

STRUCTURE OF SPARK ERODED Fe₃Si POWDER¹

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We have investigated structure, phase composition and atomic ordering in a spark eroded powder of Fe₃Si alloy by means of the Mössbauer effect and magnetization measurements. In the samples of the as-prepared powder dominating part (97%) of amorphous phase was found. The development of the atomic ordering can be described in agreement with the phases appearing in the phase diagram. The amorphous structure transforms into α bcc phase with D0₃ type atomic ordering via solid solution of Si in α -Fe (A2). Several critical temperatures were observed on a thermomagnetic curve of the as-prepared powder: temperatures of crystallization and recrystallization at about 330°C and 530°C, and Curie temperatures of amorphous, A2 and D0₃ structures of 330°C, 420°C and 550°C.

Data on crystallization and atomic ordering in Fe₃Si are important for the understanding of some nanocrystalline magnetics prepared from amorphous materials [1, 2, 3]. Fe-Si alloys above 12 at.% Si are of D0₃ ordering and it is very difficult to prepare those alloys in an amorphous state or in a crystalline state with suppressed ordering in bulk form [4, 5]. Amorphous phases were reported for thin films mostly prepared by sputtering, e.g., [6, 7, 8]. Spark erosion yields a similarly high quenching rate [9] that could allow at some conditions to prepare an Fe₃Si alloy in an amorphous state [10, 11, 12].

The Fe₃Si powder was prepared by spark erosion of an ingot prepared from pure (better than 3N) elements. Erosion was performed using Fe₃Si and Cu as electrodes and kerosene as dielectric. The powder was extracted from kerosene by sedimentation and magnetic separation. Remaining Cu particles and surface contamination by Cu and hydrocarbons were removed by a chemical method. The carbon content in the powder was below 0.005wt.%. Annealing at elevated temperatures was done in vacuum (10⁻² Pa). Mössbauer spectra were measured at room temperature by a standard transmission method. The computer processing of the spectra was reported in several previous papers, for example e.g., [12, 13], yielding intensity I of the components and their hyperfine induction B_{hf} and isomer shift δ relative to α -Fe. The atomic ordering

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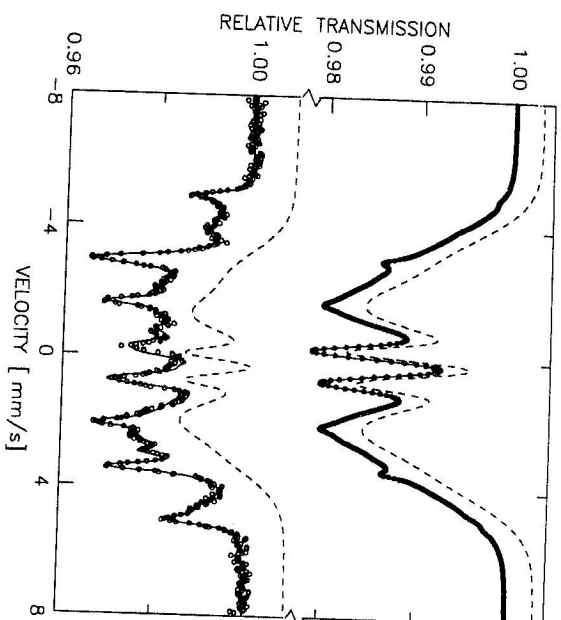


Fig. 1. Mössbauer spectra of the sample from the as-prepared powder (above) and the sample of the powder after annealing at 400°C for 275 hours in vacuum (below). The dashed lines show the shape of the function representing the amorphous components.

was estimated in a similar way as in [12, 14]. Thermomagnetic curves were measured using a vibrating sample magnetometer with a vacuum furnace.

In the spectrum of the original powder (Fig. 1) a dominating part (97%) of amorphous phase was found with $B_{\text{hf}} = 18.0$ T and $\delta_{\text{am}} = 0.219$ mm/s. The crystalline part was identified as ordered Fe₃Si. To prove the composition of the spark eroded powder the sample prepared by annealing at 1000°C for 1 hour in vacuum was investigated. Its spectrum is composed of two sextets with B_{hf} and δ of 31.31 T and 20.09 T, and 23.57 T. It corresponds well to the Fe-25at.%Si alloy with D0₃ order, i.e. to the original ingot. Therefore, changes in the chemical composition that occurred during the powder preparation and cleaning treatment can be neglected.

From the thermomagnetic curve (Fig. 2) the Curie temperatures of the amorphous part $T_{\text{am}}^{\text{cr}} \sim 330^\circ\text{C}$ and for the crystalline state after cooling from the 800°C $T_{\text{c}}^{\text{cr}} \sim 550^\circ\text{C}$ were estimated. The $T_{\text{am}}^{\text{cr}}$ of Fe-6.5wt.%Si found in [11] was 425°C . It gives a decrease of $T_{\text{am}}^{\text{cr}}$ about 11 K per at.% Si. A decrease in T_{c}^{cr} due to the increase in Si content is also about 12 K per at.% Si [15]. A fine kink at $\sim 420^\circ\text{C}$ could indicate T_{c} of another phase. Enokizono and Narita [11] have also observed at 530°C a change in magnetic moment in the same region for Fe-6.5wt.%Si. They ascribed it to a second critical temperature for crystallization. The next critical temperature we have observed is about 520°C . It shifts the Curie temperature of the sample toward T_{c}^{cr} . Therefore

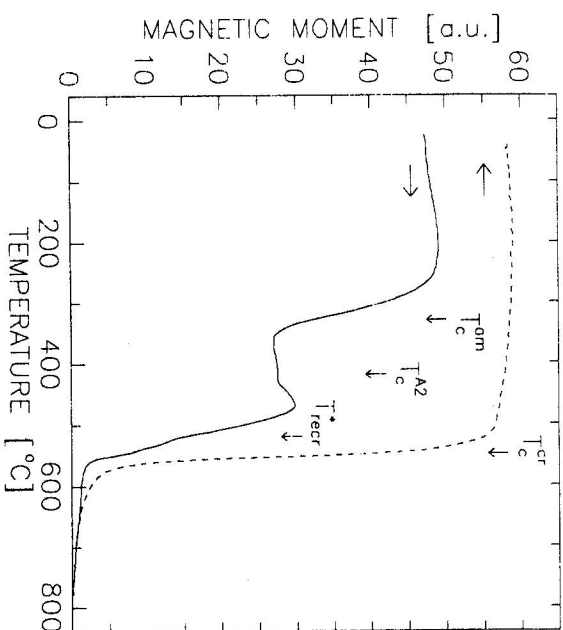


Fig. 2. Temperature dependence of the magnetic moment measured with a temperature increase of 240 K h^{-1} in the external field of 50 Oe. The fill and dashed lines correspond to increasing and decreasing temperature. The arrows show some critical temperatures.

we can ascribe this T_{recr}^* to recrystallization of the fine crystallites. Hampel et al. have observed the D0₃ superlattice diffraction peaks of Fe-Si phase in X-ray spectrum of the Fe_{73.5}Cr₁₁Nb₃Si_{13.5}B₃ amorphous alloy after annealing at this temperature [16]. The observation of grain growth in the nanophase Fe₃Si prepared by mechanical alloying [17] showed that the coarsening of nanocrystals occurs already at lower temperatures (450°C). Therefore recrystallization seems to be the most probable transformation that influences the shape of the thermomagnetic curve in this temperature region. It should be noted that the mentioned critical temperatures are true only for the temperature increase of 240 K h^{-1} used in this case.

Based on information from the thermomagnetic curve we have investigated the temperature region where crystallization of the amorphous phase occurs. In the spectrum of the powder that was annealed at 400°C for 0.5 hour the amount of the amorphous part decreased to 70% and the mean B_{hf} of the sample slightly increased to 18.3 T.

After annealing at 400°C for 207 hours crystallization was not finished yet as indicated by the monitored changes of the magnetic moment of the sample. In the Mössbauer spectrum of this sample about 60% amorphous phase with $B_{\text{hf}} = 16.8$ T and $\delta_{\text{am}} = 0.257$ mm/s could still be detected. The mean B_{hf} reached 20.05 T.

The crystalline part can be fitted as a mixture of the $60 \pm 5\%$ of D0₃ ordered structure and of the $40 \pm 5\%$ of structure with random distribution of Si atoms in α -Fe(A2). The decrease in magnetic moment observed on the thermomagnetic curve at

420°C can rather be ascribed to the Curie temperature of crystallites with A2 structure T_{c2} than to the second critical temperature of crystallization as preferred in [11].

The B_{Hr} decrease of the amorphous phase can be explained in several ways. A decrease can be induced by an increase in Si content [6, 7] or by a decrease of the volumes occupied by this phase [4]. It can also be due to an increase in density of defects in the volumes occupied by the remaining amorphous phase. An increase in its Si content would be expected as initial stage of segregation or formation of the silicon rich phase. It does not occur in this alloy. Therefore the formation of very fine volumes with remaining high defect density seems to be most probable.

The states reached by annealing of the as-quenched powder at 450°C and 475°C for 0.5 hour were very similar to that obtained by annealing at 400°C. More important changes occurred after annealing at 500°C for 0.5 hour - the amount of amorphous phase decreased to 54% and mean B_{Hr} increased to 19.8 T. The crystalline part was formed from 75% of the D0₃ ordered structure and 25% of the A2 structure. It indicates that the increase in the magnetic moment above 450°C can rather be ascribed to forced crystallization than to a change in the permeability of the material.

In conclusion we can describe the development of the phase composition and atomic ordering in agreement with phases appearing in the Fe-Si phase diagram. The amorphous structure transforms in the α phase with D0₃ type atomic ordering via solid solution of Si in α -Fe (A2). The temperature region for the formation of nanocrystals from the amorphous state starts at $T_{cr}^* \sim 330^\circ\text{C}$. The amount of the crystalline phase with predominant D0₃ structure increases more rapidly by annealing above 500°C.

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