x≤1 in steps of 10 wt.%). The powders were mixed and grounded in a planetary mill (speed 250 rpm for 20 minutes in an isopropanol medium), then these mixtures will be designated as solid-phase mixtures (SPM). Then, the crushed powders were dried in a drying cabinet at a temperature of 100 °C until the alcohol was completely removed. Raw materials were prepared by uniaxial double-sided pressing (200 MPa) from the obtained mixtures, in a steel mold. Next, the samples were placed in a graphite mold in a hot press (HP20-1000-3560- FP20 company "TERMAL TECHNOLOGY INC.", USA) and burned at a temperature of 1750 °C for 60 minutes in an Ar atmosphere with a maximum pressure of 30 MPa. The obtained tablets with a diameter of 25 mm and a height of ≈4 mm were sawn with a precision saw into 2 beams with a size of 20 x 4 x 4 mm.

Physical and mechanical tests were carried out on the beams:

1) Density of the samples was determined by the method of saturating of the body with liquid and subsequent hydrostatic weighing. Distilled water was taken as a liquid phase.

2) Flexural Strength was determined by a machine for mechanical research (Instron 5581, UK)

The calculation was carried out according to the formula:

$$\sigma_{bf} = \frac{3Pl}{2bh^2} \times 10^6, \text{ (MPa)},$$

where $P$ is the breaking force, (N); $b$ and $h$ are the width and height of the sample, respectively, (mm). The error in determining the flexural strength was ± 1%.

3) the Electrical Resistivity was measured by a four-probe method by passing a constant current through the sample in the range from 0.1 A to 1A (in increments of 0.1 A) from the beginning with the sign "+", then with the sign "-". The final voltage ($U_a$) at a given current was calculated by the formula:

$$U_a = \frac{U_+ + U_-}{2}$$

4) the Coefficient of Linear Temperature Expansion (CLTE) was determined on a high-temperature dilatometer (DIL 402 C7G of Netzsch, Germany). The sample was placed in a graphite holder and heated at a rate of 10°C/min to 1600°C.

5) Microhardness of samples was determined on Micro-hardness Tester 401/402 MVD (Shanghai) device. The diamond pyramid was used, the angles between the opposite sides of which were 136 degrees. The pyramid was pressed into the polished surface of the sample with a force of 1.95 N. the Microhardness was calculated by the formula:

$$H_V = 0.102 \frac{F}{S} = 0.102 \frac{2F \sin \theta}{D^2} = 0.1891 \frac{F}{D^2},$$

where $H_V$ – the value of microhardness Vickers; $F$ – applied force, N; $S$ – the square of the depressed area, mm$^2$; $\Theta$ – pyramid angle = 136°; $D$ – diagonal of area, mm.

3. Discussion of results

Figure 1 shows the relative density values for all compositions. The density was calculated with respect to x-ray densities of molybdenum and niobium disilicides, which is taken as 100% for pure molybdenum and niobium disilicide, and for intermediate compositions was calculated from the average corresponding to this composition. The graph shows a gradual increase in relative density with an increase in the content of NbSi$_2$. 

Figure 1. Relative density of the content of niobium disilicide in the composite (Mo_{1-x}Nb_{x})Si_2 The results of studies of the flexural strength of a series of samples are shown in the graph (figure 2).

Figure 2. The dependence of the flexural strength on the content of NbSi_2 in the composite (Mo_{1-x}Nb_{x})Si_2

The analysis of the results showed that the samples of pure molybdenum disilicide have the highest strength, then with an increase in the content the tensile strength drops to 130 MPa at 20 wt.% NbSi_2, then with an increase in the content of niobium disilicide strength does not change. Apparently, this is due to the low strength of the grain of niobium disilicide. Analysis of the microstructure of the chips showed that the solid-phase samples have an uneven structure with an island accumulation of the phase enriched with molybdenum or niobium disilicide, which leads to a decrease in the tensile strength of the composite (figure 3). The figure shows that the destruction is on the grain of disilicide, therefore, the strength of the composite itself will be determined primarily by the strength of the grain [7,8].

Figure 3. Microstructure of cleavage (Mo_{0.5}Nb_{0.5})Si_2
Since the disilicides have the property of conducting an electric current at the metal level, it was of great interest for research to influence the content of niobium disilicide on the resistivity of the composite (Mo$_{1-x}$Nb$_x$)$_2$Si$_2$. The obtained dependence of the resistivity shown in Fig. 4, has an extreme character with a maximum for the composition (Mo$_{0.5}$Nb$_{0.5}$)$_2$Si$_2$ and is 350 $\mu\Omega\cdot$cm. This type of curve is presumably due to the fact that the mixture of the tetragonal and hexagonal phases passes after sintering completely into the distorted hexagonal phase NbSi$_2$, therefore, in this case, the greatest number of defects in the structure of ceramics is observed. Open porosity in all cases did not exceed 3%. Therefore, this composite can be recommended for replacement net disilicide, molybdenum heating elements for high temperature atmospheric furnaces. Due to the greater resistivity for these furnaces, transformers of lower power will be rubbed.

Figure 4. The dependence of the electrical resistivity of the composite (Mo$_{1-x}$Nb$_x$)$_2$Si$_2$ on the concentration of NbSi$_2$ ($0 \leq x \leq 1$)

The obtained dependence of CLTE is shown in the graph (figure 5). For the solid phase of a mixture of disilicides values of CTE of composite (Mo$_{1-x}$Nb$_x$)$_2$Si$_2$ in the concentration range $0 \leq x \leq 0.3$ grow, then the value of the CTE reaches a plateau. In work [9] it was shown that for SHS composites (Mo$_{1-x}$Nb$_x$)$_2$Si$_2$ the change of crystal lattice parameters is observed with an increase in the content of NbSi$_2$. In this scenario, XRF’s looking a hexagonal lattice of niobium disilicide, while for the solid phase of the mixture of RFA regardless of the content captures the two phases of the tetragonal phase of the disilicide of molybdenum and hexagonal phase of the disilicide and niobium. It is with this that we associate a uniform decrease in tclr with an increase in the concentration of niobium disilicide.

Figure 5. The dependence of the CLTE of the composite (Mo$_{1-x}$Nb$_x$)$_2$Si$_2$ on the concentration of NbSi$_2$ ($0 \leq x \leq 1$)

Microhardness tests have shown that with an increase in the content of NbSi$_2$ in the composition of the composite, a decrease of obtained values until the composite 30% of NbSi$_2$. After that, we can see a steady decrease of obtained values. It can be observed due to the uneven distribution of hexagonal niobium disilicide and tetragonal molybdenum disilicide in solid-phase mixtures.
4. Summary

The effect of NbSi2 in the range from 10 to 90 wt% was investigated on the properties of composites (Mo1-xNbx)Si2 obtained by hot pressing a solid-phase mixture of molybdenum and niobium disilicides at a temperature of 1700°C. It was found that with an increasing level of NbSi2 in the content, the flexural strength drops to 130 MPa at 20 wt.% NbSi2, further flexural strength does not change from the content of niobium disilicide. The electrical resistivity depending on the content of niobium silicide is extreme with a maximum for the composition (Mo0.5Nb0.5)Si2. The increase in resistance is due to the distortion of the crystal lattice due to the introduction of Nb, resulting in the transition of the tetragonal phase of MoSi2 to the distorted hexagonal phase of NbSi2, which is consistent with the data of CLTE and microhardness, since in the concentration range of NbSi2 20-100 wt.% CLTE and microhardness of the composite within the error does not change.

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References

[1] Guzman I Ya 2003 Chemical technology of ceramics (Moscow) p 514
[2] Samsonov G V, Dorina L A, Rud’ B M 1979 Metallurgija Moscow
[3] https://www.kanthal.com/
[4] Yao Z, Stiglich J, Sudarshan T S 1999 Journal of Materials Engineering and Performance 8 3 291-304
[5] Govindarajan S et al. 1995 Surface and Coatings Technology 76 7-13
[6] Xiao L, Abbaschian R 1992 Materials Science and Engineering A 155 1-2 135-145
[7] Vasudevan A K, Petrovic J J 1992 Materials Science and Engineering: A 155 1-2 1-17.
[8] Hagihara K et al. 2016 Materials Letters 177 99-103
[9] Titov D D et al 2018 J. Phys.: Conf. Ser. 1134 012058