Influence of nafen nanoparticles on the strength of nickel

L E Agureev¹, B S Ivanov¹, S V Savushkina¹, I N Laptev¹, A I Kanushkin²
and G V Sivtsova¹

¹Department of nanotechnologies, SSC FSUE “Keldysh Research center”, 125438, Moscow, Russia
²LLC "Rusatom – Additive Technologies", 115409, Moscow, Russia

E-mail: trynano@gmail.com

Abstract. The article presents the results of studies of the structure and properties of pure nickel with the addition of nanofibers of aluminum oxide – nafen. The samples were obtained by spark plasma sintering of mechanically activated metal powder. The effect of nanofibers on Young's modulus and ultimate strength of nickel at 25 °C and elevated temperatures is considered.

1. Introduction
Nickel-based materials are used in various industries: aviation, astronautics, mechanical engineering, energy, and others [1]. Nickel is a universal chemically stable metal, the hardening of which can be associated with a wide range of different methods [2]: Paerls-Nabarro hardening, solid solution hardening, dislocation hardening, dispersion hardening, grain boundary hardening. Pure nickel is not used as a structural material due to its high density and relatively low strength, but its modification allows achieving a significant increase in mechanical characteristics [3].

Dispersion hardening is caused by both coherent and incoherent particles and precipitates with varying efficiency. Earlier, in works related to the strengthening of molybdenum [4] and aluminum [5–7] by introducing spherical nanoparticles of refractory oxides in an amount of 0.01–0.1 wt. %, it was shown that an increase in the ultimate strength can reach 30–300 %, compared to pure metal. The materials were obtained using powder metallurgy technologies.

It should be noted that the introduction of refractory insoluble high-modulus nanoparticles into a metal matrix in small amounts (up to 0.1 wt. %) contributes to their simpler and more uniform distribution [8, 9]. This is due to the fact that nanoparticles tend to aggregate. In addition, according to the Obraztsov-Lurie-Belov micromechanical model, based on the gradient theory of elasticity [10], a hard nanoparticle, being in a soft matrix, contributes to the formation of an interfacial hardening zone, which is characterized by increased mechanical characteristics compared to the matrix. The better the nanoparticles are distributed, the more uniform and continuous these zones are. In this case, the metal, as noted above, can significantly harden.

2. Materials and experimental methods
In the present study, experiments were carried out to modify pure nickel by introducing nanoparticles of aluminum oxide in the form of fibers. Nickel powder PNK-UT3 (20 μm, 99.9 %, GOST 9722–97) was used as a matrix. For modification, nanoparticles of aluminum oxide in the form of fibers (NafenTM, diameter 10 nm, length up to 5 μm) were used [11].
Nickel powder was activated in a planetary mill "Activator-2SL" in steel glasses. The grinding balls were made of stainless steel, 5 mm in diameter with a ratio of P: W = 1:10. Activation was carried out in isopropyl alcohol of chemical purity with the addition of a surfactant (hexamethyldisilazane). Nanoparticles of alumina fibers were dispersed in isopropyl alcohol using a UPS 3600 Bandeline ultrasonic homogenizer for 3 minutes at a power level of 50 % in a pulsed mode. The introduction of nanoparticles was carried out into nickel powder in isopropyl alcohol under the action of low power ultrasound in an ultrasonic bath for 5 minutes while stirring the solution with an overhead stirrer at a speed of 400 rpm. Then, it was dried in a vacuum drying oven at 250 °C for 10 hours. After that, the powder was sintered by the spark plasma method on the FCT Systeme Gmbh installation in the form of tablets with a diameter of 30 mm and a height of 3 mm. The sintering temperature was 950 °C, the time was 20 min, the process was carried out in argon, the pressing pressure was 50 MPa. Were obtained samples with a concentration of nanoparticles equal to 0, 0.01, 0.025, 0.05, 0.075 and 0.1 % of the mass.

For tensile tests, beads were cut from the sample pellets. The tests were carried out at 25 °C, 400 °C, 750 °C on a universal installation for mechanical testing TestSystems-VacEto (Keldysh Center). Young's modulus of nickel with additives of nanoparticles was determined on an ultrasonic unit "MUZA" at temperatures of 25 °C, 400 °C, 750 °C. For this, rectangles of 5×15×3 mm were cut from each tablet.

The structure of the samples was examined using a Quanta 600 scanning electron microscope.

3. Results and discussion

Figure 1 shows photographs of 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 1: Microstructure of nickel powder after mechanical activation.](image)

Figure 2 shows the microstructure of sintered nickel samples without nanoparticles and with 0.1 wt. % nanoparticles. The samples were etched with a solution (HNO3 + H2O + CH3COOH).

With an increase in the number of nanoparticles, the grain size significantly decreases in comparison with pure sintered nickel, on average from 8 μm to 3 μm.

The behavior of Young's modulus of nickel sintered by the IPS method looks interesting, both without and with nanoparticles. Figure 3a shows the nature of the change in Young's modulus of nickel depending on the composition in comparison with cast samples [12]. Even with an increase in the test temperature to 400 °C or more, the elastic modulus decreases by 10 % compared to tests at 25 °C. Most likely, this is due to the high surface energy of nanoparticles of aluminum oxide fibers, which contribute to the development of contact with the matrix and better adhesion. In addition,
nanoparticles interfere with the recrystallization and softening of the metal. It should be noted that there are oxide films on powder metals, incl. on nickel NiO, which can also prevent self-diffusion. The formation of chemical compounds between nickel oxide and aluminum oxide nanoparticles is not excluded, which is expressed in the formation of aluminum-nickel spinel NiAl₂O₄ [13–15].

![Figure 2](image.png)

**Figure 2.** Microstructure of sintered nickel samples.

![Figure 3](image.png)

**Figure 3.** Comparison of the dependence of the Young's modulus of nickel depending on the manufacturing method and the presence of nanoparticles (a). Comparison of the dependence of the strength of nickel and Monel alloy depending on the production method and the presence of nanoparticles (b).

Figure 3b shows the dependence of the tensile strength for Ni and Ni-0.1Nf alloys on the test temperature. At 25 and 400 °C, the curves are similar. However, at 750 °C it becomes less obvious. The increase in the strength of nickel at 25 °C is on average from 7 to 38 % (for samples with 0.01–0.1 wt. % of nanoparticles). It is known that the temperature of 350–400 °C for pure nickel is a turning point, after which the decrease in strength occurs with an extreme character, a similar picture is observed for the Monel alloy [13].
In this regard, nanoparticles of alumina fibers prevent high-temperature creep when the matrix still retains its strength properties. At 750 °C, the metal significantly softens, recrystallizes, and the effect of nanoparticles located at the grain boundaries slows down the destruction processes.

The nanoparticle has an uneven surface with convex and concave areas, chips, and an uneven composition. This can lead to the introduction of voids into the IFS, which will also lead to a state of imbalance of grain boundaries. Those on the one hand, in the early stages of sintering, nanoparticles contribute to shrinkage due to the introduction of additional defects and stresses, and on the other hand, they prevent the coarsening of matrix grains at the later stages of consolidation. Nanodispersed powders represent a nonequilibrium system with an excess of free energy. The pressure due to the presence of a curved surface with two main radii of curvature can exceed 300 MPa for particles with a size of 20 nm compared to 3 MPa for particles with a size of 1 μm [16].

4. Conclusion
1. By the method of mechanical activation of powders with subsequent introduction of nanoparticles under the action of ultrasound and spark plasma sintering, samples of nickel containing nanoparticles of aluminum oxide fibers in the range of 0–0.1 wt.% were obtained.

2. It has been established that the tensile strength of sintered nickel increases with an increase in the concentration of nanoparticles to 0.1 % by 10–40 % at room temperature. With an increase in the temperature of strength tests to 400–750 °C, the increase in strength is not so pronounced and amounts to 5–10 %, in comparison with pure sintered nickel.

3. The influence of nanoparticles on the elastic modulus of nickel has been found, which contribute to its increase by 10 % at room temperature of tests. In addition, it was noted that nanoparticles prevent the softening of nickel when the test temperature rises to 400–750 °C.

4. The general character of the change in short-term strength and Young’s modulus on the number of nanoparticles and test temperature is shown, which consists in an increase in mechanical properties with an increase in the concentration of nanoparticles in the range of 0.01–0.1 wt. % at the test temperature range of 25–750 °C.

Acknowledgements
The study was carried out with the financial support of the Russian Foundation for Basic Research within the framework of scientific project No. 20-33-70009.

References
[1] Heubner U 2000 Nickel alloys (New York, Basel, Marcel Dekker Inc.)
[2] Goldshtein M I, Litvinov V S and Bronfin M F 1986 Metallophasis of high-strength alloys (Moscow, Metallurgia)
[3] Davis J R 2000 Nickel, Cobalt, and their alloys. ASM Speciality Handbook (Materials Park, OH – ASM International)
[4] Bruckart W L and Jaffee R I 1952 Transactions Am. Soc. Metals 44
[5] Lurie S, Volkov-Bogorodskiy D, Solyaev Y, Rizahanov R and Agureev L 2016 Comput. Mater. Sci. 116 62–73
[6] Kostikov V I, Agureev L E and Eremeeva Zh V 2015 Russ. J. Non-Ferr. Met. 56 325–8
[7] Sharma A, Roh M-H, Jung D-H and Jung J-P 2016 Metallurgical and Materials Transactions A 47A 510–21
[8] Agureev L E, Kostikov V I and Yeremeyeva Z V 2016 Inorganic Materials: Applied Research 6 507–10
[9] Mironov V V, Agureev L E, Eremeeva Z V and Kostikov V I 2018 Doklady Physical Chemistry 481 110–3
[10] Lurie S, Belov P, Volkov-Bogorodsky D and Tuchkova N 2006 J. Mat. Sci. 41 6693–707
[11] Saunders Z, Noak C W, Dzombak D A and Lowry G V 2015 Journal of Nanoparticle Research 17 1–14
[12] 1921 *Nickel. Circular of the Bureau of Standards* **100** (Washington Government printing office)
[13] Bhattacharjee P P, Sinha S K and Upadhyaya A 2007 *Scr. Mater.* **56** 13–6
[14] Borkar T and Banerjee R 2014 *Mater Sci Eng A* **618** 176–81
[15] Minier L, Le Gallet S, Grin J and Bernard F 2012 *Mater. Chem. Phys.* **134** 243–53
[16] Ragulya A V and Skorokhod V V 2007 *Consolidated nanostructured materials* (Kiev, Naukova Dumka)