Study of sintered aluminum materials with nanoparticles microadditions

L E Agureev¹, S V Savushkina¹, ², ⁴, I N Laptev¹, B S Ivanov¹, A V Ivanov¹, V I Kostikov³ and Zh V Eremeeva³
¹Keldysh Research Center, Onezhskaya 8, Moscow 125438, Russia
²Moscow Aviation Institute, Volokolamskoe Shosse 4, Moscow 125993, Russia
³National University of Science and Technology «MISIS», Leninskii av. 4, Moscow 119049, Russia
E-mail: nanocentre@kerc.msk.ru

Abstract. Sintered aluminum materials with small additions (0.01-0.15 vol.%) of aluminum, zirconium and magnesium oxide nanoparticles were obtained by powder metallurgy. The microstructure of the samples and the effect of the nature and concentration of nanoparticles on the matrix grain size, density, microhardness, and corrosion resistance in 10% solutions of nitric and sulfuric acids were studied. The addition of nanoparticles led to matrix grains decrease, an increase in the density, microhardness, and corrosion resistance of sintered aluminum samples. The lowest value of grain size was shown by the sample with 0.1% vol. magnesium oxide. Sintered aluminum material with 0.05% vol. zirconium oxide nanoparticles had the highest density ~ 2.67 g/cm³. The highest Vickers microhardness at the level of 0.474 GPa was obtained for material with the addition of 0.1 vol.% Al₂O₃ nanoparticles. All samples showed significantly greater corrosion resistance in comparison with pure sintered aluminum. The samples with nanoparticles withstood 30 hours of testing, and pure aluminum dissolved in nitric acid in 15 hours, and in sulfuric acid in 10.

1. Introduction
Dispersion-strengthened metals and alloys are often used in areas of technology operating under conditions of high mechanical stress and corrosion. Composites "aluminum - ceramic particles" have a lower specific weight, an optimal ratio of strength and plasticity and sufficient corrosion resistance in combination with high operational mechanical characteristics [1-4]. Oxide particles are stable in the aluminum matrix and block the dislocations movement. As noted in [5, 6], the structure of an interfacial layer is much more complicated in comparison with intergrain boundaries, since neighboring crystallites can have not only different orientations, but also different structures. The structure of the interfacial layer is more complicated if the materials are not heterogeneous, include impurities, surface phases, voids, etc. Nanoparticles have high unrealized surface energy and affect the structure of the grain boundaries (interfacial layers) of the matrix. Even small additives (less than 0.2% vol.) can significantly affect the functional properties of the sintered material. The properties of the hardened metal depend on the uniform distribution of nanoparticles. The greatest hardening is associated with the provision of low aggregation of nanoparticles and their uniformly distribution over the matrix volume. This can be achieved by additions of nanomodifiers in low concentrations. In most works on aluminum and its alloys modification by nanoparticles, the concentration of additives...
exceeds 1% vol [7-16]. However, in recent years, attention has been specifically growing to low concentrations of nanoparticles [1-4, 17-21].

Nanoparticles aggregates located at the grain boundaries of the metal matrix lead to an introduction of defects into the grains surface during a pressing process and penetrate into the metal. The nonequilibrium structure of the grain boundaries of disperse hardened materials is due to the presence of an excess dislocation density in the interfacial layers [22]. In [5] it is noted that defects distributed within the boundaries create internal stress fields that can impede the movement of dislocations in grains and their penetration into the boundaries. To make the deformation caused by external influence, it is necessary that the induced stress field, at which dislocations in the grain move, would be higher than the field \( \sigma_i \), and also above the level of the short-range fields \( \sigma_0 \) created by dispersed particles, impurity atoms, etc. The condition for the development of intragrain deformation can be expressed as follows: \( \sigma \geq \sigma_i + \sigma_0 \).

In this work, the method of powder metallurgy was used to study the effect of small nanoparticles additions on the structure, density, microhardness, and corrosion resistance of sintered aluminum-based material.

2. Experimental setup and characterization techniques

An aluminum powder with average particle size 4 \( \mu \text{m} \) was used as a material matrix. The specific surface of the powder having a spherical particles was 0.58 m\(^2\)/g. The oxide film thickness on the aluminum powder surfaces measured by X-ray photoelectron spectroscopy was \( \sim 5 \) nm. Nanoparticles \( \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{MgO} \) were used as nanomodifiers (Table 1).

| Nanoparticles type | Average diameter, nm | Specific surface, m\(^2\)/g |
|-------------------|----------------------|---------------------------|
| \( \text{Al}_2\text{O}_3 \) | 60                   | 27                        |
| \( \text{ZrO}_2 \) | 50                   | 32                        |
| \( \text{MgO} \) | 45                   | 40                        |

Sintered materials were prepared in several stages: screening of the matrix powder (sieve - 60 \( \mu \text{m} \)); preparation of nanoparticles suspensions in alcohol; aluminum powder and nanoparticles mixing in ethanol at room temperature under the influence of ultrasound; drying the mixture in air; pressing the mixture at 400 MPa; free sintering in vacuum at 640 °C for 180 min. The structure of materials was studied using optical microscope Carl Zeiss and scanning electron microscope (SEM) Quanta 600. A density of the samples was determined by helium pycnometry using Ultrapycnometer 1200e. After measuring the pycnometric density of the samples, their closed porosity was calculated. The apparent density was measured by pycnometer after the coating of the samples by impervious to the gas varnish. The microhardness of the samples (Vickers method) was measured using Micromet 5114 instrument. Corrosion resistance was estimated by the rate of mass loss in 10% solutions of nitric and sulfuric acids.

3. Results and discussion

The average grain size of the sintered material without the addition of nanoparticles was \( \sim 7.1 \mu \text{m} \). Figure 1 shows the microstructure of aluminum samples with the addition of zirconium oxide nanoparticles in various concentrations, obtained using SEM. Slightly elongated grains, as well as aggregates of zirconium oxide nanoparticles located at the grain boundaries are visible. Grains have various sizes. They are not abnormally large. The smallest average grain size (~ 4.2 \( \mu \text{m} \)) corresponds to the nanoparticles content equal to 0.01% vol., figure 1(a). In contrast to a material with 0.01% vol. \( \text{ZrO}_2 \) in the microstructure of the samples with 0.05% vol. zirconium oxide unevenness in the size distribution of grains is observed, figure 1(b). The SEM image shows large clusters of \( \text{ZrO}_2 \) nanoparticles located at the grain boundaries. The average grain size of aluminum was \( \sim 5.6 \mu \text{m} \). The closed porosity of these samples was \( \sim 2.3 \% \). SEM images of the material modified by 0.1% vol. \( \text{ZrO}_2 \)
also show large clusters of nanoparticles located at the grain boundaries, figure 1 (c). The average grain size decreases to ~ 5.2 μm. The sample with 0.1% vol. nanoparticles has a closed porosity ~2.3%. In the Al + 0.15% vol. ZrO₂ material clusters of zirconium oxide nanoparticles are more uniformly distributed over grain boundaries, figure 1(d). Some clusters have a vermicular shape. This sample has a low closed porosity ~2.2%. The average grain size is ~ 5.4 μm. However, abnormally large grains with a size of 15–20 μm are observed. At a higher magnification, a large number of individual nanoparticles with a size of 30–40 nm located between the matrix grains is found.

Figure 2 shows the dependence of the grain size of aluminum on the content of various nanoparticles. An evaluation of the average grain size for all samples was carried out by calculating the number of crossings of grain boundaries by secants. The secants were applied to the SEM and optical microscope images. The secant must cross at least 10 grains, and at least 50 grains must be in full sight. The number of intersections was counted in the at least five sections. When determining the grain size, the average size \( L_a \), mm was calculated by the formula: \( L_a = L/N \), where \( L \) was the total length of the secants in same direction, reduced to the plane of the section; \( N \) was the total number of grains crossed by secant length \( L \). The smallest grain size (~ 3.2 μm) was obtained for sintered material with additives of 0.1 vol.% MgO.

![Figure 1](image_url)

**Figure 1.** The microstructure of the sintered material with nanoparticles additions in the amount of: a) 0.01 vol.%; b) 0.05 vol.%; c) 0.1 vol.%; d) 0.15 vol.%.
The average grain size of aluminum modified by different type and concentration of nanoparticles.

Figure 2. The average grain size of aluminum modified by different type and concentration of nanoparticles.

The density of aluminum samples containing 0.05, 0.1, and 0.15 vol.% alumina nanoparticles was measured before and after sintering. The final density increased with additive amount increase, although the samples with 0.05% vol. nanoparticles had the highest density before sintering, figure 3 (a). The total porosity of the samples after sintering for a concentration of 0.05% vol. Al$_2$O$_3$ nanoparticles was ~4.4%, for 0.1% vol. ~ 3.3%, and for 0.15% vol. ~ 4.0%. For sintered Al+ZrO$_2$ material, the sample modified by 0.05% vol. nanoparticles had the highest density (2.67 g/cm$^3$) after sintering, figure 3 (b). As in the previous case, before the sintering process the density was higher for the sample with 0.05% vol. Figure 3 (c) shows the dependence of the Al+MgO material density on the content of nanoparticles. An increase in the density of the samples up 2.62 g/cm$^3$ after sintering was observed for materials with 0.1 and 0.15% vol. The opposite effect was for concentrations of 0.01 and 0.05% vol. which is possibly associated with desorption of the dispersant or moisture at high temperature. Before to sintering the samples with 0.01% vol nanoparticles possessed the highest density.

Figure 4 shows the dependence of microhardness on the content of nanoparticles in sintered materials. The microhardness of sintered aluminum without additives was ~ 0.335 GPa. All types of nanoparticles additives led to an increase in the microhardness of aluminum. The sample with 0.1 vol.% Al$_2$O$_3$ nanoparticles showed the maximum value of 0.475 GPa. For material modified zirconium oxide, the microhardness was ~ 0.44 GPa for all samples. The least microhardness was shown by the samples with MgO additives.

All modified materials showed significantly greater corrosion resistance in solutions of nitric and sulfuric acids in comparison with pure sintered aluminum. The samples with nanoparticles withstood 30 hours of testing, and pure sintered aluminum dissolved in nitric acid in 15 hours, and in sulfuric acid in 10. The lowest mass loss rate of 1.1 mg/h was observed by the sample with 0.01 vol. % ZrO$_2$ additives, figure 5. In sulfuric acid, the material with 0.05 vol.% ZrO$_2$ nano-additives showed the best result (2.2 mg/h). The worst corrosion resistance in H$_2$SO$_4$ the sample with 0.15 vol.% nanoparticles showed. Perhaps this is due to the number and size of defects (cavities) introduced as a result of mixing the nanoparticles with aluminum powder. A nonlinear change in the corrosion resistance of aluminum sintered materials is possibly related to the shape of the interfacial layers around the nanoparticles. Nanoparticles concentrations of 0.01 and 0.05 vol.% lead to an optimal compaction level and a more correct distribution of additives in the matrix, which affects the diffusion of the oxidizing agent along the grain boundaries, preventing corrosion.
Figure 3. The dependence of aluminum samples density on the content of nanoparticles before and after sintering. a) Al₂O₃, b) ZrO₂, c) MgO.

Figure 4. Dependence of aluminum materials microhardness on the nanoparticles content.
Further improvement of microhardness, wear resistance and corrosion resistance of the sintered material can be achieved by metals alloying and applying or growing a functional surface coating, for example, from aluminum oxide [23-24].

4. Conclusions
The addition of nanoparticles led to matrix grains decrease, an increase in the density, microhardness, and corrosion resistance of sintered aluminum samples. According to the distribution of nanoparticles in the matrix, the best results were observed for aluminium materials with a minimum content of nanoparticles (Al₂O₃ - 0.05% vol., ZrO₂ - 0.01% vol., MgO - 0.01% vol.). It is associated with lower aggregation at these nanoparticles concentration and easier conditions for nanoparticles distribution inside the matrix during the mixing process. The average grain size for various aluminum composites was in the range of 3.2-5.6 μm. The lowest value corresponded to the sample with 0.1% vol. magnesium oxide and was 3.2 μm. Sintered aluminum material with 0.05% vol. zirconium oxide nanoparticles was closest to the theoretical density of aluminum and equal to 2.67 g/cm³. The highest Vickers microhardness at the level of 0.474 GPa was obtained for the sample with the addition of 0.1 vol.% Al₂O₃ nanoparticles. In 10% solutions of nitric and sulfuric acids, the samples with 0.01% vol. zirconium oxide nanoparticles had the least rate of mass decrease equal to 1.1 mg/h. With an increase in the concentration of nanoparticles up 0.05% vol. the rate of weight loss increased to 3.1 mg/h, however, a further increase in nanoparticles to 0.1 and 0.15% vol. led to a decrease in corrosion rate to 2.5 and 2.4 mg/h, respectively. In sulfuric acid, the best result (2.2 mg/h) was showed by the material with 0.05 vol% zirconium oxide nanoparticles.

Acknowledgments
The study was supported by grant from the President of the Russian Federation No. MK-54.2019.8.

References
[1] Agureev L E, Kostikov V I, Yeremeyeva Z V, Barmin A A, Rizakhanov R N, Ivanov B S, Ashmarin A A, Laptev I N, Rudshtein R I 2016 Inorg. Mater. Appl. Res. 7 507-10.
[2] Mironov V V, Agureev L E, Eremeeva Z V, Kostikov V I 2018 Dokl. Phys. Chem. 481 2 110-13.
[3] Agureev L E, Savushkina S V, Laptev I N, Ivanov A V 2019 J. Phys.: Conf. Ser. 1396 012001
[4] Kostikov V.I., Agureev L.E., Eremeeva Z.V. 2015 J. Non-Fer. Met. 56 3 c. 325-28
[5] Chuvildeev V N 2004 *Nonequilibrium grain boundaries in metals. Theory and applications.* (Moscow: Fizmatlit)

[6] Bokshtein B S, Yaroslavtsev A B 2005 *Diffusion of atoms and ions in solids* (Moscow: MISiS)

[7] Hosking F M, Portillo F, Wunderlin R. Mehrabian R 1982 *J.Mater.Sci.* **17** 2 477-98

[8] Maruyama B, Hunt W P 1999 *JOM* **11** 59-61

[9] Srivatsan T S, Mattingly J 1993 *J. Mater. Sci.* **28** 611 - 20

[10] Pandey A B, Chawla N 1999 *JOM* **51** 11 69-72.

[11] Kang Y C, Chan S L I 2004 *Mater. Chem. Phys.* **85** 438-43

[12] Ma Z Y, Tjong S C, Li Y L 1997 *Mater. Sci. Eng., A* **225** 125-34

[13] Mazahery A, Osfadhabani M 2011 *J. Compos. Mater.* **45** 24 2579-86.

[14] Zebjarad S M, Sajjadi S A, Vahid Karimi E Z 2008 *Res. Let. Mater. Sci.* 1-4

[15] Ansary Yar A, Montazerian M, Abdizadeh H, Baharvandi H R 2009 *J. Alloys Compd.* **484** 400-4

[16] Hemanth J 2009 *Mater. Sci. Eng., A* **507** 110-13

[17] Sukhodaev P O, Redkin V E, Bogdanova T A, Kuznetsov V A 2017 *J. Siberian Federal University. Eng. Technol.* **10** 3 317-26

[18] Roudini G, Rasti Ghahfarokhi A, Behzadmehr A 2017 *IOP Conf. Series: Mat. Sci. Eng.* **201** 12-26

[19] Lurie S, Volkov-Bogorodskiy D, Solyaev Y, Rizahanov R, Agureev L 2016 *Comput. Mater. Sci.* **116** 62-73

[20] Kishore Babu N, Kallip K., Leparoux M., Al Ogab K A. 2016 *Mater. Des.* **95** 534–44

[21] Kallip K, Kishore Babu N, Khaled A. Al Ogab K A, Kollo L, Maeder X, Arroyo Y, Leparoux M 2017 *J. Alloys Compd.* **714** 133-43

[22] Kosevich V M, Ievlev V M , Palatnik I S, Fedorenko A I 1980 *The structure of intergranular and interphase boundaries* (Moscow: Metallurgy)

[23] Agureev L et al. 2018 *Metals* **8** 6 459

[24] Savushkina S V, Agureev L E, Ashmarin A A, Ivanov B S , Apelfeld A V, Vinogradov A V 2017 *J. Surf. Invest.* **11** 6 1154–58