Cermet materials reinforced with a small addition of spinel nanoparticles for molten salt power systems

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Abstract. This work is devoted to developing of new cermets for molten-salt power systems, promising for use in aviation, rocket and space technology, and power engineering. The production of cermets in the nickel-aluminum alloy system – 35 wt. % aluminum oxide by the method of mechanical activation and spark plasma sintering was carried out. It was found that the addition of 5 wt. % yttrium oxide, as well as small quantities (0.1 wt. %) of aluminum-magnesium spinel nanoparticles, increase the strength of the cermet at elevated temperatures. Cermets have high strength at room and elevated temperatures, which amounted to 480-530 MPa at 20 °C and 430-470 MPa at 750 °C. The microstructure of cermets was characterized by the presence of elliptical regions, the grains in which were significantly smaller than the grains in the surrounding matrix. This structure allows to effectively harden the material because elliptical areas are obstacles to crack propagation. Elliptical zones have length ranged 100 to 200 μm and width 5 to 20 μm. It was found that the material of the NiAl-Al₂O₃ system at 20 °C and 800 °C contains the phases NiAl, Al₂O₃, and Ni₂Al₃. Composite composition NiAl-Al₂O₃-Y₂O₃ at 20 °C and 800 °C retains the three-phase composition of NiAl, Al₂O₃, and Y₂O₃. Both materials are stable up to 800 °C.

1. Introduction

In recent years, interest in liquid salt energy systems has increased [1-6]. Such installations can be used in aviation, rocket and space techniques in advanced engines, as well as terrestrial, space and planetary-based solar installations [2,6,7]. However, such systems’ machinery parts operating conditions are extremely aggressive (high temperature, oxidizing environment, radiation, and mechanical stresses). Therefore, the main task is to develop new structural materials for use in such harsh conditions. Promising candidates for this are materials based on nickel, aluminum, and also with additions of oxides of various nature, for example, Al₂O₃ and others [8-15]. Such systems are heat-resistant, resistant to strong oxidants and radiation. The methods of dispersion and disperse strengthening found application in the creation of heat-resistant materials based on nickel back in the 60s of the 20th century. Some similar technological methods are still used today. For example, a nickel alloy with 2% of thorium oxide of the mass was obtained in the USA. It was found that the oxidation resistance of nickel with thorium dioxide particles is 3-5 times higher than that of pure nickel [16]. In 1992-2000 Ni (35 vol. %) - Al₂O₃ composites were created by reaction hot pressing. The ultimate bending strength of such a material was 613 MPa [17]. The high mechanical properties in comparison with similar materials are explained by the authors because of the better adhesion of Ni and Al₂O₃ and the containment of cracks in ceramics by nickel. Many researchers note the high prospects of composites based on nickel and its alloys with additions of oxide materials. An increase in the amount of the oxide component in the nickel matrix...
leads to an increase in the composite's mechanical strength and tribological properties [18,19]. For example, when the content of silicon oxide in the nickel matrix changed from 3 to 9%, the ultimate strength increased from 500 to 600 MPa, and the hardness (HV) from 170 to 260. Besides, the use of refractory compounds nanoparticles in low concentrations for strengthening metal and cermet composites is one way to improve the functional properties of new materials significantly. The use of nanoparticles in small amounts (no more than 0.1%) promotes their better distribution in the matrix with a minimum number of aggregates, which reduces the level of material defectiveness [20-25]. According to the Obraztsov-Lurie-Belov theory, an interfacial layer with properties different from the matrix (figure 1) around the nanoparticle could be formed [25].

Figure 1. Scheme of uniform distribution of solid nanoparticles and interphase strengthening zones in the matrix [25].

The addition of both nanoparticles of aluminum-magnesium spinel and micro- and submicron particles of yttrium oxide to cermet based on the NiAl-Al₂O₃ system should contribute to its strengthening according to the classical mechanisms of strengthening composite materials. Information could be found elsewhere [26].

The purpose of this work was to develop a cermet material and its composition with high strength at elevated temperatures, which could be used in molten salt systems for various machine parts (in turbo-pumps, impellers, journal bearings, gears, for example). Besides, the main aim of research is to study the influence of small amount of spinel nanoparticles on microstructure and strength of NiAl-Al₂O₃ cermet materials.

2. Materials and experimental methods
Powder of NiAl alloy (PN70Yu30) was used as a matrix; with 35 wt. % Al₂O₃ powder, 5 wt. % Y₂O₃ powder, and 0.1 wt. % MgAl₂O₄ nanoparticles were used in additives. Mixing was carried out in a planetary mill “Activator-2SL” with a ratio of balls of 1:10, balls of Al₂O₃ 5 mm in diameter, isopropyl alcohol and a surfactant additive were used as a dispersion medium. The mixing time was 15 min in an argon atmosphere. Sintering of cylindrical samples with a diameter of 30 mm and a height of 2 mm was carried out by the spark plasma method on FCT Systeme GmbH installation at a temperature of 900 °C for 18 min. Nanoparticles were introduced into the matrix by exposure to ultrasound in isopropyl alcohol. For bending tests, beads were cut from the sample pellets. They were carried out at 25 °C and 750 °C on a universal installation for mechanical testing TestSystems-VacEto (Keldysh Research Center) in accordance with GOST 25.604-82 [27]. For this, rectangles of 5x15x3 mm were cut from each tablet and used for three-point bending test. High-temperature X-ray phase analysis was performed at 20 °C and 800 °C in vacuum. High temperature exposure was 15 min. The structure of the samples was examined using a Quanta 600 scanning electron microscope.
Figure 2 shows the powders of the prepared mixtures of charge materials. After mixing, the oxide particles have a fragmentation shape. The particles size ranges from submicron to 30 μm. The dark gray areas on the microstructure illustrate the nickel-aluminum alloy powder.

![Figure 2. Powders of charge materials: (a) NiAl-Al₂O₃-0.1MgAl₂O₄, (b) NiAl-Al₂O₃-Y₂O₃-0.1MgAl₂O₄.](image)

Figure 3 shows the microstructure of cermet samples after sintering. As you can see, the grains have a smoothed shape. The size of oxide particles ranges from submicron values to 50 μm.

![Figure 3. Microstructure of sintered composites: (a) NiAl-Al₂O₃-0.1MgAl₂O₄, (b) NiAl-Al₂O₃-Y₂O₃-0.1MgAl₂O₄.](image)

3. Results and discussion

Figure 2 illustrates the microstructure of nickel powder before and after mechanical activation in a planetary mill. Nickel particles after activation had a more uniform size distribution, in contrast to the
untreated powder. Figure 4 shows the fracture structures of cermet specimens tested at different temperatures. A good distribution of components (ceramic and metal components) is clear. However, areas with submicron grains were found in the structure of the composite. Most likely, this happens due to the segregation of nanoparticles during mixing.

![Figure 4](image_url)

**Figure 4.** Structure of NiAl-Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-0.1MgAl<sub>2</sub>O<sub>4</sub> composite fractures at different test temperatures: (a) 20 °C, (b) 750 °C.

Figure 5 shows a crack propagation in a composite structure modified with yttrium oxide. It can be seen that areas with submicron grains impede its movement and force it to slow down, changing its trajectory. Previous studies [25,26,28] have shown composites' effectiveness with a similar structure but for aluminum matrix.

As a result of X-ray phase analysis (figure 6), it was found that the material of the NiAl-Al<sub>2</sub>O<sub>3</sub> system at 20 °C and 800 °C contains the phases NiAl, Al<sub>2</sub>O<sub>3</sub>, and Ni<sub>2</sub>Al<sub>3</sub>. Composite composition NiAl-Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> at 20 °C and 800 °C retains the three-phase composition of NiAl, Al<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>. Both materials are stable up to 800 °C.

Figure 7 shows the change in the ultimate three-point bending strength of NiAl-Al<sub>2</sub>O<sub>3</sub> composites with spinel nanoparticles at 20 °C and 750 °C. It was found that the addition of 5 wt. % of yttrium oxide increases strength at room temperature and elevated temperatures by an average of 10%.

Based on the typical microstructures shown in figures 4 and 5, we can say that cermets are obtained reinforced not only by the addition oxides, such as Y<sub>2</sub>O<sub>3</sub> and aluminum-magnesium spinel nanoparticles but also by the elliptical structures formed. This structuring makes it possible to increase cermets crack resistance because elliptical regions are effective barriers to crack propagation. Similar results were previously obtained on metal systems based on aluminum, reinforced with refractory compounds of various natures [28-30]. Still, there were no similar results on systems containing intermetallic compounds and ceramics with higher physical density.

As a result of NiAl-Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-0.1MgAl<sub>2</sub>O<sub>4</sub> samples X-ray phase analysis at 20 °C and at 800 °C, it was found that they have sufficient phase stability for such an operating temperature range, the main phases being NiAl, Y<sub>2</sub>O<sub>3</sub>, and α-Al<sub>2</sub>O<sub>3</sub>. 
Figure 5. Crack in the composite: (a), (b), (c) crack area microstructure at different magnifications, (d) scheme of crack propagating.

Figure 6. Results of X-ray phase analysis of the obtained composites: (a) 20 °C, NiAl-35Al₂O₃, (b) 800 °C, NiAl-35Al₂O₃, (c) 20 °C, NiAl-35Al₂O₃-5Y₂O₃, (d) 800 °C, NiAl-35Al₂O₃-5Y₂O₃.
Figure 7. Change in the three-point bending strength of composites depending on the composition and test temperature.

Mechanical tests of cermets at room and elevated (750 °C) temperatures have shown that the material of NiAl-Al₂O₃-Y₂O₃-0.1MgAl₂O₄ system has a strength of 530 and 480 MPa, respectively, which opens up the possibility of their use in turbopump units of molten salt power systems. Addition of 0.1 wt. % spinel nanoparticles in cermet NiAl-Al₂O₃ increases its strength by an average of 6% at room temperature and 12% at elevated temperatures. It is known that nanoparticles of refractory substances, which strengthen metals and alloys, are obstacles to the movement of dislocations [31]. Also, they contribute to high temperature creep resistance along the grain boundaries. Based on the results of mechanical tests of cermets with spinel nanoparticles, it was found that the addition of 5 wt. % yttrium oxide increases their strength by 10% at room and elevated temperatures. This may be because the yttrium oxide particles have a smaller size than aluminum oxide and contribute to the intermetallic compound's precipitation hardening. Also, yttrium oxide improves composite because it has a lower CTE than matrix components.

4. Conclusion
As a result of the study, samples of cermets of the composition NiAl-Al₂O₃-Y₂O₃-0.1MgAl₂O₄ and NiAl-Al₂O₃-Y₂O₃-0.1MgAl₂O₄, reinforced with aluminum-magnesium spinel nanoparticles, were obtained.

It is shown that the introduction of 5 wt. % yttrium oxide microparticles and 0.1 wt. % MgAl₂O₄ nanoparticles into cermet is based on the NiAl – 35 wt. % Al₂O₃ increase its strength by an average of 15-20% at room and elevated temperatures.

The performed X-ray phase analysis at 20 °C and 800 °C showed the stability of the cermets phase composition. In addition, cermets demonstrate high strength and stability at room and elevated temperatures, which are 480-530 MPa at 20 °C and 430-470 MPa at 750 °C. The presence of yttrium oxide microparticles and aluminum-magnesium spinel nanoparticles in small amounts contributed to an increase in the mechanical characteristics of cermets at working temperatures. Strengthening is facilitated by developed interphase contacts due to the addition of spinel nanoparticles, a low CTE with the addition of yttrium oxide, and a good distribution of components in cermet.

The composites' structure contains areas with large grains of 5-20 μm and regions in the form of ellipses with micron and submicron grains. The presence of areas with fine grains helps to inhibit cracks. The cracks have to bend while passing through this submicron grains zones and lose its energy. This should positively affect on the prospects for use new cermets in molten-salt power system units, in
aviation, rocket and space techniques, and power engineering, operating under increased mechanical loads.

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