Structural phase changes during deformation of FeCo-V alloys by torsion under high pressure

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Abstract. The effects of high pressure torsion at 77 and 295 K on the phase composition of soft magnetic alloys (FeCo)100-xVx (x = 0 - 6.0) were studied by X-ray structure analysis, transmission electron microscopy and magnetometry. It was established that HPT leads to the suppression of excess γ-phase in alloys containing 3.0–6.0% V. It was concluded that the observed effect was a consequence of the martensitic transformation γ→α, due to deformation, along the lines of TRIP effect. It was established that suppression of the paramagnetic γ-phase leads to a noticeable increase in the specific magnetism of saturation.

1. Introduction

FeCo alloy with an equiatomic ratio of components belongs to the class of soft-magnetic materials and at room temperature has a very high saturation magnetic moment among existing ferromagnetic materials [1]. However, effective implementation of the unique magnetic properties of this alloy encounters serious difficulties due to its high tendency to brittle fracture. It was established that embrittlement is mainly due to the formation of long-range atomic ordering in the form of B2 [2, 3]. As a rule, FeCo is alloyed with vanadium to increase ductility. It favorably affects ductility, but leads to a certain decrease in high magnetic characteristics [4]. The latter is mainly due to the release of paramagnetic γ-phase (FCC) upon alloying with vanadium, as well as the decrease in the magnetic moment of the matrix α-phase of FeCoV [5]. In a number of works, concentration boundaries of the existence of a two-phase region (α+γ) when alloying FeCo with vanadium were determined, but the results obtained were rather contradictory. Thus, according to [6,7], γ-phase is formed in alloys containing more than 2 at% V, and according to [8,9] - containing more than 2.5-3.0 at% V. In [10], a very high boundary concentration of vanadium (5%) was indicated, and in [11] - a very low one (1.5%). Such variations in the critical concentration are obviously associated with some difference in the ratio of components in alloys and in the modes of their preliminary heat treatment. Is it possible to avoid the negative effect of vanadium on the magnetic properties of FeCo alloy, while maintaining a sufficiently high ductility?

Recently, it was discovered that severe plastic deformation (SPD) can effectively influence not only the grain size of polycrystalline materials based on Fe, Ni, and Cu and other metals, but also
substantially transform their phase composition [12-14]. Alloys based on Fe–Co were also subjected to SPD [15–18], however, the main focus was on the formation of a microgranular structure and its effect on mechanical and magnetic properties. In this work, we attempted to influence not only the structure, but also the phase composition of ferromagnetic FeCo-V alloys containing various concentrations of vanadium, using SPD at different temperatures. When alloying with vanadium, the equiatomic ratio of iron and cobalt atoms was preserved in ternary alloys. The main goal of the research was to systematically study the effect of severe plastic deformation by high-pressure torsion (HPT) on the tendency to form in vanadium-alloyed alloys a paramagnetic γ-phase, which has a negative effect on ferromagnetic properties.

2. Experimental

Alloys (FeCo)\(_{100-x}\)V\(_x\) (x =0; 1.5; 3.0; 4.5; 6.0) were melted in a vacuum furnace in the form of rods with a diameter of 10 mm. After that, 0.5 mm thick discs were made of them and annealed in an argon atmosphere at a temperature of 800°C for 50 hours, after that they were cooled to room temperature at a rate of 100 deg./h. The disc-shaped samples of all alloys were subjected to plastic deformation of HPT at room (295 K) and cryogenic (77 K) temperatures at \(N = \frac{1}{4}, \frac{1}{2}, 1, 2, 3, 4 \) and 6, where \(N\) is the number of full revolutions of a movable anvil at quasi-hydrostatic pressure of 6 GPA and at a rotational speed of a movable anvil of 1 rpm. The value of a true logarithmic strain \(\varepsilon\) in the process of HPT was determined by the formula [10]:

\[
\varepsilon = \ln(1 + \left(\frac{\phi \cdot r}{h}\right)^2)^{0.5} + \ln\left(\frac{h_0}{h}\right),
\]

where \(r\) and \(h\) are respectively, the radius and height of the sample in the form of a disk, \(\phi\) is the rotation angle of a movable anvil. The value \(\varepsilon\) in accordance with (1) ranged from 5 to 9.

X-ray structure analysis of the samples before and after SPD was performed on a Rigaku Ultima IV diffractometer using Co K\(_{\alpha}\) radiation and a graphite monochromator. Diffraction patterns were taken according to Bragg-Brentano method in the range of 30-125 degree angles at 0.1 degree intervals. Analysis of diffraction patterns was carried out using a modified Rietveld method. The volume fraction value of γ-phase \(C_\gamma\) was determined as a structural parameter before and after HPT. The obtained X-ray patterns were processed using Rigaku PDXL program (Rigaku Corp., Japan) [19], which took into account the Debye-Waller factor, the Lorentz polarization factor, as well as crystallographic texture. The error in determining the volume fraction of γ-phase did not exceed 5%. The minimum non-zero value \(C_\gamma\) was 1 volume %.

Submicroscopic studies were performed using JEM 1400 transmission electron microscope at an accelerating voltage of 120 kV using a high-resolution dark field technique. Measurement of specific saturation magnetic moment \(\sigma\) was carried out at room temperature. The experiments used VSM – 250 vibration magnetometer. Intensity of the constant magnetic field varied within 80 - 640 kA/m with a minimum step of 0.8 A/m. The device was calibrated against a reference sample of pure nickel. Almost perfectly round samples devoid of cracks were selected for the studies. The \(\sigma\) values were averaged over the measurement results of four different samples for each deformation mode. An error in measuring the \(\sigma\) value did not exceed 3%.

3. Results and discussion

Figure 1a shows the dependence of γ-phase \(C_\gamma\) volume fraction on the vanadium concentration in the initial (before HPT) state of the alloys studied. In FeCo and FeCo-1.5% V alloys the γ-phase was not detected. At higher concentrations of vanadium, a smooth increase in \(C_\gamma\) value from 2.0 to 6.7 volume % is observed as the vanadium content increases from 3.0 to 6.0 %, respectively. After deformation processing using HPT method at 295 K, the character of dependence \(C_\gamma\) (% V) changes significantly (Fig. 1 b–d). The effect of suppressing γ-phase formation in alloys with a high vanadium content is observed. This effect is more pronounced, when the deformation value at HPT is higher.
after $N = 0.5$, $\gamma$-phase is not observed only in the alloy with 6.0% V, then after $N = 1$, it is not detected in two alloys with 6.0 and 4.5% V. Finally, after $N = 2$, $\gamma$-phase is absent in three alloys with 6.0, 4.5, and 3.0% V. The values $C_\gamma$ in the studied alloys after HPT vary within 3-4 volume %.

Figure 1. Dependence of the $\gamma$-phase volume fraction $C_\gamma$ on the content of vanadium in FeCo-V alloys before HPT (a) and after HPT at 295 K: $N = 1/2$ (b), 1.0 (c), 2.0 (d).

Figure 2 shows the dependence of the maximum vanadium concentration in the studied FeCo-V alloys, for which $\gamma$-phase is noted, on the deformation value $N$ in the HPT process at different temperatures ($% V_{\text{max}}$). A clear pattern is observed: the larger the deformation value at HPT, the lower the value of $% V_{\text{max}}$. The dependences observed in Fig. 2 indicate that HPT at room temperature reduces the value of $% V_{\text{max}}$ more effectively than deformation at cryogenic temperature.

Figure 2. Dependence of the maximum content of vanadium in the alloy, where $\gamma$-phase is observed, based on value $N$ at 77 and 295 K.

Fig. 3 shows typical electron microscopic images of FeCo-4.5 %V alloy microstructure in the initial state (before HPT) (a – c) and after HPT ($N=1$) at 77 K (d). A similar structure was observed in
the initial state of alloys with 3.0–6.0 %V. Thin layers of γ-phase are located, as a rule, between the packaged martensite plates of α-phase (Fig. 3b-c). After HPT, regardless of the temperature and deformation value, γ-phase was observed or was not noted, or was observed in the form of nanoparticles of 10-50 nm size, having a spherical or elongated shape (Fig. 3d). Based on X-ray and electron microscopic data, an average size of γ-phase nanoparticles increased from 10 to 50 nm as the concentration of vanadium in the alloy increased, respectively, from 3.0 to 6.0%.

Figure 3. Structure of FeCo-4.5% V alloy before HPT (a-c) and after HPT (N=1; 77 K); a is a microelectron diffraction pattern, b is a dark field in the α-phase reflection, c, d is a dark field in the γ-phase reflection.

Figure 4 shows the measurement results of the specific saturation magnetic moment $\sigma$ for FeCo and FeCo-6.0% V alloys depending on $N$ (on deformation value e) after HPT at room temperature. If the value of $\sigma$ for the binary FeCo alloy practically does not change with the value $N$ (slightly decreases), then in the alloy doped with 6.0% V, as the HPT deformation increases, a noticeable increase in $\sigma$ is observed by about 15%. As a consequence, the $\sigma$ value for a ternary alloy with 6.0% V after HPT ($N = 4$) approaches noticeably a similar characteristic $\sigma$ of FeCo binary alloy. As a result, the difference in values $\sigma_i$ is reduced by approximately twofold (Fig. 4).

Figure 4. Dependence of the specific saturation magnetic moment $\sigma$ on value $N$ (295 K) for FeCo and FeCo-6% V alloys.
So we see that HPT tends to decrease the excess $\gamma$-phase volume fraction in the structure of FeCo-(3.0-6.0)% V alloys as SPD value increases. After $N \geq 2$ at 295 K and after $N \geq 3$ at 77 K, the release of $\gamma$-phase in the studied alloys is completely suppressed regardless of the vanadium content (Fig. 2).

It is well known that in FeCo-V alloys, when cooled in a high-temperature region (750-900°C), $\gamma$ (FCC) $\rightarrow \alpha$ (BCC) polymorphic transformation is observed, which occurs according to the diffusion mechanism at % V <2.0 and martensitic mechanism at % V $\geq 2.0$ [1]. In the latter case, packet martensite is formed in the entire volume of the alloy, and only then, during subsequent slow cooling an excess $\gamma$-phase is formed at the boundaries of martensitic crystals and fragments. The results of electron microscopic studies presented in Fig. 3a-c confirm these regularities. It should be noted that the high-temperature $\gamma$-phase composition corresponds to the content of the main components in the alloy, while excess $\gamma$-phase observed at room temperature in alloys with 3.0-6.0% V is substantially enriched with vanadium atoms. According to [20], the excess $\gamma$-phase in FeCo-2.0% V alloy is enriched with cobalt and vanadium (65% Co and 22% V) and does not undergo a low-temperature phase transformation $\gamma \rightarrow \alpha$ when cooled to 77 K. In alloys with (3.0-6.0)% V, containing an excess $\gamma$ phase, with small $N$ values in HPT process at 295 and 77 K, a noticeable change in its morphology is observed. Nanoparticles uniformly distributed in $\alpha$-phase are observed, an average size of which changes with increasing vanadium content and depending on the deformation temperature (Fig. 3d).

The complete disappearance of $\gamma$-phase particles in the structure (Fig. 2) is most likely due to the martensitic transformation $\gamma \rightarrow \alpha$ during HPT process. During plastic deformation, the effect of appearance of martensitic phases which are not formed during heat treatment, is associated with the expansion of martensitic transformations’ temperature range caused by plastic deformations [21]. In our case, we are talking about severe plastic deformation. The reason for this phenomenon is that plastic deformation leads to a noticeable increase in the thermodynamic stimulus of martensitic transformation at relatively low temperatures [22].

Displacement of martensitic point $T_M$ with the application of effective external stresses $\sigma(e)$ can be described by the Clayperon equation:

$$\frac{dT_M}{d\sigma} = \varepsilon_o(VT_o / \Delta H) ,$$  

where $\varepsilon_o$ is the internal deformation of transformation; $\Delta H$ is the change in the enthalpy of transformation; $V$ is the volume of grams per mole of substance; $T_o$ is the thermodynamic equilibrium temperature of $\gamma$ and $\alpha$-phases.

Since all values in the right-hand side of equation (2) are constant in the first approximation, the amount of martensitic phase at a given temperature increases linearly with an increase in critical stress $\sigma_o(e_o)$ corresponding to the martensitic transformation during SPD.

With $N(e_o) \geq 2$, all $\gamma$-phase nanoparticles in our case underwent the martensitic transformation $\gamma \rightarrow \alpha$ in HPT process at 295 K and with $N(e_o) \geq 3$ at the temperature of 77 K. A more effective effect of HPT at room temperature as compared with HPT at 77 K suggests that thermally activated processes may play a certain role in a martensitic $\gamma \rightarrow \alpha$ transformation. A similar result was obtained by us earlier in the study of martensitic transformation $\alpha \rightarrow \omega$ into $\alpha$-Ti in HPT process at various temperatures [23]. Formation of the martensitic $\omega$-phase was observed at earlier deformation stages at 295 K compared with deformation at 77 K.

The discovered martensitic transformation $\gamma \rightarrow \alpha$ during HPT in FeCo-(3-6)% V alloys is essentially similar to the activation of TRIP effect (martensitic transformation due to plastic deformation [24]). The only difference is that the martensitic transformation is caused not by ordinary plastic deformation, but by SPD.

An interesting feature of the discovered effect is that suppression of $\gamma$-phase as the volume of deformation $N(e)$ increases first occurs in the alloy with a high content of V (6%) with $N \geq 0.5$ (295 K) and $N \geq 1.0$ (77 K) (Fig. 2). Further, as $N(e)$ increases, the limiting vanadium content in the alloy, where the existence of $\gamma$-phase is still observed, decreases linearly (Fig. 2).

This effect can be explained by the following reasons:
1. As the vanadium content in the alloy increases, the relative content of vanadium in γ-phase increases noticeably [20]. Accordingly, as % V grows, critical stress $\sigma_{cr}$ can decrease and, consequently, deformation value $e_{cr}$, at which the martensitic transformation occurs, stimulated by SPD.

2. An average particle size of γ-phase at HPT up to the martensitic transformation $\gamma \rightarrow \alpha$ (Fig. 3d), as we established, grows noticeably from 10 nm to 50 nm with increasing % V in the alloy. As it is known, there is a size effect, in which the incentive to martensitic transformation in nanoparticles decreases significantly as the particle size of the initial phase decreases [25]:

$$M = M_o - K_Md_{av}^{-1/2}, \quad (3)$$

where $M$ is the transformed volume fraction in the martensitic transformation; $M_o = K_1(T^* - T_d)$; $T^*$ is the thermodynamic equilibrium temperature of γ and α - phases; $T_d$ is the deformation temperature; $d_{av}$ is the average particle size of γ-phase; $K_M$ and $K_1$ are constants.

In our case, a similar effect described by equation (3) can lead to relative stabilization of γ-phase particles with a smaller size $d_{av}$ in alloys with a lower vanadium content.

The effect of suppressing the γ-phase formation under the influence of HPT is clearly confirmed by the nature of the change in the specific saturation magnetic moment $\sigma$ (Fig. 4). Since γ-phase has a paramagnetic nature [26], its disappearance in alloys with (3.0-6.0)% V leads to a noticeable increase in $\sigma$ value and, as a consequence, to an increase in the efficiency of their use as high-strength soft magnetic materials with high magnetic induction. In this case, an optimal heat treatment mode, which does not lead to the reappearance of γ-phase in the structure, apparently, can eliminate the undesirable increase in the coercive force observed under the influence of HPT.

4. Conclusions
1. It was established that HPT at temperatures of 77 and 295 K leads to the disappearance of an excess γ-phase in the magnetically soft FeCo-V alloys containing 3.0-6.0% V.
2. It was shown that the observed effect was most likely a consequence of activation of martensitic transformation $\gamma \rightarrow \alpha$ during HPT by analogy with the TRIP effect.
3. It was found that the complete disappearance of γ-phase occurs as the deformation value increases during HPT, first in alloys with a high vanadium content and under the influence of HPT at 295 K.
4. It was established that the effect of paramagnetic γ-phase suppression in the studied alloys was accompanied by a noticeable increase in the specific saturation magnetic moment.

Acknowledgments
The work was performed under the State task of the Ministry of Science and Education of Russia No. 2017/113 (2097) and under the grant of the Russian Foundation of Basic Research No. 18-02-00398.

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