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PROPERTIES OF Fe-36%Ni INVAR WITH NANOCRYSTALLINE STRUCTURE

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Abstract. Temperature dependencies of saturation magnetization and temperature coefficient of linear expansion for the Fe-36%Ni alloy have been studied in different structural states obtained by severe plastic torsion straining under quasi-hydrostatic pressure and following annealing at different temperatures. The studies have revealed the decrease in the coefficient of thermal expansion for the invar alloy within the temperature range 20-100 °C from severe plastic deformation, as well as the generation of superlattice segregation in it.

1. INTRODUCTION

The Fe-Ni base alloys are widely used in various fields of industry. One of their most important characteristics is a temperature coefficient of linear expansion (TCLE) [1,2]. In the Fe-36%Ni alloy its value within the temperature range from 0 to 100 °C is about zero and $(1\text{-}2)\cdot 10^{-6}$ °C^{-1} at room temperature. It is assumed that a low value of this coefficient for this alloy is conditioned by the competition of magnetic and heat contributions below Curie temperature near the magnetic transition and the fact that the heat expansion of the material is compensated by the negative magnetostriction [3].

The changes in the properties of materials from structure refinement due to severe plastic deformation till the true logarithmic strain value e = 3 and above have been studied thoroughly in recent years [4]. Such deformation can cause essential changes in the properties of materials. For example, a value of the yield stress for the Fe-36%Ni alloy from severe plastic deformation by equal channel angular pressing increases from 300 to 800 MPa [5]. Similar to [5] the structure transformation to the mean fragment and grain size of about 100 nm described in [6] was also due to severe plastic deformation by equal channel angular pressing. The temperature coefficient of linear expansion was measured in [5] at room temperature after each cycle of deformation. In [6], the sample of the Fe-36% Ni alloy subjected to 12 cycle equal channel angular pressing and following annealing was studied. After multiple cycle pressing and after each annealing the tem-

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perature dependence of the TCLE was measured. Both papers revealed the decrease in the value of TCLE from equal channel angular pressing. However, in [5] the decrease by 200% was observed only after the first cycle of pressing. Following cycles led to recovery of TCLE in this case, whereas according to the results from [6] the twelve cycle pressing led to the decrease in TCLE of the material by a factor of 2 on average within the temperature range from the room temperature to 150 °C.

The present paper considers the temperature dependence of TCLE $\alpha(T)$ and the temperature dependence of saturation magnetization $\sigma(T)$ for the Fe-36%Ni alloy in different structural states obtained by severe plastic torsion straining under quasi-hydrostatic pressure and following annealing at different temperatures.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

Severe plastic deformation of the Fe-36%Ni alloy was realized by torsion under quasi-hydrostatic pressure [7] to the true logarithmic strain value e=7. For producing samples with different structures the deformed samples were subjected to step by step annealing at temperatures 125, 225, 350, 480, and 500°C for 30 minutes. The structure was studied by a transmission electron microscope JEM 2000EX. The measurement of the coefficient of thermal linear expansion of the samples was carried out using a dilatometer Dh 1500 RHP ULVAC SINKU-RIKO during heating at the rate 2 °C/min. The saturation magnetization $\sigma(T)$ was measured by automatic vacuum magnetic scales [8] during heating and cooling of the samples at the rate 15°C/min. The temperature dependencies $\alpha(T)$ and $\sigma(T)$ were measured for several cycles consecutive increasing the upper temperature of each cycle. On attaining the upper temperature at each cycle of measurement, the samples were annealed for 30 minutes.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The structure of the alloy after severe plastic deformation (Fig. 1a) consists of fragments which are mainly less than 100 nm in size. The fragments are almost equiaxed and separated by relatively narrow boundaries. The fragment disorientation exceeds 5-10 degrees. The reflexes on electron diffraction patterns taken from an area of 0.5 μm^2, i.e. from several fragments, are arranged in circles. Along with the fragmented structure, the areas with a less perfect cellular structure are observed in the alloy after deformation. The cellular size is about 200-500 nm, their boundaries are wider and contour broken. The reflexes on the electron diffraction patterns from these areas are slightly blurred in the azimuth direction

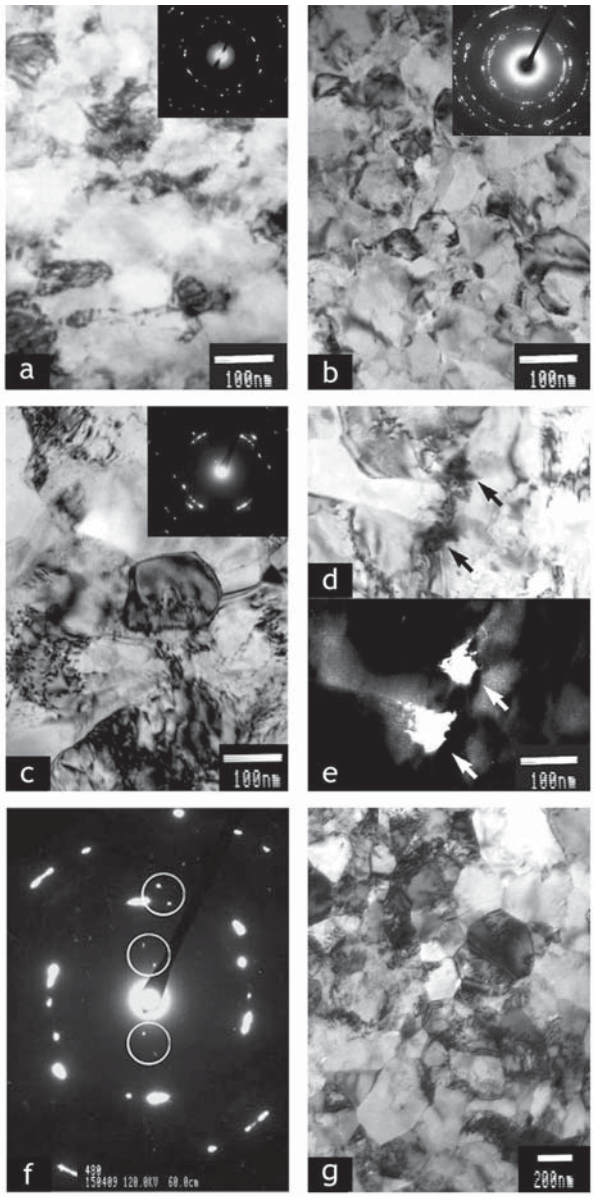

Fig. 1. Microstructure and electron pattern of alloy Fe-36%Ni, subjected to severe plastic deformation (a) and following annealing for 30 minutes at temperatures: (b) 350, (c,d,e,f)-480, g) 500 °C. Superstructure reflexes typical for ordered phase are marked by circles (e) which images in bright (d) and dark (e) fields are indicated by arrows.

and typical of low angle (weakly disorientated) disorientated cellular structure.

Following annealing at 280 °C resulted in the decreased volume fraction of the cellular structure. The fragment boundaries became thinner and more distinct. The reflexes on the diffraction patterns are arranged in a circle more uniformly, i.e. the disorientation of fragment boundaries is increased.

The annealing at 350 °C led to noticeable changes in the structure. Typical recrystallized areas consisting of crystallites about 100 nm in size are observed in the structure (Fig. 1b). The diffusion contrast and the presence of extinction contours being an evidence of long range internal stresses indicate the non-equilibrium state of grain boundaries. Areas of cellular structure are not observed at all.

After annealing at 480 °C, the fragmented structure almost completely transformed to the granular one (Fig. 1c) consisting of equiaxed crystallites with the mean size of about 200 nm. In addition the presence of ordering phase segregation is observed (Figs. 1d, 1e, and 1f). Some electron diffraction patterns (Fig. 1f) contain superlattice reflexes apt to an ordering crystal lattice [9]. Dark field images obtained from such reflexes (Fig. 1e) show that these reflexes are from ordering phase parts about 50 nm in size (indicated by arrows). The particles are located at grain boundaries. Such segregation might appear at more earlier annealing stages but they were not revealed because of the difficulty of their identification.

Annealing at the temperature 500 °C is accompanied by further growth of grains (250 nm) and microstructure transformation (Fig. 1g). Analyzing the diffraction patterns of the microstructure, one can see grains with a banded contrast intrinsic to equilibrium boundaries.

The temperature dependencies of TCLE under study have a non-linear character and for some cycles of measurement they are non-monotonic (Fig. 2). The least value of TCLE is observed in the sample at once after severe plastic deformation (curve 1) in the temperature range from the room temperature to 100 °C being interesting in terms of practical application. At the room temperature $\alpha(T_{r.t.}) = 0.7 \cdot 10^{-6}$ °C^{-1}. Annealing at the temperature 125 °C did not lead to any essential changes in the $\alpha(T)$ dependence (curve 2). Due to further annealing steps at temperatures 225 °C, 280 °C, and 350 °C (curves 3, 4, and 5), the values of TCLE within the temperature range from the room temperature to 100 °C increased. The measurement made at heating up to 500 °C of the sample annealed at 350 °C has shown $\alpha(T_{r.t.}) = 2.4 \cdot 10^{-6}$ °C^{-1}. Annealing at 500 °C led to some decrease in TCLE within the mentioned temperature range (curve 6), $\alpha(T_{r.t.}) = 1.6 \cdot 10^{-6}$ °C^{-1}. The unusual non-monotonic behavior of the $\alpha(T_{r.t.})$ dependence is observed during heating from the room temperature to 280, 350, and 400 °C (curves 3,4,

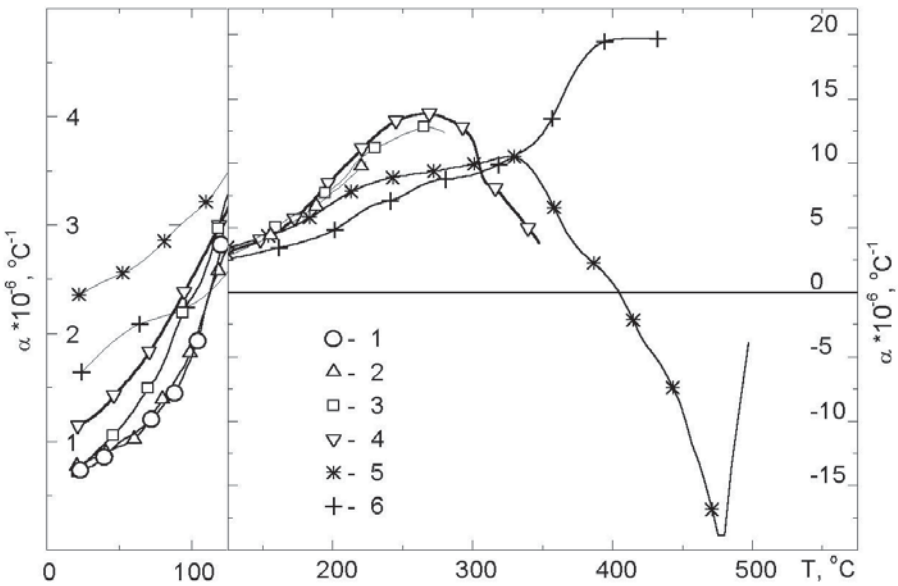

Fig. 2. Temperature dependencies of TCLE for the severely deformed Fe-36%Ni alloy obtained at upper temperatures increased consecutively up to 1 –125, 2 – 225, 3 – 280, 4 – 350, 5 – 500 °C. Curve 6 - annealing of the sample at 500 °C.

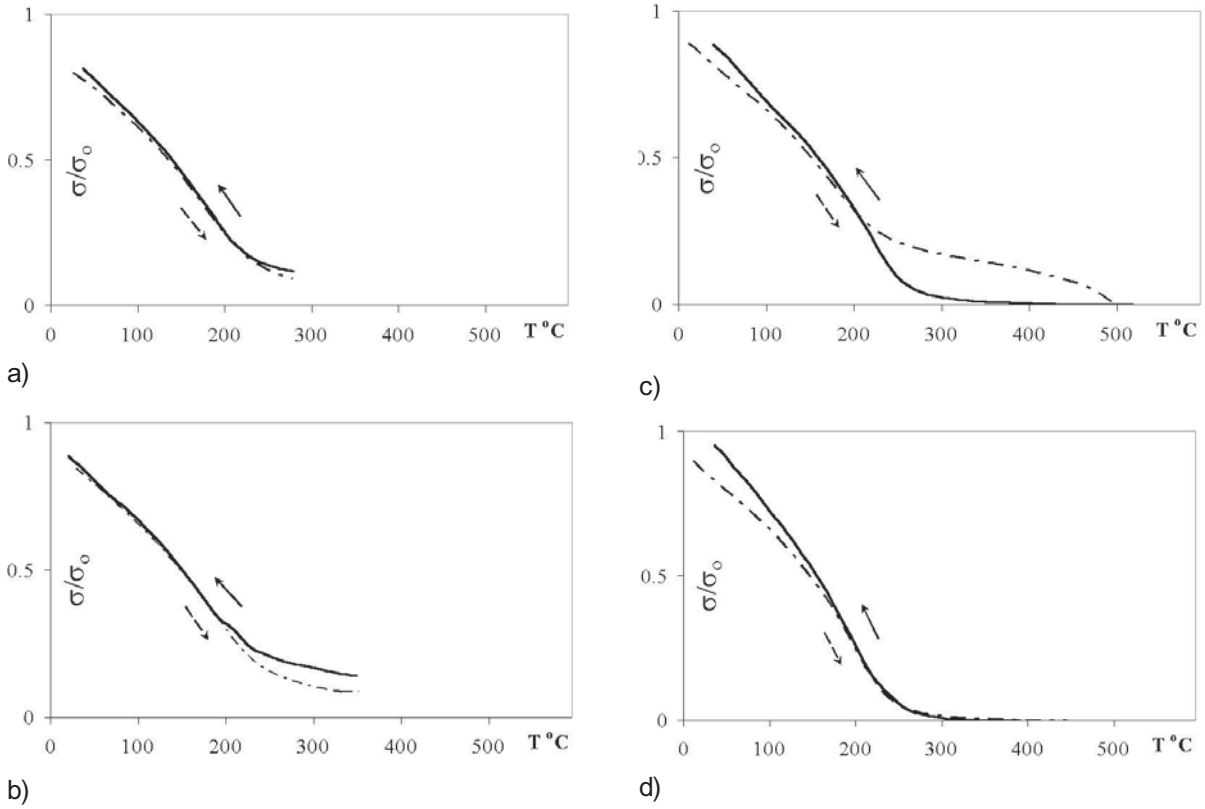

Fig. 3. Temperature dependencies of saturation magnetization for the severely deformed Fe-36%Ni alloy obtained at upper temperatures increased consecutively up to a) 280, b) 350, c) 500, d) 800 °C. σ_0 – saturation magnetization of the alloy at room temperature in the coarse-grained state.

and 5, respectively). At consecutive heating up to 280 and 350 °C after some initial growth in TCLE there occurs a sharp decrease in the value TCLE with increasing temperature above 270 °C. At subsequent heating up to 500 °C such a decrease is observed above the temperature 340 °C. In the latter case TCLE grows sharply above 480°C.

The measurements have shown that the behavior of the temperature dependence of saturation magnetization changes from one cycle to another as the upper temperature of measurement is increased consecutively (Fig. 3). The $\alpha(T)$ curve obtained after annealing of the sample at 500 °C is typical for the coarse-grained alloy Fe-36%Ni (Fig. 3d). Moreover, the shape of this curve in the temperature range of magnetic transition and above it is adequate both for the measurement at heating and the one at cooling, the Curie temperature T = 260 °C corresponding to the reference data [10]. The value of saturation magnetization at room temperature for this state is maximum. The $\alpha(T)$ dependencies for the alloy sample at once after severe deformation and for the sample subjected to annealing up to 350 °C (Fig. 3a,b and heating curve in Fig. 3c) are characterized by the presence of the additional plateau in the high temperature range. Moreover, the value of saturation magnetization does not decrease to zero at 260 °C. The temperature of their ferromagnetic-paramagnetic transition exceeds the Curie temperature for the coarse-grained sample. The curves obtained at heating to the upper temperatures of measurement do not coincide with the ones obtained at following cooling. The cooling curve is above the heating one. Besides, successive heating of the sample increases steadily the value of saturation magnetization. After heating up to 500 °C and annealing at the same temperature (Fig. 3d) the additional plateau on the $\alpha(T)$ dependence disappears and following heating up to 800 °C and cooling do not lead to its restoration.

4. DISCUSSION

The severe plastic deformation up to the true logarithmic strain value e = 7 of the Fe-36%Ni alloy leads

to formation of a fragmented structure with a mean grain size of about 100 nm. Annealing with a consecutively increase in temperature at first leads to formation of a nanocrystalline structure and then to growth of grains and improvement of the structure. The sample annealed at the temperature of 500 °C (Fig. 2) has the TCLE dependence being most close to the classic one [2,11]. Due to such annealing the structure of the alloy subjected to severe plastic deformation underwent essential changes and its grain size has grown from 100 to 250 nm. The decrease in the value TCLE from severe plastic deformation correlates with the known data on the decrease in TCLE in invar alloys due to plastic deformation [12-14]. Consequently, the sharp decrease in TCLE above 270 and 340 °C revealed in the states obtained after annealing at 280 and 350 °C cannot be explained reasoning from the known data.

The occurrence of the additional plateau in the high temperature range of the temperature dependence of saturation magnetization for the samples subjected to severe plastic deformation and following annealing till 350 °C (Fig. 3) testifies the formation of a new phase in the structure of the alloy and the Curie temperature of this phase exceeds the value *T* for the Fe-36%Ni alloy in the conventional coarse-grained state. The growth of the plateau with increasing annealing temperature indicates that the volume fraction of this phase increases at heating. Annealing at 500 °C led to disappearance of this phase. Consequently, the decrease in the value of saturation magnetization to zero at 500 °C testifies that the Curie temperature of the phase formed is above 500 °C.

According to the equilibrium state diagram at temperatures above 345 °C, the Fe-36% Ni alloy is solid solution with f.c.c. lattice [15]. Below 345 °C, the equilibrium state of the alloy presents a structure with ordered $FeNi_3$ impurities in the matrix of nickel depleted Fe solid solution. However, in the conventional coarse-grained state the diffusion processes are extremely retarded below 500 °C. That is why in conditions of processing material by rapid cooling from a melt the intermetallic state is not realized. On the other hand, it is known that the investigations of nanocrystalline metals with a mean grain size of about 100 nm produced by severe plastic deformation have shown that their diffusion processes are increased by several orders as compared to the coarse-grained state [4,16]. Such behavior is due to the large volume fraction of grain boundaries and their specific state. The grain boundaries are in a non-equilibrium state and their physical width is about 10 nm. Consequently, the nanocrystalline structure formed in the Fe-36%Ni alloy can contribute to precipitation of intermetallic phase $FeNi_3$ particles in it. In this connection, one can naturally assume that ordering takes place at grain boundaries. The data of microstructural studies testify the presence of an ordered phase at grain boundaries in the structure of the alloy under consideration.

The presence of this phase allows explaining the results of measurement of saturation magnetization. The Curie temperature for it is 611 °C [17]. The increase in the volume fraction of the ordered phase with increasing temperature can be explained by the acceleration of diffusion processes, on the one hand, and the occurring transformation of the fragmented structure to the granular one, on the other. As follows from the state diagram the increase in the temperature above 500 °C leads to dissolution of the $FeNi_3$ in the invar alloy and formation of homogeneous f.c.c. solid solution. The increased grain size and more uniform microstructure prevent the repeated generation of the intermetallic compound after cooling and following heating of the alloy. The increased value of TCLE within the range from 100 to 270 °C at heating up to 350 °C can also be explained by the presence of $FeNi_3$ impurities in the structure of the Fe-36% Ni invar alloy. The sharp decrease in TCLE above 270 °C at heating up to 350 °C and above 340 °C at heating up to 500 °C is not due to the decrease in TCLE itself. It can be attributed to the change in the specific volume of the material due to the intensification of the process of ordering phase generation with increasing temperature. As known, the ordering of structure causes the reduction of the material volume [18]. For a number of double alloys this decrease is about 0.4% [19]. Let us assume that the decrease in TCLE within the range (340, 480 °C) at heating up to 500 °C (curve 5 in Fig. 2) occurs mainly due to the sample reduction from ordering. Reasoning from the curve one can estimate that a value of reduction is about 0.02%. Then, assuming that ordering in the material is localized at grain boundaries with the effective width 10 nm and the mean grain size 100 nm, one can obtain that the specific change of the volume in sites of ordering is about 0.1%. This value differs from the value 0.4%. However, taking into account the fact that with heating the material the traditional increase in TCLE is added to the process of reduction due to generation of the ordering phase one the compatibility between the data estimated and the literature ones can be considered satisfactory. The sharp growth of the $\alpha(T)$ curve above 480 °C can be attributed to the retarded generation

of the intermetallic phase due to grain growth and transformation of grain boundaries from the non-equilibrium state to the equilibrium one.

5. CONCLUSION

The fragmented structure with a mean grain size of about 100 nm was formed in the Fe-36% Ni alloy from severe plastic torsion straining under quasi-hydrostatic pressure. Annealing at 350 °C led to formation of the nanocrystalline structure with a mean grain size of 100 nm.

Torsion straining under quasi-hydrostatic pressure led to the decrease of the TCLE value near room temperature by more than twice.

The transformation of the fragmented structure to the granular one at heating of the sample severely deformed and the non-equilibrium state of grain boundaries in its nanocrystalline structure led to generation of the intermetallic $FeNi_3$ phase in the f.c.c. solid solution of the Fe-36% Ni alloy.

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