Effect of deformation nanostructuring on thermal expansion and phase composition of Fe - 36% Ni alloy

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Abstract. The influence of deformation nanostructuring and subsequent annealing on the temperature dependence of the thermal expansion coefficient of the Fe-36% Ni Invar alloy is studied. The nanostructured state was obtained by severe plastic deformation via high pressure torsion in Bridgman anvils. An "anomalous" contraction of the nanostructured Fe-36% Ni alloy was detected during heating in certain temperature ranges. The phase composition of the nanostructured Invar was studied to explain the behavior of the thermal expansion coefficient. The revealed anomalies of the coefficients are explained by the formation of a bcc phase not observed in the Fe-36% Ni Invar alloy in the coarse-grained state. The formation of this phase becomes possible due to a significant increase in the diffusion coefficient as a result of nanostructuring.

1. Introduction
Invar alloys of the Fe-Ni system have found wide application in modern engineering and instrumentation due to the anomalously low value of the coefficient of thermal expansion (CTE) – α(T) ≈ 1.6⋅10-6 °C-1 [1]. For the first time, unique properties of Invar were found in the Fe-36% Ni alloy by Guillaume at the end of the 19th century. It is known that the chemical compositions of the Fe-36% Ni alloy and its deformation processing influence the CTE. Alloying elements or impurities commonly lead to an increase of the CTE while plastic deformation reduces the latter. Therefore, one can assume that deformation nanostructuring can reduce the CTE of the Invar alloy.

Today, there are many works [3-5] on the study of nanostructured (NS) materials, since they have properties that are not characteristic for materials in the coarse-grained (CG) state. Deformation nanostructuring also influences the phase composition of alloys, for example, leads to the suppression of martensitic [6] or polymorphic hcp-fcc [7] transformations. Accordingly, the study of the properties of the Fe-36% Ni alloy in the NS state can broaden its application and, undoubtedly, is of scientific interest.

The aim of this work is to study the CTE of the Fe-36%Ni alloy after deformation nanostructuring by high pressure torsion and upon annealing. To explain the temperature dependence of the CTE of the Invar alloy in different structural states, its phase composition was studied.

2. Experimental
The NS samples were obtained by severe plastic deformation (to a true strain of e = 7) via the high-pressure torsion method in Bridgman anvils. The average crystallite size of the processed sample was about 100 nm [8].
The dependences of CTE on temperature $\alpha(T)$ were measured using a Dh 1500 RHP ULVAC SINKU-RIKO dilatometer. The heating rate of the samples was 2 $^\circ$C/min. Measuring the temperature dependences $\alpha(T)$ consisted of several cycles. The specimen was heated from room temperature to maximum temperature and then annealed at this temperature for 30 minutes, then cooled inside the device to room temperature. After that, the measurement of this sample was repeated, but it was heated to the next maximum temperature. To exclude bending deformation during heating, a sample in the form of a plate (0.1 x 4.5 x 7.4 mm$^3$) was fixed in special slots of two quartz cylinders. The length of the plate exceeded the depth of the slits by 0.8 mm, which provides mechanical contact with the dilatometer sensor.

The phase composition of samples in a different structural state was investigated by X-ray diffraction analysis at room temperature. To obtain different structural states, the samples after deformation nanostructuring were annealed in vacuum for 1 hour at 300, 400, 420 and 480 $^\circ$C.

3. Results and discussion

Figure 1 shows the temperature dependences of the CTE $\alpha(T)$ of the Fe - 36% Ni Invar alloy in the NS state (square symbols) and after annealing at 280 $^\circ$C (circle symbols), 350 $^\circ$C (rhomb symbols), 500 $^\circ$C (triangle symbols) and 800 $^\circ$C (the solid line) for 30 minutes. These dependences have a non-linear character and for some cases of measurements they are non-monotonic. The non-monotonic behaviour of the $\alpha(T)$ curves is observed during heating from room temperature to 280 $^\circ$C, 350 $^\circ$C and 500 $^\circ$C (see curves with symbols of a circle, a rhomb and a triangle, respectively, in figure 1). All the curves show that the CTE sharply decreases when the annealing temperature of the measured sample is reached. The CTE decreases even to negative values when the specimen is heated above 350 $^\circ$C, which corresponds to its annealing temperature, and after reaching above 480 $^\circ$C, the value $\alpha(T)$ increases sharply. Such a non-monotonic temperature dependence of CTE is not observed in the CG Fe-36% Ni Invar alloy (see the dashed curve in figure 1) [9]. However, figure 1 shows that the curve $\alpha(T)$ for the NS Invar annealed at 800 $^\circ$C (the solid line in figure 1) practically coincides with the curve of the CGFe - 36% Ni alloy (the dashed line). This indicates that the annealing of the NS Invar at 800 $^\circ$C leads to the formation of a grain structure similar to the CG state.

To explain the anomalous contraction of the NSFe-36% Ni Invar alloy during heating above 350 $^\circ$C, the phase composition of the alloy in different structural states was studied by X-ray diffraction analysis. Figure 2 shows X-ray diffraction patterns of the NS Fe-36% Ni alloy in the as-processed state (a) and after annealings at 300 $^\circ$C (b), 400 $^\circ$C (c), 420 $^\circ$C (d) and 480 $^\circ$C (e). The peaks in the diffraction patterns obtained from the sample after deformation nanostructuring (see figure 2 a) correspond to the fcc lattice $\gamma$-Fe. However, the peaks have a lower intensity and a greater width than in the case of the CG sample, which is due to the structural nonequilibrium and high internal elastic stresses in the sample arising due the process of nanostructuring.

![Figure 1. Temperature dependences of the CTE $\alpha(T)$ of Fe - 36% Ni Invar alloy in the NS state (square symbols) and after annealing at 280 $^\circ$C (circle symbols), 350 $^\circ$C (rhomb symbols), 500 $^\circ$C (triangle symbols) and 800 $^\circ$C (the solid line) [8]. The dotted line shows the dependence $\alpha(T)$ for Invar in the CG state [9].](image-url)
The peaks appearing in the X-ray diffraction patterns after annealing of the NS samples at 350 °C, 400 °C and 420 °C (figure 2 b-d) correspond to the bcc lattice of α-Fe. As the annealing temperature increases, the intensity of the bcc peaks increases and reaches a maximum value at 420 °C (figure 2 d). A further increase in the annealing temperature leads to the dissolution of α-Fe, and the bcc phase peaks are not observed in the diffraction pattern at 480 °C (figure 2 e). Note that at temperatures below 500 °C, ordered phases of FeNi and/or FeNi$_3$ can form in Fe-Ni alloys [10]. However, it is impossible to reliably confirm (or refute) the presence of these phases using the X-ray diffraction method, since the lattice parameters of the main γ-phase and intermetallic phases practically coincide (see figure 2).

Figure 2. X-ray diffraction patterns of the NS Fe-36% Ni (a) alloy and after annealing at 300 °C (b), 400 °C (c), 420 °C (d) and 480 °C (e) for 1 hour. $I/I_0$ is the relative intensity, reduced to the intensity $I_0$ of the (111) γ-Fe peak.

Figure 3 shows the dependences of the CTE at 20 °C $\alpha_{20/0}$ (square symbol) and the height of the diffraction peaks (101) for the bcc phase $I/I_0$ (circle symbol) on the annealing temperature $T_{an}$ of the NS Fe-36% Ni alloy. On the $\alpha_{20/0}$ curve one can see that the CTE increases with increasing $T_{an}$ and after annealing at 420 °C, it reaches a value of 2.48×10$^{-6}$ °C$^{-1}$. At this temperature, the intensity of the diffraction peaks of the bcc phase reaches a maximum. Thus, the degradation of the properties of invar at room temperature is related to the separation of the bcc phase during annealing of the NS Invar at temperatures above 350 °C. Similar behavior was previously found in [11, 12]. The contraction of the sample observed in the CTE temperature dependence of the Invar alloy annealed at 350 °C (curve with rhomb symbols in figure 1) is associated with the dissolution of the less dense bcc phase during heating above $T_{an}$. The α-phase is completely dissolve at 480 °C and the diffraction peaks, corresponding only to the main fcc phase, are observed (figure 2 e), i.e. the structure becomes completely single-phase. This leads to a sharp increase in the value of the CTE (see curve with rhomb symbols in figure 1).

The $\gamma \rightarrow \alpha$ transition, usually not observed in Fe-Ni alloys with a Ni content of more than 33%, found in the annealed NS Fe-36% Ni alloy became possible due to an increase in the diffusion coefficient by several orders of magnitude after deformation nanostructuring [13, 14]. The results obtained in this work can extend the use of the Fe-36% Ni Invar alloy in various industries due to the detected influence of the annealing temperature after deformation nanostructuring on CTE.
words, by varying the value of $T_{\text{an}}$, one can create an Invar specimen with a certain value of thermal expansion.

![Graph](image)

**Figure 3.** Dependence of the CTE at 20 °C $\alpha_{20^\circ C}$ (square symbol) and the height of the diffraction peak (101) bcc phase $I/I_0$ (circle symbol) on the annealing temperature $T_{\text{an}}$ of the NS Fe - 36% Ni alloy.

### 4. Conclusions

The formation of a nanosized structure in the Fe-36% Ni Invar alloy using deformation by high pressure torsion and subsequent annealing leads to an increase in CTE at 20 °C at certain annealing temperatures. This behavior is associated with the separation of the bcc phase during annealing, which is not observed in the CG Fe-36% Ni alloy. In addition, the observed shortening in the NS Invar upon reheating after annealing at 350 °C is due to the dissolution of the less densely packed bcc phase. The formation of this phase becomes possible due to a significant increase in the diffusion coefficient as a result of deformation nanostructuring.

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