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COMPARISON OF SPARK–SYNTHETIZED AND MELT–SPUN Fe–Ni–C NANOCRYSTALLITES[1]

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Phase composition and magnetic properties of spark synthetized powders and melt–spun ribbons of Fe–Ni–C alloys were studied by means of Mössbauer spectroscopy. In both cases α– and γ–iron phases, $\theta-, \epsilon-$, and some transition carbides were identified. In powders, graphite and further non–magnetic component containing Fe–Ni were detected, the latter was ascribed to iron–nickel clusters in graphite. In the Fe–12wt.%Ni–4wt.%C ribbon the transformation of γ–Fe–Ni to a ferromagnetic state was observed after severe deformation. Subsequent tempering at 523 K induced a reversal transformation to the antiferromagnetic state. This effect was ascribed to the influence of the high defect density on mean interatomic iron atom distances which (in agreement with a theoretical prediction) could change the mgnetic state.

The rapid solidification produces various metastable phases and structures. It appears especially in materials based on an Fe–C system, which forms a large number of structures and phases in dependence on heat and mechanical treatment [1, 2, 3, 4, 5, 6]. Most problems arise in the study of fine particles that often exhibit properties differing from those of a bulk material. Therefore new structures and phase compositions can be expected in materials prepared by rapid solidification from a melt, gas or plasma. In this paper we compare the phase composition and structure of two types of Fe–Ni–C nanocrystallites: melt–spun ribbons and powders prepared by spark synthesis.

Two methods of rapid cooling were used for sample preparation: melt spinning yielding ribbons about $15\mu m$ thick and 1mm wide of Fe–12wt.%Ni–4wt.%C (samples R12–4) and Fe–3wt.%Ni–4wt.%C (samples R3–4), and spark synthesis between electrodes of pure Fe–10wt.%Ni in kerosene for the production of a powder (samples P) [7, 8, 9]. The as–prepared samples are denoted R12–4/A, R3–4/A, and P/A. The tempering was done in vacuum 10^{-3} Pa for 1 hour at 523 K (samples R12–4/T, R4–3/T, and P/T). Plastic deformation of the ribbons (samples R12–4/D and R3–4/D) was

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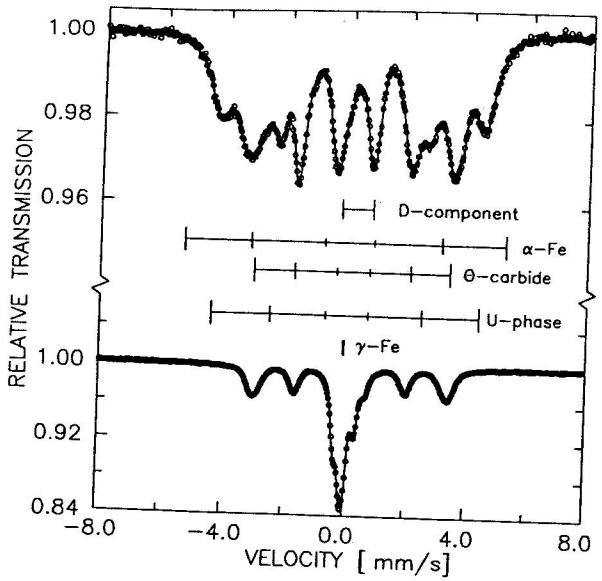

Fig. 1. Mössbauer spectra of the spark–synthetized $(Fe–10wt.\%Ni)_{1-y}C_y$ powder (top) and Fe–12wt.%Ni–4wt.%C ribbon (bottom). The combs label the position of some spectrum components.

performed by mortaring. Details are given in ref. [10]. The samples R12–4/DT and R4–3/DT were prepared by the tempering of the deformed state.

Mössbauer spectra were measured at room temperature using the transmission method. They were analyzed by means of a standard procedure and calibration was done with standard α–iron foil. Relative areas of individual components of spectra are supposed to roughly correspond to the distribution of Fe atoms between individual phases.

Fine irregular eutectic was observed as a basic microstructure of ribbons. The spark–synthetized powders consist of black mat particles of wide range of forms and sizes composed of iron rich particles wrapped in graphite debris.

A quantitative analysis of iron containing phases was gained from Mössbauer spectra. Two examples are shown in Fig. 1. The spectra were deconvoluted into 6 components [8, 9]. The results of the analysis are summarized in Table 1. The α–component (sextets with $B_{hf} = 35 \div 32.5$ T) represents the α–phase Fe–Ni(–C). The γ–component without magnetic splitting corresponds to the non–magnetic γ–phase. It is composed of a singlet (isomer shift δ = -0.05 mm/s) , and a doublet (δ = 0.02 mm/s and quadrupole splitting σ = 0.7 mm/s).

The components ascribed to carbides [8, 9] (sextets with $B_{hf} = 24 \div 11$T) are labelled as θ and TC, corresponding to cementite with mean B_{hf} = 20.5 T and to transition carbides, respectively. In this component we supposed ε–carbide with B_{hf}

Table 1. Intensities of components of spectra

Sample	α	U	θ	TC	γ	D
R12–4/A	-	.02	.32	.13	.53	-
R12–4/D	.20	.14	.26	.23	.17	-
R12–4/DT	.17	.03	.34	.14	.32	-
R12–4/T	-	-	.29	.12	.59	-
R3–4/A	.08	.02	.43	.08	.39	-
R3–4/D	.21	.11	.41	.13	.14	-
R3–4/DT	.43	-	.35	.20	.02	-
R3–4/T	.41	-	.50	.06	.03	-
P/A	.01	.31	.18	.41	.01	.08
P/T	.19	.06	.20	.43	.03	.09

of about 24, 17 and 13T [11], χ–carbide with B_{hf} of about 22, 18.5 and 11 T [11], Fe_7C_3 carbide B_{hf} = 23, 18.5 and 16 T [12] and faulted cementite. The carbides might be microsyntactically intergrown likely as θ'–particles formed at early third stage of martensite tempering [13, 14]. These particles are composed of very thin alternating layers of individual carbides, the structures of which are closely related with each other.

In addition to the above mentioned common phases, a U–component (represented by broad distribution of sextets with $B_{hf} = 32 \div 25$ T) has been observed. In the powder, a further non–magnetic component D (doublets with δ of about 0.34mm/s and mean quadrupole splitting σ = 0.85 mm/s) was detected. It is most probably due to Fe atoms in graphite [9].

In as–prepared samples the α–phase content is low and the carbides represent an important part of the spectrum in both ribbons and powder. In the ribbons, the other dominating component is the γ–phase, the U– component content being negligible. On the other hand, in the powder the U–component content is high and that of the γ–phase is negligible.

In the ribbons, the U–component (and also the α–phase) formed after severe deformation. The sum of U– and α–intensities was approximately equal to the decrease of the intensity of the γ–component. The θ–component was reduced by about 25% and the transition carbides TC increased by about the same amount. The changes after tempering were different. In the sample R12–4/DT almost the entire U– component was transformed back to γ and the lost amount of the θ–component was restored. Tempering without previous deformation caused a slight increase in γ–intensity (of about 10%). The same tempering of samples from R3–4 alloy caused the decomposition of the γ–phase and the U–component into an α–phase and carbides in both as–quenched and deformed states. In the powder, most of the U–component was decomposed into an α–phase and carbides after the same tempering (sample P/T).

The U–component with $B_{hf} = 32 \div 25$ T can be ascribed to a distorted close–packed lattice configuration. A similar component with B_{hf} = 27 T was found in mechanically synthetized carbides of the Fe–C system and was interpreted as hexagonal carbide of the disordered $\varepsilon L'3$ type which is, in fact, also the distorted close–packed lattice

configuration [15]. In the case of ageing of martensite, the component with B_{hf} of about 27 T may also be due to a similar distortion configuration, which can be supposed in the last step before formation of hcp ε–carbide [5]. A ferromagnetic γ–phase was found in the rapidly quenched $(Fe_{1-x}Ni_x)_{92}C_8$ alloy. In the range of $x = 0.4 \div 0.25$ hyperfine induction $B_{hf} = 33$ T at 4.2 K. Below $x = 0.25$ it decreases with decreasing x and disappears at $x = 0.15$ [16].

In the case of the ribbons, the distortion is induced by a hard deformation of the γ–phase which causes the transformation of the antiferromagnetic state to a ferromagnetic one. The most probable cause is the influence of a high defect density on mean atomic distances. In agreement with the theoretical prediction, this may change the magnetic state. After annealing, the antiferromagnetic state is restored, at least in the presence of a higher Ni–content (12wt.%) and after tempering at 523 K. In alloys with a lower Ni–content, the decomposition into an α–phase and carbides takes place at that temperature and no detection of changes in primary phases is possible.

In the case of spark–synthetized powders the distortion is supposed to be due to coherence, the orientation relationship or complex bonds with the hexagonal net of graphite. In contrast to pure Fe–C system [9], the presence of Ni increases the content of the ferromagnetic U–component and decreases that of the non–magnetic D–component.

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