

The Role of Nickel in the Formation of Phases of High Chromium Alloys of Cementite Composition upon Mechanical Synthesis and Subsequent Annealing

A. L. Ulyanov^{a, *}, A. I. Ulyanov^a, A. A. Chulkina^a, V. A. Volkov^a, and A. V. Zagainov^a

^aUdmurt Federal Research Center, Ural Branch, Russian Academy of Sciences, Izhevsk, 426067 Russia

*e-mail: ulyanov@udman.ru

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Abstract—After medium and high temperature annealing, X-ray diffraction, Mössbauer spectroscopy, and magnetic measurements are used to study phase transformations and patterns of the redistribution of Ni and Cr in high-chromium alloys of cementite composition produced via mechanical synthesis.

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INTRODUCTION

Cementite is an important structural constituent of plain and alloyed carbon steels. It determines their strength and other physical properties. The effect alloying elements have on formation of phases (cementite in particular) under conditions of mechanical synthesis has not been studied in any detail. Obtaining cementite doped with carbide forming (Cr) or non-carbide forming (Ni) elements during the mechanical synthesis and subsequent annealing of cementite alloys was discussed in [1–3]. It is of interest to study the effect Ni has on the formation of phases during the mechanical synthesis and subsequent annealing of alloys of high chromium cementite composition.

EXPERIMENTAL

Samples of cementite $(\text{Fe}_{0.9-x}\text{Cr}_{0.1}\text{Ni}_x)_{75}\text{C}_{25}$, where $x = 0, 0.05$, and 0.10 , were prepared via 16 h of the mechanical alloying (MA) of powdered carbonyl iron (grade, OSCh 13-2; purity, 99.98%); nickel and chromium (purity, 99.9%), and graphite (purity, 99.99%) in an argon environment inside a Pulverisette-7 ball planetary mill. The powdered samples were annealed for 1 h in an argon environment using a setup for measuring magnetic susceptibility $\chi(T)$ as a function of temperature. Our X-ray study was performed using a Miniflex 600 diffractometer with $\text{CoK}\alpha$ radiation. Mössbauer spectra were recorded at liquid nitrogen temperature ($T = 77$ K) using a YaGRS-4M spectrometer upon steady acceleration with a $^{57}\text{Co}(\text{Rh})$ source of γ radiation. The distribution functions of ultrafine magnetic fields were recovered from the

spectra using a generalized regularized algorithm of inverse ill-posed problems [4].

RESULTS AND DISCUSSION

Figure 1 presents the data from our X-ray analysis of $(\text{Fe}_{0.85}\text{Cr}_{0.10}\text{Ni}_{0.05})_{75}\text{C}_{25}$ and $(\text{Fe}_{0.80}\text{Cr}_{0.10}\text{Ni}_{0.10})_{75}\text{C}_{25}$ alloys as a function of the annealing temperature. It can be seen that the mechanically alloyed samples of both compositions contained 51–57 vol % of cementite, 37–39 vol % of the amorphous phase, and small amounts of α -Fe and χ - Fe_5C_2 . Figures 2a and 2b show the results from Mössbauer spectroscopy after MA (spectra 1). As in our X-ray analysis, the Mössbauer data show that most of the sample was composed of alloyed cementite, and the maximum of its $P(H)$ function lay in the field $H \approx 200$ kOe. Other phases are also reflected in the spectra, along with the $P(H)$ functions of the considered alloys (the most intense components are at $H \approx 100$ kOe for χ - Fe_5C_2 and $H \approx 330$ kOe for α -Fe). The distribution of the $P(H)$ function for the amorphous phase lies in the 200 to 300 kOe range of fields. Cr and Ni are distributed between the phases upon the phase transformations that occur during MA. However, no appreciable variations in the $P(H)$ function are observed for the considered compositions, due to the weak effect of Ni atoms in the vicinity of Fe atoms have on the average ultrafine magnetic field in the cementite lattice [3]. It can nevertheless be seen in Figs. 2a and 2b (spectra 1) that the distribution of the $P(H)$ function for the cementite of both alloys is in a fairly wide range of fields, due to their high doping with chromium. Doping with Ni atoms can be detected by magnetic measurements. Figure 3 shows the relative magnetic susceptibility of the alloys as a

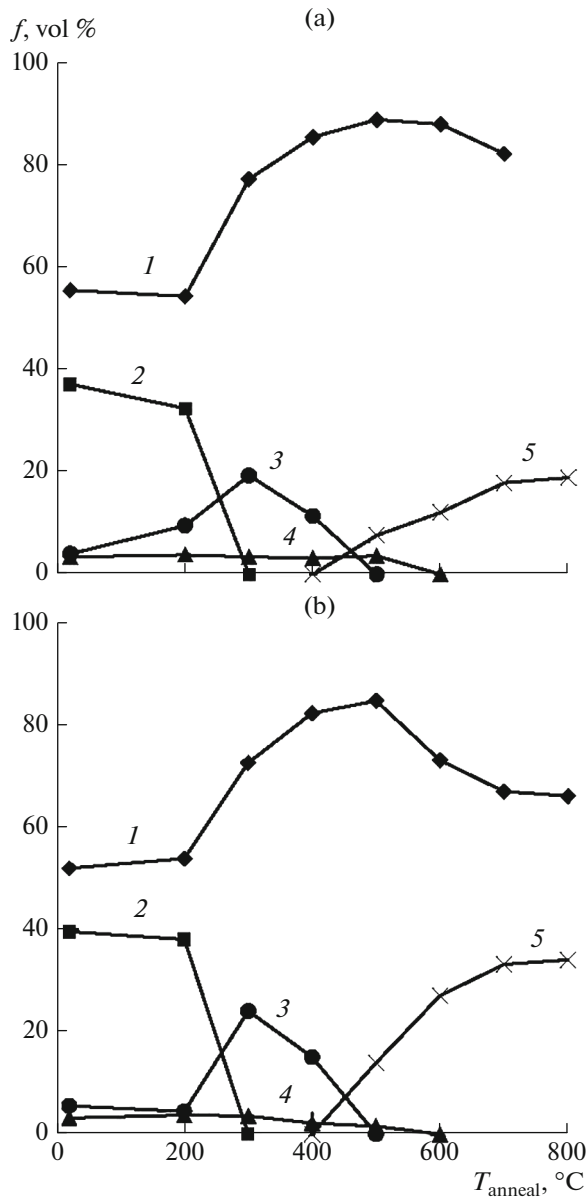


Fig. 1. Phase composition of our alloys as a function of annealing temperature: (a) $(\text{Fe}_{0.85}\text{Cr}_{0.10}\text{Ni}_{0.05})_{75}\text{C}_{25}$ and (b) $(\text{Fe}_{0.80}\text{Cr}_{0.10}\text{Ni}_{0.10})_{75}\text{C}_{25}$. Phases: (1) cementite, (2) amorphous phase, (3) χ carbide, (4) ferrite, (5) austenite.

function of temperature. Maxima and inflections are observed when the ferromagnetic phases cross Curie point T_C on the $\chi(T)$ curves, and the doping of phases with one element or another can be estimated from their temperatures. It is known that Cr doping lowers and Ni doping raises the T_C of cementite [2, 3]. Curves 1 in Fig. 3, obtained upon heating our samples, are characterized by extended maxima in the ranges of temperature and reflect the crossing of the Curie points of cementite and the amorphous phase formed during MA. Meanwhile, the position of the maximum

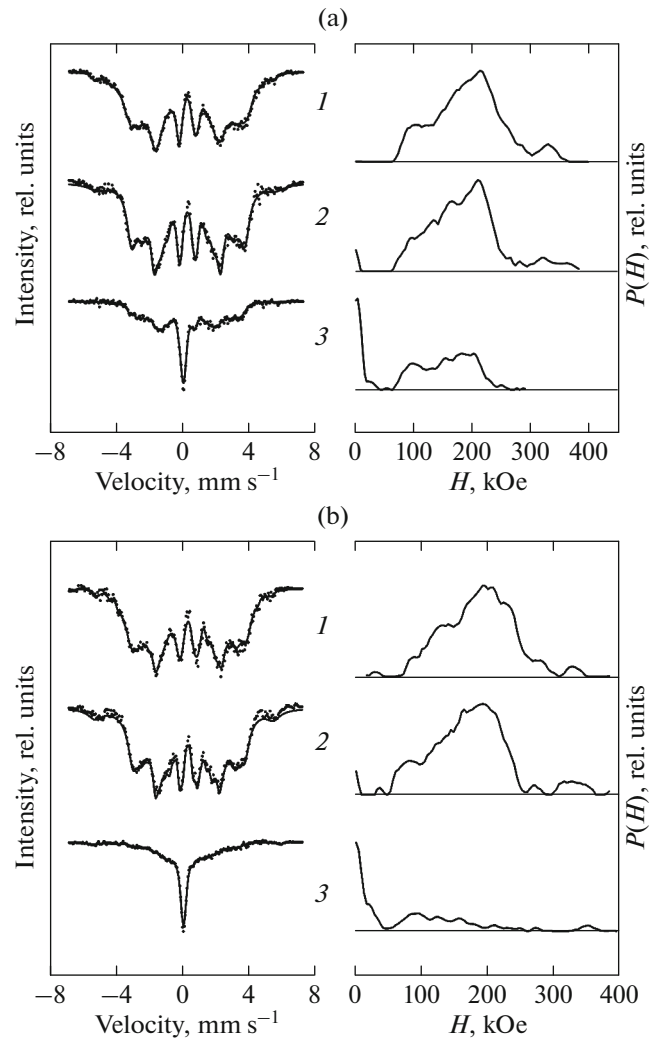


Fig. 2. Mössbauer spectra and $P(H)$ functions of our alloys: (a) $(\text{Fe}_{0.85}\text{Cr}_{0.10}\text{Ni}_{0.05})_{75}\text{C}_{25}$ and (b) $(\text{Fe}_{0.80}\text{Cr}_{0.10}\text{Ni}_{0.10})_{75}\text{C}_{25}$: (1) mechanical synthesis; (2) annealing at 500°C; (3) annealing at 800°C.

on the abscissa remains virtually the same when the Ni content is raised from $x = 0$ to $x = 0.1$ ($T_C \approx 60^\circ\text{C}$). This means the cementite was doped mainly with chromium. Small amounts of nickel can also be dissolved in cementite, though it is difficult to determine the effect it has on the behavior of the $\chi(T)$ curves of the alloys after MA.

At $T_{\text{anneal}} = 300^\circ\text{C}$, the amorphous phase of the alloys crystallizes with the formation of cementite and χ -carbide (curves 1, 2, and 3 in Fig. 1). It can be seen in Fig. 3c that curve 2 of function $\chi(T)$ has two inflections near the maximum. This means the alloy contained cementite with different Curie points, and thus with different doping. The first inflection, in the region of lower temperatures, corresponds to cementite doped with chromium; the second one, in the region of higher temperatures, corresponds to cemen-

tite enriched with nickel, which emerges as a consequence of the crystallization of the amorphous phase, which contains a considerable number of Ni atoms. It should be noted that at $x = 0.05$ (Fig. 3b), the second inflection on curves 2 and 3 is barely visible, due to low content of Ni in the alloy.

Two processes occur during annealing in the range of 400 to 500°C: the transformation of χ -carbide into cementite, and the decomposition of cementite enriched with Ni, which forms as a consequence of the crystallization of the amorphous phase. The second process is much slower than the first, so the content of cementite is maximal at $T_{\text{anneal}} = 500^\circ\text{C}$ (curves 1 in Fig. 1). At the same annealing temperature, the cementite enriched with nickel disappears almost completely, as can be seen from the absence of the second inflection on curves 4 of functions the $\chi(T)$ in Fig. 3. The released Ni atoms are segregated on phase grain boundaries and form austenite with iron and carbon atoms (curves 5, Fig. 1), the amount of which at $T_{\text{anneal}} = 800^\circ\text{C}$ is as high as 20 and 38 vol % for $(\text{Fe}_{0.85}\text{Cr}_{0.10}\text{Ni}_{0.05})_{75}\text{C}_{25}$ and $(\text{Fe}_{0.80}\text{Cr}_{0.10}\text{Ni}_{0.10})_{75}\text{C}_{25}$, respectively. It should be noted that austenite is not uniformly doped with Ni. The portion of austenite with a Ni content of <30 at % is in a paramagnetic state (the constituent at $H = 0$ kOe in Figs. 2a and 2b, spectra 2). The portion of austenite with a Ni content of >30 at % is in a ferromagnetic state [5] with Curie temperatures of $\sim 450^\circ\text{C}$ for $(\text{Fe}_{0.80}\text{Cr}_{0.10}\text{Ni}_{0.10})_{75}\text{C}_{25}$ (Fig. 3c, curve 4) and $\sim 280^\circ\text{C}$ for $(\text{Fe}_{0.85}\text{Cr}_{0.10}\text{Ni}_{0.05})_{75}\text{C}_{25}$ (Fig. 3b, curve 4). In the $P(H)$ functions (spectra 2 in Figs. 2a and 2b) the intervals of fields H of ferromagnetic austenite and cementite overlap, and it is impossible to separate them. The decomposition of cementite enriched with Ni and the redistribution of dopant atoms upon annealing increase the remaining cementite's degree of doping with chromium. Upon an increase in the annealing temperature, there is thus a slight displacement of the maxima on curves 4 toward lower measured temperatures, compared to curves 3 in Fig. 3. Decomposition of the remaining regions of cementite weakly doped with nickel was observed upon a further rise in the annealing temperature. It should be noted that the higher the Ni content in the alloy, the greater the intensity of cementite decomposition in the region of higher annealing temperature (curves 1 in Figs. 1a and 1b). The decomposition of cementite upon annealing at higher temperatures raised the content of austenite in the sample even more.

Mössbauer phase analysis qualitatively confirmed our X-ray studies. We can see from spectra 3 in Figs. 2a and 2b that after annealing the alloy at 800°C, the austenite was in a partial paramagnetic state (the constituent at $H = 0$ kOe). The wide distribution of fields in the range of 50 to 300 kOe can be attributed to the coexistence of two phases in the sample: cementite doped with Cr and ferromagnetic austenite doped with Ni. Their $P(H)$ functions lie in

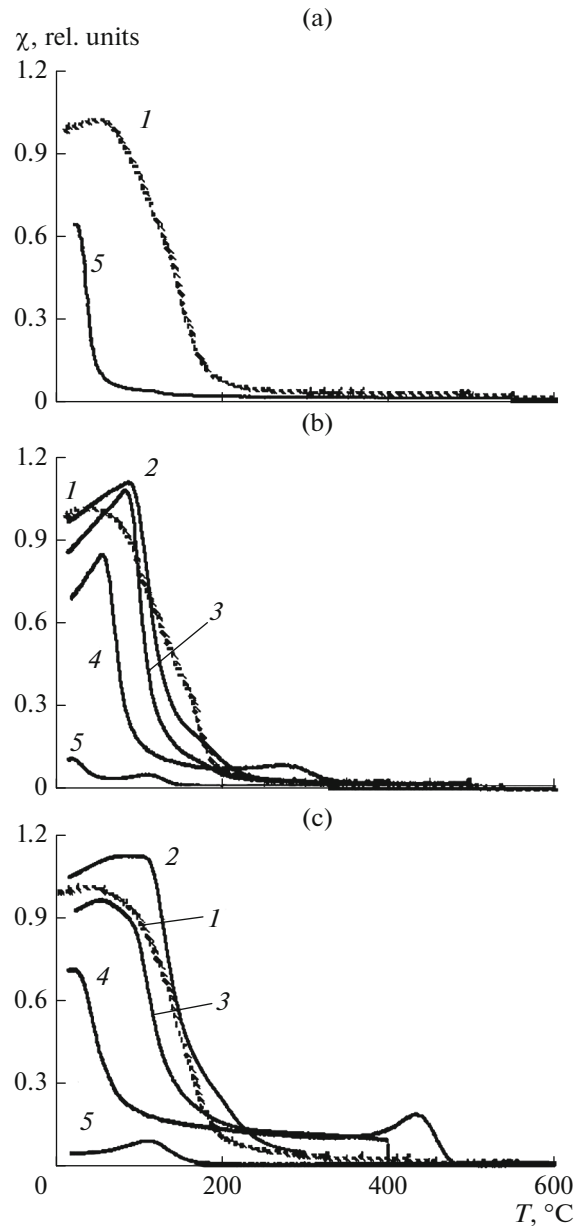


Fig. 3. Dependences $\chi(T)$ of mechanically synthesized alloys $(\text{Fe}_{0.9-x}\text{Cr}_{0.10}\text{Ni}_x)_{75}\text{C}_{25}$, where (a) $x = 0$, (b) $x = 0.05$, and (c) $x = 0.10$, as a function of the temperature of heating (T) and cooling of the same samples after annealing at: (2) 300; (3) 400; (4) 500; (5) 800°C.

the same range of fields. For ferromagnetic austenite, $T_C \approx 100^\circ\text{C}$ (curves 5 in Figs. 3b and 3c), while the T_C of cementite doped with chromium lies in the range of negative temperatures.

CONCLUSIONS

It was shown that the mechanical synthesis of $(\text{Fe}_{0.9-x}\text{Cr}_{0.1}\text{Ni}_x)_{75}\text{C}_{25}$ powders where $x = 0.05$ and 0.10 yields samples composed of cementite, an amor-

phous phase, and amounts of χ -carbide and α -Fe. After mechanical synthesis, cementite is doped mainly with chromium. Nickel also dissolves in cementite, but in limited amounts. The amorphous phase is doped with chromium and nickel, the latter more than the former.

It was found that after low temperature annealing, the alloys contained cementite with different types of doping. The cementite formed as a consequence of mechanical synthesis was doped mainly with chromium. The cementite resulting from crystallization of the amorphous phase was doped with both chromium and nickel.

Doping with nickel led to formation of austenite, which acts as a binder in cementite–austenite composite after high temperature annealing.

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