Effect of nanostructuring on the thermal expansion and saturation magnetization of Fe - 36% Ni and Fe - 50% Ni alloys

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Abstract. Nanostructured samples of Fe - 36% Ni (Invar alloy) and Fe - 50% Ni alloys with a fragment size of about 100 nm were obtained by high pressure torsion using Bridgman anvils. The formation of the nanostructure leads to a decrease in the coefficient of thermal expansion of the Fe - 36% Ni and Fe - 50% Ni alloys by 2.2 and 1.2 times, respectively. Annealing of the Fe - 36% Ni alloy after nanostructuring leads to the formation of a dispersed bcc phase, which is not observed in the coarse-grained Invar alloy. The release of this phase affects the anomalous growth of thermal expansion (above the values typical for a coarse-grained Invar alloy) and the retention of saturation magnetization at temperatures above the Curie temperature of 260 °C. It is found that heating the nanostructured Fe - 50% Ni alloy above the Curie temperature (460 °C) saves the saturation magnetization. By analogy with the results for the Fe - 36% Ni, it can be assumed that this is due to the appearance of a dispersed bcc ferromagnetic phase. Detailed structural analysis will be carried out in future works.

1. Introduction
Alloys of the Fe-Ni system are distinctive materials due to the fact that the variation in the amount of dissolved Ni atoms in Fe has a significant effect on the physical properties of an alloy. A unique alloy of this system is Invar [1], which contains 36% Ni and has an abnormally low value of the coefficient of thermal expansion (CTE) equal to \( \alpha \approx 1.6 \cdot 10^{-6} \, \text{C}^{-1} \) in a certain temperature range. Due to this, it has found wide application in modern technology and instrument making. However, a change in the nickel content by only ±5% leads to a sharp increase in the CTE. For example, for the Fe-50%Ni alloy, it has a value as high as \( \alpha \approx 8.9 \cdot 10^{-6} \, \text{C}^{-1} \) [1].

An important disadvantage of Fe-Ni alloys, limiting their application is their low strength and hardness. For example, the tensile strength of the alloy Fe - 36% Ni is less than 500 MPa [2,3], and the tensile strength of a strip made of Fe - 50% Ni alloy is about 450 MPa. To date, the method of alloying with Be [4], Mo or W [5] atoms is used to harden the Fe - 36% Ni alloy, which most often leads to an increase in the CTE. Another effective method for increasing the strength properties of alloys is deformation nanostructuring. It was established in [6] that the microhardness of the Fe - 36% Ni alloy in the nanostructured (NS) state was 4250 MPa, although in the coarse-grained (CG) state it was 1300 MPa [3]. Nanostructured materials are not only characterized by high strength but also have unique physical properties that are not typical for materials in the CG state [7, 8, 9, 10, 11]. Therefore,
A detailed study of the effect of severe plastic deformation on the properties of Fe-Ni alloys in different structural states is of fundamental and practical interest. The present work is devoted to the study of the effect of deformation nanostructuring on the CTE and saturation magnetization of alloys of the Fe-Ni system: Fe - 36% Ni and Fe - 50% Ni. This work is a continuation of the previous works of the authors on the investigation of the phase composition and thermal expansion of Invar alloy in different structural states, from nanocrystalline to microcrystalline ones [7, 9,10].

2. Experimental

Nanostructured samples of the alloys Fe - 36% Ni (Invar) and Fe - 50% Ni were processed by severe plastic deformation using high pressure torsion on Bridgman anvils. The deformation was carried out up to the true logarithmic strain value of $e = 7$. The structures of Fe - 36% Ni and Fe - 50% Ni alloys after nanostructuring are shown in figures 1, a and b, respectively. It can be seen, that the alloys have a structure consisting of equiaxed fragments with a size of about 100-200 nm. Fragment boundaries are relatively thin. Reflexes on electron diffraction patterns obtained from several fragments are arranged in a circle. To obtain a different structural state, the samples after severe plastic deformation were annealed in a vacuum for 45 min and then cooled with the oven. Annealing of alloys after nanostructuring leads to the formation of equiaxed grains, and their average size increases monotonically with the annealing temperature $T_{an}$.

![Figure 1. TEM images and diffraction patterns of NS Fe - 36% Ni (a) and Fe - 50% Ni (b) alloys obtained by severe plastic deformation.](image)

The coefficient of thermal expansion $\alpha(T)$ is measured on a Dh 1500 RHP ULVAC SINKU-RIKO dilatometer. The NS samples are heated in the process of measuring $\alpha(T)$ at a constant rate of 2 °C/min and then cooled with the oven. The microstructure is studied using transmission electron microscopy (TEM) on a JEM-2000EX operated at 120 kV. Changes in the dependence of the saturation magnetization on the temperature and annealing time are carried out by automatic magnetic vacuum microbalance [12]. The magnetic field, which is enough to achieve saturation, is 240 kA/m.

3. Results and discussion

Figure 2 shows the CTEs at 20 °C of the Fe - 36% Ni and Fe - 50% Ni alloys after deformation nanostructuring as functions of the annealing temperature. It can be seen, that severe plastic deformation leads to a decrease in the coefficient $\alpha_{20 \degree C}(T)$ by 2.2 and 1.2 times for Fe - 36% Ni (a) and Fe - 50% Ni (b) alloys, respectively. In [13], a decrease in the CTE of Invar alloy (Fe - 35% Ni - 0.49% Mn) was also observed after the plastic deformation by upsetting with the strain $e = 1.1$, which was explained by the arising distortion of the crystal lattice. This results in the weakening of the interatomic interactions and contributes to the appearance of negative bulk magnetostriction.
Annealing leads to an increase in the thermal expansion of the alloys, due to a decrease in the defects density, which reduces the distortion of the crystal lattice. After annealing at 500 °C, the value of $\alpha_{20 \, ^\circ \text{C}}$ of both alloys approaches the one typical for the CG state. However, on the $\alpha_{20 \, ^\circ \text{C}}(T_{\text{an}})$ curve for the Fe - 36% Ni alloy, an anomalous increase in the CTE is observed in the interval $T_{\text{an}} = 350 – 420$ °C. This is due to the precipitation of a less close-packed bcc phase in the Fe - 36% Ni alloy, which was previously discovered by the authors in the NS Invar alloy using X-ray diffraction analysis [10]. The deterioration of the Invar properties during the separation of the bcc phase in the Invar alloy obtained by electrodeposition was observed in [14]. At the annealing temperature above 420 °C, the ferromagnetic bcc phase dissolves, which decreases $\alpha_{20 \, ^\circ \text{C}}$ to the values characteristic of CG Invar. The abnormal formation of the bcc phase after annealing of the NS Fe - 36% Ni alloy became possible due to a sharp increase in the diffusion capacity of alloys after deformation nanostructuring associated with nonequilibrium grain boundaries [15, 16, 17].

Figure 2.

Figure 2. Thermal expansion coefficient at 20 °C $\alpha_{20 \, ^\circ \text{C}}$ as the function of annealing temperature $T_{\text{an}}$ for the NS Fe - 36% Ni (squares) and Fe - 50% Ni alloys (circles). The dashed line shows the CTE values corresponding to these alloys in the CG state.

Figure 3 shows the changes in the saturation magnetization of the Fe - 36% Ni (a) and Fe - 50% Ni (b) alloys during heating after deformation nanostructuring. One can see that the $\sigma(T)/\sigma_0$ curves show the preservation of the saturation magnetization of the studied alloys at $T$ above the Curie temperature ($T_c = 260$ and 460 °C for Fe - 36% Ni and Fe - 50% Ni, respectively). In figure 3, the Curie temperature is shown with a vertical dashed line. It should be noted that upon cooling of NS alloys after annealing at 500 °C (blue curves in figure 3 (a) and (b)), it appears only at $T_c$, which is typical for alloys in the CG state. The retention of the saturation magnetization at $T > T_c$ for the Fe - 36% Ni alloy is associated with the formation of the ferromagnetic bcc phase, which dissolves during annealing at 500 °C [10, 18]. It was found in [18], that as a result of the annealing of the NS Invar alloy, about 10%
of the bcc phase was formed. Presumably, the formation of the bcc phase also occurs in the Fe - 50% Ni alloy, which leads to the observed magnetization of the alloy above the Curie temperature.

![Figure 3. Saturation magnetization of the Fe - 36% Ni (a) and Fe - 50% Ni (b) alloys after nanostructuring as the function of temperature. The saturation magnetization, $\sigma_0$, of NS alloys at room temperature after annealing at 500 °C.](image)

4. Conclusions
Using severe plastic deformations by high pressure torsion on Fe - 36% Ni and Fe - 50% Ni alloys, a NS with fragment sizes of about 100-200 nm is obtained. It is found that the formation of the NS state leads to a decrease in the CTE of the Fe - 36% Ni and Fe - 50% Ni alloys by 2.2 and 1.2 times, respectively, in comparison with the CG state. This is due to the effect of nonequilibrium grain boundaries on the magnetic subsystem of alloys and interatomic interaction, leading to an increase in negative magnetostriction [13].

After annealing of NS Invar alloy above 300 °C, an anomalous increase in thermal expansion above the CTE of the alloy in the CG state is observed. This is due to the formation of a less densely packed bcc phase [10, 18], which is not typical for the cast Fe - 36% Ni alloy. The formation of the bcc phase occurs due to an increase in the diffusion capacity of NS alloy [15, 16].

In the NS Fe - 36% Ni and Fe - 50% Ni alloys, anomalous retention of saturation magnetization is observed at temperatures above the Curie temperature (260 and 460 °C, respectively), which occurs due to the release of the ferromagnetic bcc phase, which dissolves after annealing at 500 °C.

The data obtained show that by varying the annealing temperature after deformation nanostructuring of Fe - 36% Ni and Fe - 50% Ni, it is possible to achieve the required thermal expansion value of alloys under study while maintaining their magnetic properties in a wide temperature range. Also, deformation nanostructuring leads to an increase in the mechanical properties of alloys [6], which is an important parameter for expanding the scope of their application.

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