The impact of a sintering additive from Al,Mg,Y-oligomer on the physicochemical properties of MoSi₂ ceramic

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Abstract. We investigated the effect of a triple oxide additive (Al₂O₃-MgO-Y₂O₃) obtained by a new method on ceramics properties based on MoSi₂. The ternary oxide was obtained from a ceramic-forming oligomer. Ceramic MoSi₂ samples were obtained by hot pressing of molybdenum disilicide with ternary oxide 1, 3, 5, 10 wt% at 1650 °C and 30 MPa. The graphs of the dependence of density, bending strength and electrical resistance on the content of Al₂O₃-MgO-Y₂O₃ are presented. It was found that as the additive level was increased, the flexural strength increased to 89 MPa. The specific electrical resistance, depending on the oxide additive content, is extreme with a maximum for a composition containing 1 wt% Al₂O₃-MgO-Y₂O₃.

1. Introduction

Nowadays, there is a great need for materials that can work at high temperatures without destruction and preserve the original properties. Ceramics based on molybdenum disilicide are currently used to create heaters that can operate in an atmosphere of air at temperatures of 1600-1700 °C without destruction. Several factors contribute to this: the formation of a protective coat of SiO₂ on the surface of the material, and high electrical conductivity. High hardness, high heat resistance, is a set of properties that allows the use of MoSi₂ to create heating elements for the high-temperature furnaces [1]. However, the material has a number of disadvantages, including high initial ductility, low mechanical strength, low electrical resistance, and the inability to work at temperatures below 900 °C. The most part of the problems can be solved by additives introduction. For example, earlier, the authors of work [2] showed that the introduction of the WSi₂ additive leads to decreasing of the porosity and an increase of the bending strength by 40%, compared to pure disilicide obtained by hot pressing. The influence of yttrium and zirconium oxides on the properties of MoSi₂-based ceramics was studied in work [3]. Studies have shown that obtained samples had a fine-crystalline structure with a closed intercrystalline porosity lying in the range of 2-5%. The introduction of Y₂O₃ and ZrO₂ additives increased the bending strength values to 280 and 292 MPa, while the strength of pure disilicide was 150 MPa. In work [4], the author studied the influence of Sc₂O₃ and Y₂O₃ on the physical and chemical properties of MoSi₂-based ceramics was investigated. The results of the conducted studies showed that the introduction of 5 wt. % addition of Sc₂O₃ leads to increasing the three-point bending strength up to 1081 MPa. Disilicides are known to
have good electrical conductivity comparable to metals. The electrical resistivity of pure molybdenum disilicide is 21.6 $\mu\Omega\cdot\text{cm}$. The authors of work [5] investigated the effect of Lu$_2$O$_3$ and 3*Y$_2$O$_3$-5*Al$_2$O$_3$ (YAG) oxide additives on the electrical resistivity of MoSi$_2$-based ceramics. It is shown that both additives contribute to increasing of the conductivity of ceramics from $10^2$ ($\mu\Omega\cdot\text{cm}$)$^{-1}$ to $10^5$ ($\mu\Omega\cdot\text{cm}$)$^{-1}$, however, the difference of the intensities, authors attribute to different grain sizes of Lu$_2$O$_3$ and YAG.

A study of the literature has shown that the use of oxide additives has a positive effect on the mechanical properties of the material, reduces the sintering temperature, and controls the material's electrical resistivity. In this paper, we report on creating MoSi$_2$ ceramics using Al$_2$O$_3$-MgO-Y$_2$O$_3$ (YAG+MgAl$_2$O$_4$) as sintering additives. The article presents the research on the effect of the concentration of the sintering additive on the electrophysical properties of ceramics at room temperature and physical and mechanical properties.

2. Experimental part

Commercial high-purity MoSi$_2$ powder (LLC "Plasmaterm", Moscow) obtained by magnesium-thermal reduction was used as a starting material. The triple oxide additive Al$_2$O$_3$-MgO-Y$_2$O$_3$ was acquired by a new method developed at the SSC RF "GNIChTEOS". The process is based on the condensation of alkoxyalumoxane in the chelated form, hydrous yttrium acetylacetonate and magnesium acetylacetonate in an organic solvent (acetoacetyc ester). After that, the solvent was driven off, and the mixture was pyrolyzed at a temperature of 700°C as the result ceramic powder was obtained [6]. The method makes it possible to obtain high-purity raw materials of the required composition. Based on the phase diagram (figure 1), a compound of the composition xAl$_2$O$_3$-yMgO-zY$_2$O$_3$ was selected, where x=0.58 mol.%., y=0.21 mol.%, with a melting point of 1600 °C. This temperature corresponds to the initial sintering temperature of pure molybdenum disilicide [7].

![Phase diagram](image)

**Figure 1.** The phase diagram of the ternary system Al$_2$O$_3$-MgO-Y$_2$O$_3$

The powders were mixed and grounded in a planetary mill in an isopropanol medium for 2 hours. The crushed powders were placed in a drying cabinet until the alcohol was removed entirely. Raw materials were prepared by uniaxial double-sided pressing (200 MPa) in a steel mould with 25 mm. Dense ceramic samples were obtained by hot pressing (HP20-1000-3560- FP20 company "TERMAL TECHNOLOGY INC.", USA) in a graphite mould at a temperature of 1650 °C for 30 minutes in an
argon medium with a maximum specific pressure of 30 MPa. Ceramic samples with a diameter of 25 mm and a height of ≈ 5 mm were cut with a precision saw into beams with a size of 20 × 5 × 5 mm.

Physical and mechanical tests were carried out on the beams:
1) The density was studied by the method of saturation of the body with liquid and subsequent hydrostatic weighing. Distilled water was used as the liquid phase.
2) Three-point bending strength was determined by a machine for mechanical researches (Instron 5581, U.K.)

The calculation was carried out according to the formula:

\[ \sigma_{bf} = \frac{3PL}{2bh^2} \times 10^6 \text{, (MPa)}, \]  
(1)

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 symbol "-". The final voltage (\( U_a \)) at a given current was calculated by the formula:

\[ U_a = \frac{U_+ + U_-}{2} \]  
(2)

3. Results and discussion

The powder obtained after pyrolysis organomagnesiumoxanittriumoxanalumoxanes was characterized by XRD analysis and it was shown that after pyrolysis up to 750°C, the amorphous powder at 900°C, there is a halo of the dispersed phase and/or highly disordered due to polymorphic transformation of the structure of the low-temperature phase \( \eta \)-Al\(_2\)O\(_3\). XRD analysis of the powder after pyrolysis at 1500°C showed that the mixture consists mainly of alumomagnesium spinel MgAl\(_2\)O\(_4\)-77% aluminium-yttrium garnet Y\(_3\)Al\(_5\)O\(_{12}\)-23% (figure 2). In work [7], a thermochemical transformation scheme of organomagnesiumoxanitтрoxanalumoxanes was shown. It was established that ceramic samples based on organomagnesiumoxanittrixanalumoxanes are an oxide system \( x\text{MgO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{Y}_2\text{O}_3 \) microparticles of aluminium-magnesium spinel and aluminium-yttrium garnet (0.5 to 1.0 microns), are uniformly located along the boundaries of corundum grains (size from 3.0 to 5.0 microns). Which should prevent grain-boundary slippage. This effect reduces the high-temperature creep (creep) of the ceramic.

Pyrolyzed at 700°C, organomagnesium oxanittriumoxanalumoxane in powder form was used as a sintering additive for MoSi\(_2\) ceramics. Figure 3 shows the study of the density of the obtained ceramic samples with different content of the triple oxide additive (1, 3, 5, 10 wt.%). It is shown that an increase in the additive content leads to an increasing in the density of the samples. There is a significant increase in the density for the MoSi\(_2\)+5 wt.% composition of 5.85 g/cm\(^3\) compared to the value of 5.58 g/cm\(^3\) for the MoSi\(_2\)+3 wt.% composition.
Studies of the dependence of the flexural strength on the additive content (figure 4) have shown that an increase of the content of the triple oxide additive leads to an increasing of the strength values. When using 3 wt.% of the additive Al₂O₃-MgO-Y₂O₃ the value of the ultimate strength increases almost twice, relative to the composition with a content of 1 wt.% of the additive (from 48 MPa to 89 MPa). A further increase of the additive content leads to a slight increasing in strength. These results correlate with provided studies of density. A decrease in the value of the intercrystalline porosity leads to an increase in the samples' strength.

Figure 3. The dependence of the density of ceramic samples on the content of the additive Al₂O₃-MgO-Y₂O₃

Disilicides have good electrical conductivity. The studied dependence of the electrical resistance (figure 5) has an extreme character with a maximum for the composition of MoSi₂+1 wt.%. It is shown that the introduction of 1 wt.% of the additive leads to an increasing of the electrical resistance value to 45 μω*cm, which is almost twice higher than the value for pure MoSi₂ (25 μω*cm). A further increase of the content leads to a gradual decreasing of the values. The additive content increase may be related
to a decrease in the samples' porosity values because the additive, crystallizing during cooling, fills part of the pores.

Figure 5. Dependence of the specific electrical resistance of ceramic composites on the content of the additive $\text{Al}_2\text{O}_3-\text{MgO}-\text{Y}_2\text{O}_3$

4. Conclusion

In collaboration with the SSC RF "GNIIChTEOS", ceramic-forming oligomers containing Al, Mg, and Y were synthetized. Based on the oligomers, oxide additives $x\text{Al}_2\text{O}_3-y\text{MgO}-z\text{Y}_2\text{O}_3$ (where $x=58$ mol.%, $y=z=21$ mol.%) were obtained, which forms magnesium aluminium spinel and yttrium-aluminium garnet in the process of sintering the composite at 1500°C. Dense ceramic composites were obtained by hot pressing of the MoSi$_2$ with the sintering additive $\text{Al}_2\text{O}_3-\text{MgO}-\text{Y}_2\text{O}_3$ from 1 to 10 wt.%. It is shown that with an increase in the concentration of the sintering oxide additive, the density of MoSi$_2$ composites increases from 5.45 g/cm$^3$ to 5.95 g/cm$^3$, respectively, for MoSi$_2$ +1 wt.% and MoSi$_2$ + 10 wt.% Al$_2$O$_3$-MgO-Y$_2$O$_3$, with a decrease in the open porosity of ceramics from 3% to 1.2%. The flexural strength of the composite increases in the concentration ranges from 1 to 3 wt.% of the additive and then goes to the plateau (from 3 to 10 wt.% of oxide). The destruction of the samples goes along the intergranular boundaries, respectively, the strength of the composite is determined by the strength of the additive. The introduction of an oxide additive leads to an increasing of the resistivity with a maximum at 1 wt.% of the additive (43 $\mu\Omega$*cm), which is related with 2 factors: the dielectric contribution of the oxide additive and the highest porosity of the composite with 1 wt.% of the additive (about 3%).

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