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COMPARISON OF Fe_3Si NANOCRYSTALS PREPARED BY MECHANICAL ALLOYING AND SPARK EROSION[1]

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Phase composition of ball milled and spark eroded powders of Fe_3Si alloy are investigated. While in the as-prepared ball milled powders a crystalline part prevails, in the spark eroded powder dominating part (97%) of an amorphous phase was found. Development of the phase composition after different heat treatment in temperature range 573 – 1173 K tends to equilibrium which is different for the ways of preparations.

Interest on information about Fe_3Si has been increasing in connection with nanocrystalline magnetic systems prepared from amorphous materials [1, 2]. Classical technologies have not been successful in the preparation of Fe-Si alloys with more than 12 at.% Si in an amorphous state or in a nanocrystalline state in a bulk form [3]. Amorphous phases were for thin films mostly prepared by sputtering, e.g., [4]. Mechanical alloying and spark erosion were found to be promising preparation techniques of fine crystalline and/or amorphous powders [7, 8, 9, 6]. In this paper we are reporting investigation of phase composition of ball milled and spark eroded Fe_3Si powders in dependence on conditions of preparation and on subsequent heat treatment.

Mechanically alloyed Fe_3Si powders were prepared by ball milling of pure iron (0.999) and silicon (0.999) powders in atomic ratio 3:1. Parameters of the milling process were time of milling and environment (argon, toluene). The M1 powder was prepared by milling in Ar for 30 hours. The powder M2 was obtained after additional milling of M1 for 20 hours in toluene. The weight ratio of balls to original amount of powders was 4.8.

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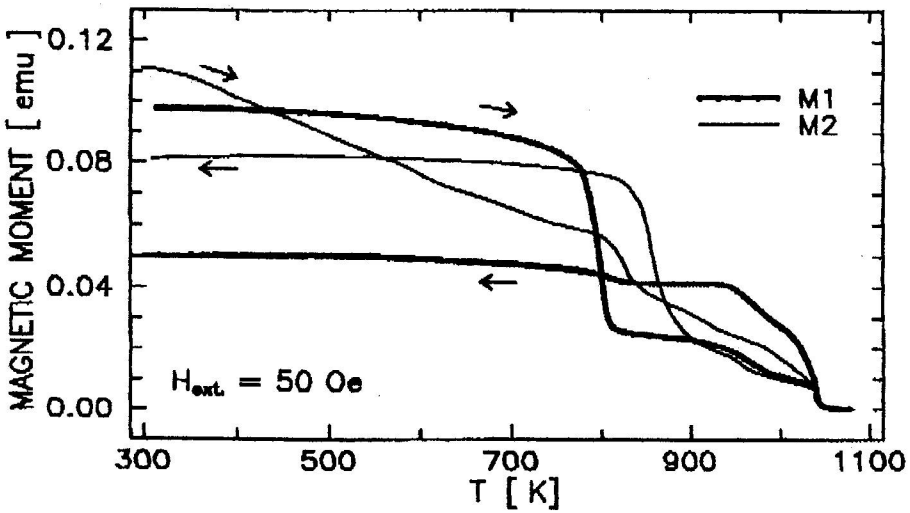

g. 1. Thermomagnetic curves of M1 and M2 powders.

For preparation of the powder E1 by spark erosion a cast ingot melted from pure better than 0.999) elements was used. Erosion was performed using Fe_3Si and Cu as ectrodes and kerosene as dielectric. The detailed information about the particle size istribution and cleaning of the powder were given in [6, 10].

Annealing at elevated temperatures was carried out in Ar or in vacuum (10^{-2} Pa). or determination of critical temperatures DTA and thermomagnetic curves were meaured in temperature range from 300K up to 1473 K and 1073 K, respectively. Structure nd phase composition of powders were investigated by means of x-ray diffraction and össbauer spectroscopy. X-ray measurements by Debye-Scherrer method using Co K_α elded lattice parameter and mean particle size. ^{57}Fe Mössbauer spectra were measured room temperature by a standard transmission method. The computer processing of e spectra was described in, e.g., [6].

In the X-ray diffraction analysis of M1 and M2 powders, iron with minor changes in ttice parameters was only identified. In the Mössbauer spectra two components were stinguished: crystalline, which was ascribed to deformed α–Fe, and amorphous Fe-Si. mounts of amorphous phase were 36% and 46% for M1 and M2, respectively. The ermomagnetic curves (Fig.1) indicate first changes at 610 K and 600 K, respectively, r the increasing temperature. Next more important kinks observed at about 795 K by oth method can be ascribed to Curie temperature T_c of the Fe_3Si phase. Besides that vo additional critical temperatures were identified - at 930 K (more pronounced for M1) nd at 1040 K which are in a good agreement with T_c of the α–FeSi containing about at.% Si and α–Fe , respectively. The T_c of crystalline phases are confirmed on curves r decreasing temperature. Positions of the above mentioned critical temperatures are good agreements with the DTA curves.

In the Mössbauer spectrum of the E1 powder about 97% of amorphous phase was

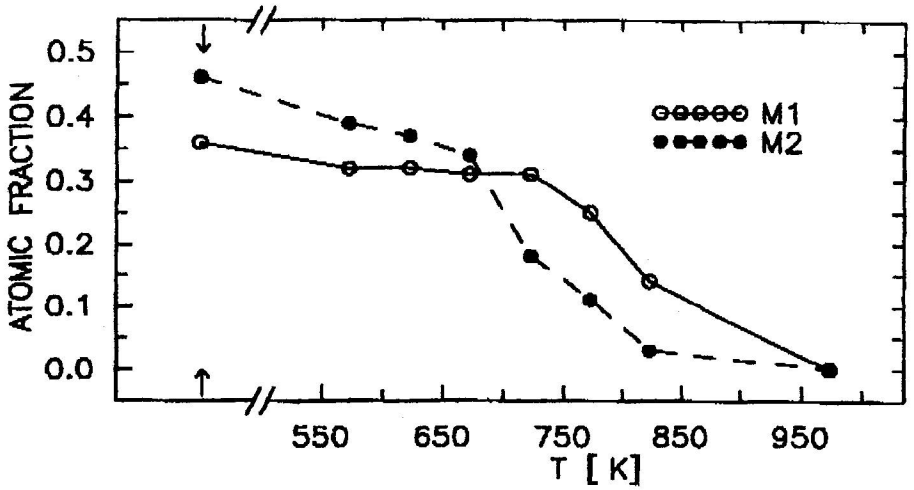

Fig. 2. Changes in atomic fraction of the amorphous phase in M1 and M2 powders in dependence on annealing temperature. The arrows label as-prepared state.

found accompanied by fine traces of a crystalline phase, which was identified as Fe_3Si.

The thermomagnetic curve of the E1 powder is very similar to that published in [10]. At the decreasing temperature the Curie temperatures of the amorphous phase $T_c^{am} \sim 600$ K and the crystalline phase Fe_3Si $T_c^{cr} \sim 805$ K were estimated. The large amount of amorphous phase in E1 powder allowed to detect T_c^{am} more precisely than in M1 and M2 samples.

According to DTA and TMC the heat treatment up to 1073 K induces crystallization of the amorphous phase and recovery and recrystallization of the remaining crystalline phases. Changes in phase composition of M1 and M2 powders after annealing in temperature range 573 - 1073 K for 20 hours in vacuum derived from Mössbauer spectra are shown in Fig. 2. There are two ranges differing in the rate of decrease of the amount of amorphous phase. The first parts characterized by slight changes are terminated at 723 K and 673 K, respectively. In the second parts completed at 973 K and 823 K, respectively, all the volume of the amorphous phase transforms to crystalline phases. If we used these data for derivation of activation energies of the crystallization, we obtained for the first range for M1 and M2 powders 0.08×10^{-19} J and 0.09×10^{-19} J, respectively. For the second range the values are 0.54×10^{-19} J and 0.46×10^{-19} J, respectively. In similar investigations of E1 sample, activation energy of 0.39×10^{-19} J was obtained for the second range only. Changes of the phase composition in E1 after annealing below 673 K were negligible. The activation energies are in good agreement with values for crystallization Fe_3Si crystallites in nanocrystalline alloys $Fe_{77.5-x}(Cu_{0.25}Nb_{0.75})_xSi_{13.5}B_9$, x=0,1,2,3,4 [11].

The x-ray investigation yields an estimation of mean particle size d in the powders and it confirms the results of the Mössbauer phase analysis. In the powder M2 after vacuum annealing at 673 K for 10 hours d was about 15 nm, while after annealing at 573 K the line broadening due to the presence of amorphous phase does not allow its

determination. After annealing of M2 at 823 K and 923 K for 30 minutes in Ar the d increases to d=54.5 nm and d=73.9 nm, respectively. To compare d for M1 and M2, they were annealed at 793 K for 9 hours in Ar. This heat treatment formed M1 and M2 powders with d=30.4 nm and d=26.6 nm, respectively.

After annealing at 973 K for 20 hours in vacuum, the phase compositions of all powders were compared. In the M1 and M2 following phases were found: 11.4% and 10.8% of α–Fe, and 88.6% and 89.2% of Fe_3Si, respectively.

There is a difference in distribution of Si between the phases detected. In the M1 the phases are closer to the stoichiometric Fe_3Si and to pure α–Fe than in the M2. However, for a more precise analysis more detailed investigations using additional TEM studies are requested. In the spectrum of E1 Fe_3Si phase was only detected. It was represented by two sextets with B_{hf} of 31.31 T and 20.09 T and the mean B_{hf} of 23.57 T. This corresponds to the original Fe_3Si alloy.

Comparison of activation energies for M1 and M2 with E1 powders shows that annealing at lower temperatures probably induced recovery of the finest Fe_3Si grains and α–Fe in M1 and M2. At higher temperatures crystallization of amorphous phase dominates. Both the crystallization temperatures and the products of the crystallization process depend on the preparation conditions of the powders submitted to annealing. In the case of our mechanical alloying procedure as described, the components are apparently not mixed at the atomic level to such an extent as to give rise to a one-phase nanocrystalline system. The equilibrium phase composition of the M samples actually tends towards a mixture of α–Fe and Fe_3Si. On the other hand the obviously more thorough mixing in the spark-eroded particles results in the nanocrystalline product, whose composition is close to the original ingot - Fe_3Si. Even for the given preparational technique the changing conditions lead to various stabilities of the amorphous phase as seen from the varying crystallization temperatures and the associated activation energies.

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