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ELECTRICAL AND MAGNETIC PROPERTIES

On the Role of Atomic Ordering in the Formation of a High-Coercivity State in Iron–Cobalt–Vanadium Alloys

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Abstract—Processes that occur in the iron–cobalt–vanadium alloy with 52% Co and 7% V (vicalloy) upon heating to 1000°C and cooling have been studied by the dilatometric and magnetometric methods. It has been found that upon heating two phase transitions occur in the alloy, namely, *B*2-type atomic ordering in the α phase and a polymorphic α ⟶ γ transformation, whose temperature intervals differ considerably. An analysis of the dependences of the coercive force and the hardness of the alloy on the annealing temperature has shown that the maximum magnitudes of these parameters correspond to the ordering temperatures in the α phase. There was made an assumption that the magnetization reversal process in the alloy tested is related to the displacement of ferromagnetic domain walls and their pinning at the boundaries of antiphase domains ordered by the *B*2 type.

Keywords: vicalloy, coercive force, atomic ordering, magnetocrystalline anisotropy, antiphase domain

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INTRODUCTION

The magnetic alloys of the iron–cobalt–vanadium system with 50–52% Co and 5–13% V revealed in the first half of the 20th century, which are called "vicalloy" [1], belong to the group of magnetically hard materials. Depending on the amount of vanadium, the coercive force of the alloys varies between 4.0 and 24.0 kA/m, the residual induction is between 1.25 and 0.6 T [1, 2].

A distinguishing feature of vicalloys is their high plasticity, which allows one to obtain the above-indicated magnetic properties in metallic ribbons up to 100 μm thick. This fact, along with the high temperature stability of magnetic characteristics, makes the vicalloys virtually irreplaceable for producing active parts of rotors of synchronous hysteresis motors (SHM) [3]. The dependence of the coercive force of the alloys on the vanadium concentration allows using them for producing a wide assortment of the SHMs with working fields of 4–24 kA/m [4].

A large number of studies has been devoted to the investigation of the nature of a high-coercivity state in the vicalloys [5–8]. Today, the most widespread notion is the one, according to which a high coercive force of these alloys is related to the forward and reverse α ⟶ γ transformations. The high-temperature fcc phase transforms into a bcc phase either upon air cooling from 1000°C (alloys with 5–9% V) or upon plastic deformation to no less than 80% (alloys with 10–13% V). The subsequent tempering in the temperature range of 550–670°C leads to a partial α ⟶ γ transformation, which results in the formation of a two-phase structure, in which disperse (probably, single-domain) regions of the ferromagnetic α phase are surrounded with the paramagnetic γ phase.

According to the existing magnetic-hysteresis theory [9], the magnetization reversal in an ensemble of single-domain particles is realized by the magnetization-vector rotation, and the magnitude of the coercive force is determined by the energy of stray fields of the particle. Generally, such mechanism of magnetization reversal is typical of many magnetically hard alloys, in particular, of the alloys of Fe–Ni–Al–Co–Ti (YuNDKT) [10, 11] and Fe–Cr–Co (KhK) [12, 13] systems.

In addition to the polymorphic α ⟶ γ transformation, atomic ordering in the α phase occurs in these alloys upon heating, with the formation of a *B*2 superstructure. This fact was mentioned in [5], and the existence of ordering was testified by neutron diffraction in [7, 8] for the alloy containing 10.5% V.

However, it was not possible to unambiguously evaluate the role of atomic ordering in the formation of a high-coercivity state of the vicalloys, since in the alloy chosen for experiments in [7, 8] the temperature intervals of ordering and α ⟶ γ transformations coincided.

In this work, the effect of atomic ordering on the coercive force was studied on the alloy with 7% V, the temperature intervals of atomic ordering and polymorphic transformation in which differ considerably, as will be demonstrated below.

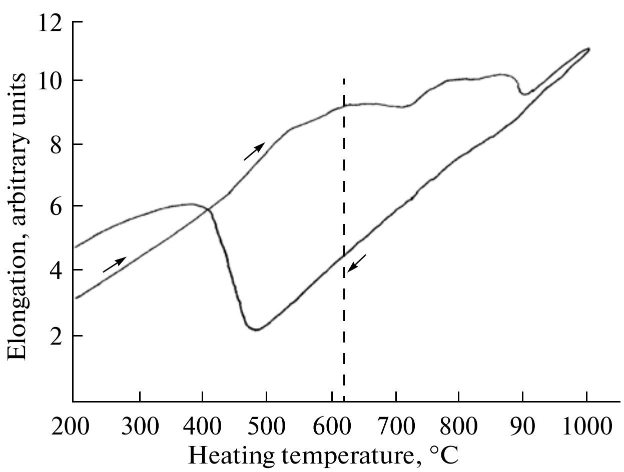

Fig. 1. Dilatogram of a vicalloy with 7% V upon heating to 1000°C and cooling (dashed line demonstrates the annealing temperature for producing a high-coercive state).

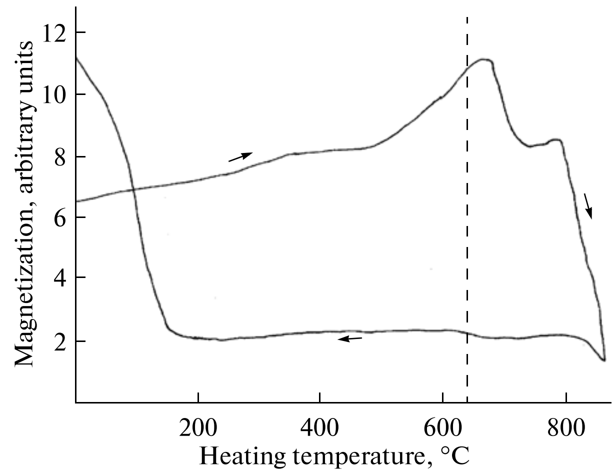

Fig. 2. Variation of the magnetization of vicalloy during heating and cooling in the temperature range from 20 to 860°C (dashed line demonstrates the annealing temperature for producing a high-coercive state).

EXPERIMENTAL

For our studies, we have chosen a commercial vicalloy containing 7% V, which is used for producing monolithic active parts of rotors of SHMs. The alloy was melted in a vacuum induction furnace with the use of pure charge materials. The smelt was cast into ingots weighting 10 kg. The chemical composition (wt %) was as follows: 52.0 Co, 6.85 V, 0.1 Si, 0.31 Mn, 0.07 C, 0.004 S, and Fe for balance.

The ingots obtained were subjected to forging in a temperature range of 1000–1150°C (into billets 30 mm thick), gouging, and hot rolling in the same temperature range to a strip 3.0 mm thick. The samples for testing were produced from a hot-rolled strip. As the initial state, we chose the state that is formed in the hot-rolled samples after air cooling from 1000°C.

The temperature intervals of phase transformations in the alloy during heating and cooling were determined by dilatometric and magnetometric methods. The rate of the temperature change in dilatometric and magnetometric tests was 10 K/min. The thermomagnetic measurements were carried out at a magnetizing-current frequency of 1000 Hz; the magnetic field strength was 5 kA/m.

The coercive force and hardness were measured on samples subjected to heat treatment according to different regimes. The measurements of the coercive force were performed using parallelepiped-shaped samples with dimensions of 5 × 2.5 × 20 mm in a magnetic coil that ensured a magnetizing field of 40 kA/m. The magnetic field of this strength provided a saturation magnetization of the samples. The hardness was measured by a standard technique.

RESULTS AND DISCUSSION

Dilatometric analysis demonstrated that several features are observed in the dilatogram upon heating (Fig. 1), namely, a plateau in the temperature range of 550–700°C, a maximum at 800°C, and two falls upon further heating. After the second fall, starting from the temperature of 912°C,there takes place an increase in the sample length stipulated by the thermal expansion of the high-temperature γ phase. The subsequent cooling in the range of 475–400°C leads to a rise of the dilatometric curve related to the $\gamma \longrightarrow \alpha$ transformation, which is accompanied by a volume increase.

The temperature dependence of magnetization also exhibits a number of features (Fig. 2). With increasing temperature, the magnetization first increases, then, in the temperature range of 380–450°C, there is observed a plateau, after which the magnetization increases again, passes through a maximum at 650°C, and then, after a slight rise, decreases quickly. This decrease can be caused by both the $\alpha \longrightarrow \gamma$ transformation and approaching the Curie temperature of the α phase.

The temperatures, at which there are observed plateaus in the dilatograms and maxima in the magnetograms, correspond to the annealing temperatures at which the alloy achieves the maximum coercive force and hardness (see table).

A decrease in the length of the sample and a decrease in the magnetization, which can be caused by the beginning of the $\alpha \longrightarrow \gamma$ transformation, are observed at higher temperatures. This means that the achievement of a high-coercivity state is related to processes that occur in the αphase itself upon heating and is not related to the $\alpha \longrightarrow \gamma$ transformation and the formation of the paramagnetic γ phase.

Magnetic and mechanical properties of a vicalloy with 7% V after different heat treatments

Heat treatment regime		Coercive force, kA/m	Hardness, *HRC*
1000°C, holding for 15 min, air cooling		4.8	38.0
1000°C, holding for 15 min, air cooling, annealing for 30 min at temperatures	400°C	4.8	44.0
	620°C	9.2	57.0
	800°C	6.7	38.0

This conclusion is also confirmed by the results of the dilatometric analysis of cooling of the samples heated to different temperatures: after heating to temperatures below 750°C, the dilatogram does not contain any features which could indicate the occurrence of the $\gamma \longrightarrow \alpha$ transformation (Fig. 3). This means that upon heating to 750°C, the $\alpha \longrightarrow \gamma$ transformation does not occur. The results of the magnetometric determination of the quantity of the γ phase that is formed upon heating testify to the same: the γ phase does not appear up to 750°C (Fig. 4).

The X-ray diffraction investigation of the alloy after tempering, which provided the maximum coercive force (620°C), showed that its structure consists of the α phase without signs of the presence of any other phases.

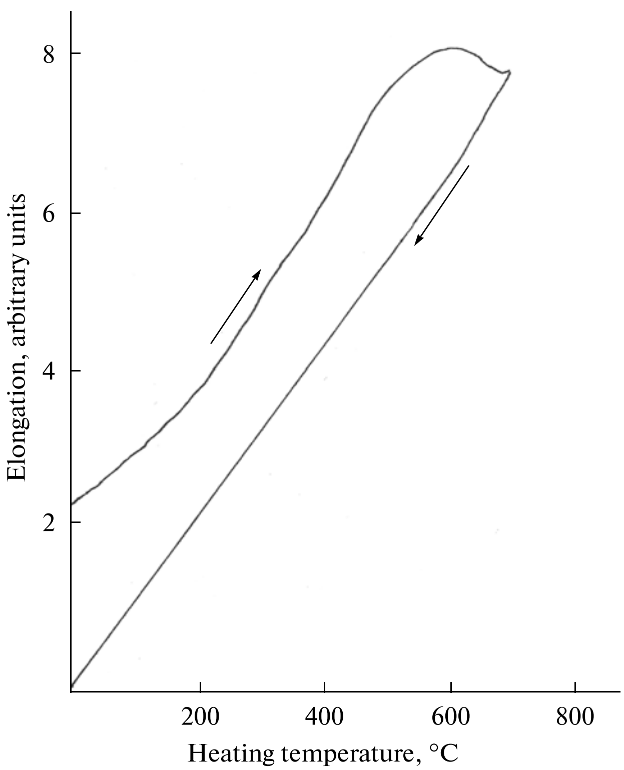

Fig. 3. Dilatogram of the vicalloy upon heating to 690°C and cooling.

The results obtained in this work give grounds to assume that the high-coercivity state in the vicalloys is stipulated by the formation of a *B*2-type superstructure in the α phase rather than by the presence of a two-phase $\alpha + \gamma$ structure [5–8].

Let us consider the main arguments in favor of this assumption.

In the Fe–Co alloys, two types of phase transitions have been established reliably, namely, atomic ordering with the formation of a *B*2-type superstructure, and a polymorphic $\alpha \longrightarrow \gamma$ transformation [14]. The ordering temperature is 730°C, the ordering rate depends on the temperature, and at temperatures close to that commonly used for annealing of vicalloys, this rate is sufficient for the long-range order to be completed in several minutes [15].

The temperature of the polymorphic transformation in the Fe–Co alloy with 50% Co lies above 900°C [14]. The alloying with vanadium decreases this temperature. Besides, between the transformations during heating ($\alpha \longrightarrow \gamma$) and during cooling ($\gamma \longrightarrow \alpha$), there appears a hysteresis, which rapidly increases with increasing vanadium concentration and decreasing the temperature range of transformations [5]. In the alloys with 10–13% V, the temperature of the poly-

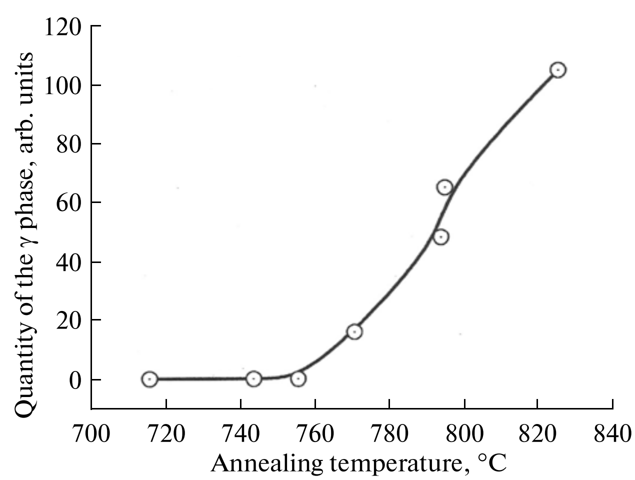

Fig. 4. The amount of the γ phase upon heating of the vicalloy as a function of the annealing temperature.

morphic transformation is below room temperature, and the formation of the α phase requires that the γ phase be deformed. Due to the hysteresis, the α phase obtained upon cooling from 1000°C (in alloys with a vanadium content below 9%) or upon deformation (in alloys with larger vanadium concentrations) is stable at temperatures above 650°C.

Depending on the vanadium concentration in the alloy, the temperature of the polymorphic transformation can lie both above and below the temperature of atomic ordering. At a certain concentration of V, the temperature intervals of these transformations can overlap, as it takes place in the alloy with 10.5% V studied in [7, 8].

In the alloys with a vanadium content less than 10%, in particular, in the alloy with 7% V investigated in this work, there is observed a fundamentally other situation. In this case, the temperature of atomic ordering is substantially less than the temperature of the $\alpha \longrightarrow \gamma$ transformation, and the temperature intervals of two phase transitions are well separated. In addition, the temperature interval of the $\alpha \longrightarrow \gamma$ transformation in the alloy containing 7% V is located above the annealing temperature that is used for producing a high-coercivity state (620°C); therefore, the γ phase is not formed during such tempering, and, hence, cannot be responsible for the appearance of high magnitudes of the coercive force. The above purports that the high-coercivity state that appear in the vicalloy containing 7% V (and, probably, in other alloys of this type) is traceable to the process of atomic ordering in the α phase.

The experimental results obtained in this work and the literature data [15, 16] allow us to formulate an assumption about the possible mechanism of formation of the high-coercive state in the alloy investigated.

It has been found for certain that the maximum of the coercive force corresponds to a single-phase ordered state. Consequently, the process of magnetization reversal in the vicalloy containing 7% V occurs via the displacements of a ferromagnetic domain walls (FDWs), and the magnitude of the coercive force is determined by the degree of pinning of the FDWs at structural defects. In [15], it has been demonstrated that during atomic ordering with the formation of the *B*2-type superstructure in the alloys of a close composition (2–3 at % V), there are formed antiphase domains. The boundary that separates one domain from another represents a region inside which the atomic-order parameter η changes from the magnitude typical of a domain to zero. Correspondently, the magnetic parameters that depend on η, in particular, the energy of the magnetocrystalline anisotropy K, change upon passing from one domain to another, and form in the crystal an energy relief, which determines the degree of pinning of the FDWs.

The possibility of such a mechanism in the alloys of the $L1_0$ type was considered in [16], where the magnitude of the coercive force was determined by the slope of the $K(\eta)$ dependence. In these alloys, upon atomic ordering, there takes place a transition from a cubic lattice to a tetragonal one, which leads to an abrupt growth of the magnitude of the magnetocrystalline anisotropy, which, in turn, provides a steep K(η) dependence and, correspondingly, quite high magnitudes of the coercive force. But in the alloys we investigated in this work, upon atomic ordering by the *B*2 type, the cubic lattice is preserved. Therefore, we cannot expect an abrupt growth of the magnetocrystalline anisotropy. Hence, the $K(\eta)$ dependence appears to be considerably flatter, which results in lower values of the coercive force.

CONCLUSIONS

The experimental study of phase transitions in the vicalloy-type alloy with 7% V, in which the temperature intervals of the atomic ordering in the αphase and the polymorphic $\alpha \longrightarrow \gamma$ transformation are clearly separated, has demonstrated that the tempering temperature (620°C) at which the high-coercivity state is realized fall within the temperature interval of ordering and is located well below the temperature of the start of the $\alpha \longrightarrow \gamma$ transformation. This proves that the process responsible for the formation of a high-coercivity state is ordering that occurs in the α phase.

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