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Ordering and phase separation in alloys of the Fe–Co system

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Abstract

$Fe_{50}Co_{50}$, $Fe_{65}Co_{35}$ and $Fe_{35}Co_{65}$ alloys heat treated at temperatures from 500 to 1300 °C have been studied by means of the X-ray diffraction phase analysis and transmission electron microscopy. Phase separation of a solid solution has been found at 900–1300 °C. That phase separation takes place in all the surface layer in the shape of alternating α and γ layers of width about 0.5 μm each. Phase separation in the interior bulk of the alloys occurs in the form of precipitation of the Co-enriched fcc particles occupied no more than 10% of the bulk. The B2 phase precipitated in the temperature region of ordering also occupies no more than 10% of the bulk of an alloy. Ordering and phase separation regions are divided on the Fe–Co phase diagram by the narrow region of a solid solution. At lowering temperature below 550 °C the phase transformation accompanied with a small increase of the lattice parameter takes place. Comparing this phase transformation with the phase transformation in the $Fe_{60}Cr_{30}Co_{10}$ alloy at the same temperature the conclusion has been made that this is precisely the transformation which at the conditions of the existence of the $\alpha_1 + \alpha_2$ cell microstructure brings about the increase of coercive force. The results obtained are shown in the updated Fe–Co phase diagram.

Keywords: Disordered and ordered materials; Precipitation; Transmission electron microscopy; X-ray diffraction

1. Introduction

According to the well-known Fe–Co phase diagram [1], the wide region of solid solutions has the fcc structure above 970 °C and bcc one below 970 °C, during which the Curie temperature coincides with the temperature of the α–γ phase transformation for the compositions contained 15–70% Co. However, using conventional X-ray diffraction phase analysis it has been found recently that phase separation of a solid solution into α and γ particles takes place at temperatures up to 1000 °C [2]. Authors of Ref. [2] have considered presence of γ particles below line of α–γ transformation as the result of the formation of the Co-enriched particles in the depleted α-solid solution. That phase separation is possible if a tendency towards phase separation occurs in the Fe–Co alloys at the temperatures mentioned. However, the X-ray diffraction has found phase separation only in the surface layer to a depth of 70 μm [2].

Further study performed by means of transmission electron microscopy (TEM) has shown that the phase separation of a Fe–Co solid solution into particles enriched and depleted with Co takes place not only in the surface layer, but in the bulk of an alloy as well [3]. Nevertheless, if in the surface layer the total phase separation occurs and quantity of clusters enriched and depleted with Co approximates the relation 50:50, then in the bulk of the Fe–Co alloy the particles of γ-phase, i.e. the particles strongly enriched with Co, occupy a small (about 10%) part of the alloy [3]. Although heat treatment of a specimen has been performed in the evacuated quartz ampoules [2,3] a suspicion arises whether the phase separation in a thin surface layer of a Fe–Co alloy is the result of oxidation occurred at the surface of a specimen, especially as there is little information on morphology of the surface layer under phase separation. Authors of Ref. [3] reasoned that the microstructure of the surface layer consists of rather coarse γ- and α-particles because these particles are well resolved by convention X-ray diffraction.

The reasonably wide region in the form of a cupola, in which B2 long-range ordering takes place throughout the bulk of alloys is observed around the equiatomic composition at temperatures below 730 °C [1]. It is agreed that a fully ordered Fe–Co alloy, attainable through a normal annealing procedure, possesses the optimum soft magnetic properties [4]. That is the reason why a lot of authors have devoted primary attention for the study of B2 ordering in the Fe–Co system [4–8]. Some authors, for example, authors of Ref. [9] reasoned that it is possible to determine the

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degree of order on evidence of saturation–magnetization measurements, that some antiphase domains are formed at ordering, that heat treatment at temperatures below 730 °C brings about the simultaneous rise in the lattice parameter and order parameter.

Estimating the quantity of the B2 ordered phase in a disordered A2 solid solution by ratio of intensities between $(1\,0\,0)_{B2}$ and $(2\,0\,0)_{A2}$ reflections at the electron diffraction patterns, one can come to recognize that even in the alloy of stoichiometric composition $Fe_{50}Co_{50}$ the B2 phase occupies only about 10% of the bulk of the alloy [3]. This leads us to the conclusion that B2 ordering is unlikely to exert any effect on the magnetic properties of Fe–Co alloys.

Formation of the phase separation microstructure at temperatures above 730 °C and the microstructure of ordering below 730 °C points to the fact that the phase transformation “phase separation-ordering” takes place in the Fe–Co alloys at 730 °C. The nature of this transformation has been studied with the help of the X-ray photoelectron spectroscopy [3]. A specimen of the $Fe_{50}Co_{50}$ alloy has been heated in the camera of a spectrometer. Measurements have been carried out in 100° intervals. The spectra at 700 °C and below have a two-band structure characteristic of systems with an insignificant overlap of the d-bands. This form of spectra differs strongly from the one of the valence bands of pure iron and pure cobalt. That difference is connected by strengthening the localization of 3d-valence electrons on Fe atoms in comparison with pure iron. Strengthening the localization of d-electrons on Fe atoms at the expense of surrounding Co atoms inhibits Fe–Fe interaction and, therefore, favors the tendency towards ordering.

When temperature in camera is increased up to 900 °C and above, the spectra resemble the superposition of the valence bands of pure iron and pure cobalt. It is possible if localized d-electron shell is ruptured and d-electron hybridization takes place on the Fe and Co atoms at the expense of the overlap of their d-electron shells. That hybridization brings into decay of chemical bonds Fe–Co, i.e. into strengthening chemical bonds Fe–Fe and Co–Co. As the result, the tendency towards phase separation takes place. By this is meant that the phase transition “phase separation-ordering” occurred at a level of changes in the electron structure is a cause of the subsequent phase transformation proceeding at a level of changes in microstructure, for example, the $A2 \rightarrow A2 + B2$ transition.

At 550 °C a small peak of the specific heat and a small increase of the lattice parameter are observed in Fe–Co alloys [4,6]. This phenomenon has been named as a “550 °C anomaly”. As the result of that increase of the lattice parameter the elastic stresses arise and microstructure resembled martensite plates is formed in the alloys water-quenched from 550 °C [3]. As this takes place, neither coercive force nor induction of magnetic saturation change noticeably. In this connection, the transformation is not held to refer to the magnetic one [3]. The nature of this transformation will also be considered in the present paper.

Although some modified Fe–Co phase diagram is exhibited in Ref. [3] the boundaries of existence of the phase separation region and the region of a “550 °C anomaly” are not specified in it. Therefore, here we will attempt to evaluate these boundaries and point to some other peculiarities of the Fe–Co phase diagram.

2. Experimental procedure

The ingots of $Fe_{65}Co_{35}$, $Fe_{50}Co_{50}$ and $Fe_{35}Co_{65}$ compositions were melted in vacuum from high purity components. The ingots were hot forged. The blanks were heat treated at high temperatures (1100–1300 °C) and then quenched in water. The specimens for TEM and X-ray diffraction phase analysis were cut out from the blanks heat-treated. Subsequent heat treatment was carried out in the evacuated quartz ampoules. The X-ray diffraction phase analysis and precise measurement of the lattice parameter were conducted with the help of Co Kα radiation at a room temperature as well as at high temperatures in a vacuum chamber operated at the temperatures up to 1000 °C. The TEM studies were carried out with the help of an EM-125 electron microscope operated at 125 kV.

3. Results and discussion

3.1. Phase separation

Fig. 1 shows fragments of the X-ray diffraction patterns near the $(1\,1\,0)_\alpha$ line. Specimens of the $Fe_{50}Co_{50}$ alloy have been heat treated at 1200 °C for 1 h and then water-quenched. The X-ray diffraction patterns have been obtained from the surface of specimens cleaned from oxides by a finely dispersed emery paper. At the surface of specimen the γ-phase dominates to a depth of 10 μm (curve 1). Quantity of α-phase is almost equal to one of γ-phase in a depth range of 10–50 μm (curves 2 and 3). The α-phase dominates at a depth of 60–70 μm (curves 4 and 5). So, Fig. 1 demonstrates that phase separation of the $Fe_{50}Co_{50}$ alloy occurs not only in the A2 region of the Fe–Co phase diagram, as expected in Ref. [3], but in the A1 region as well. It can be seen that the $(1\,1\,0)_\alpha$ and $(1\,1\,1)_\gamma$ lines are quite broadened. That broadening results from a high temperature water quenching entailed high elastic stresses in specimen. This water quenching is necessary to fix the high-temperature structural state of the alloy.

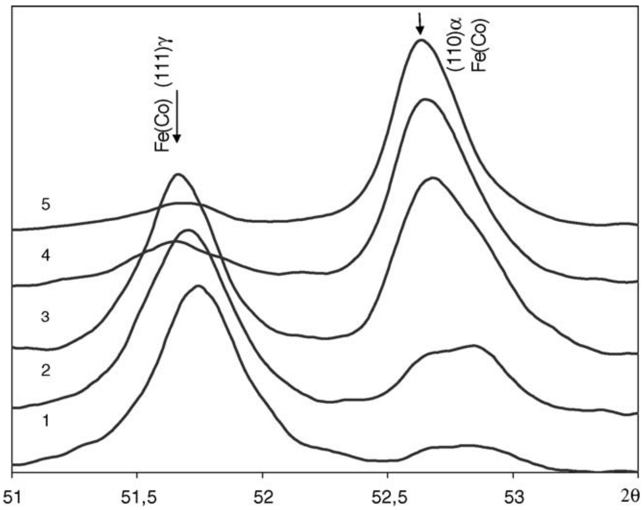

Fig. 1. $Fe_{50}Co_{50}$ alloy water-quenched from 1200 °C for 1 h in water. Fragments of the X-ray diffraction patterns in the vicinity of the $(1\,1\,0)_\alpha$ line. X-ray diffraction patterns are obtained at the different distances from the surface of a specimen: 1–0, 2–30, 3–40, 4–60, and 5–70 μm.