SOFT MAGNETIC NANOCRYSTALLINE POWDERS OBTAINED BY MECHANICAL GRINDING.

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Abstract: Amorphous powders have been produced by mechanical grinding of untreated and embrittled amorphous ribbon precursors. It is established that the Fe$_{86}$Zr$_7$B$_5$Cu$_1$ amorphous alloy shows a much higher affinity towards mechanical crystallization than Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_2$ under similar milling conditions. While the low frequency soft magnetic properties of nanocrystallized hot pressed compacts are inferior compared to the nanocrystallized ribbon cores, their high frequency behavior was superior which can be further enhanced by improving the particle insulation.

Introduction

Different magnetic applications need complexly shaped cores that are not easily formed from ribbons or wires. As powder metallurgy techniques are widely used to shape these cores, soft magnetic powder materials suitable for compaction and densification in the desired shape are of considerable interest. Results of Kawamura et al. [1] indicate that amorphous powder needs lower pressure to achieve the same degree of compaction than the crystallized material. It is due to its lower hardness and lower viscosity during hot consolidation which is connected to the free volume of the amorphous structure. This is why we decided to investigate in the present work the effect of mechanical grinding to amorphous ribbons. Particle size decreases with milling time and the minimum particle size is advantageous for successful compaction. On the other hand, crystalline fraction is also increasing with milling time. For this reason we have studied the influence of milling time to find the time window where the most suitable powder for compaction is attained.

The behavior of Fe-Si-B-Nb-Cu was investigated in some reports [2,3]. Both, the crystallization of the melt quenched ribbon and the re-amorphization of nanocrystalline ribbon under ball milling have been observed [4,5]. The Fe-Zr-B-Cu alloy fits the general trend. While the system can be prepared by mechanical alloying [6] the crystallization of the melt quenched ribbon during ball milling was also reported [7]. Here we compare the tendency of these two alloys to mechanical crystallization when milled in the same equipment under similar conditions. We also present some preliminary results on the soft magnetic properties of the consolidated cores obtained from amorphous powder.

Experimental details

Finemet type Fe$_{73.5}$Si$_{13.5}$B$_3$Nb$_3$Cu$_1$ and Fe-Zr based Fe$_{86}$Zr$_7$B$_5$Cu$_1$, approximately 20 μm thick amorphous ribbons were prepared by melt-spinning in a vacuum chamber with partial H$_2$ atmosphere. The amorphous nature of the precursor ribbon was checked by X-ray diffraction.
Mechanical milling was performed using a home built apparatus of similar design as the SPEX machine, operating at low frequency (160 rev./min) but high amplitude, permitting a 10 cm maximum travel length. Stainless steel vial and tungsten carbide balls sealed under argon were used. The mass ratio of ball to powder was 12:1. The structural evolution of the milled powder was followed by calorimetric, magnetic and Mössbauer measurements.

DSC measurements were carried out in a Perkin-Elmer DSC-2 differential scanning calorimeter with 20 K/min heating rate. The usual temperature and energy calibration procedures were applied. The room temperature $^{57}$Fe Mössbauer spectra were recorded by a standard constant acceleration spectrometer using 25 mCi $^{57}$Co in Rh matrix source. The measured spectra are fitted with the usual six-line patterns of Lorentzian line shape. The thermomagnetic measurements are made in a Faraday balance working in the 0-800 °C temperature and in the 0-1 T magnetic field range. The temperature calibration was checked by using the Curie points of nickel and iron standards.

**Results and discussion**

The milling process was performed until the melt-spun ribbon pieces was comminuted down to a maximum 100 μm powder size. This corresponds to about 100 h in the case of our milling equipment. The sieved powder with a particle size less than 100 μm was used for subsequent consolidation.

Fig. 1a and 1b present the thermomagnetic curves for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ and Fe$_{66}$Zr$_7$B$_6$Cu$_1$ alloys respectively in the as-quenched and ball milled state.

*Fig. 1: Magnetization versus temperature measured in a dc field of $H=400$ kA/m*
On the heating curves besides the Curie temperatures of the amorphous and the bcc phases also the crystallization can be clearly observed. For all samples the $T_c$ of the bcc phase is lower in the heating run than that of measured during the cooling. It shows that Nb or Zr captured in the supersaturated solid solution during the nanocrystal formation is rejected from the bcc phase in the fully crystalline state, as it is also established by a detailed thermomagnetic study [8]. For the Finemet alloy an increase of the $T_c$ of the amorphous phase is observed after the nanocrystallization. It is interpreted by Hernando et al. [9] via the exchange enhancement of the $T_c$ originating from the high Fe moment bcc Fe-Si grains. No $T_c$ is detected for the amorphous intergranular layer in Zr based alloys. It is partly due to the lower value of the $T_c$ and partly due to a different interfacial structure and thus modified coupling between the phases. The influence of these factors to the temperature dependence of the initial permeability was also discussed for unmilled ribbons [10].

For the ball milled Finemet alloy a third $T_c$ can also be observed on heating corresponding to the Fe$_2$B compound which is much more visible on both cooling curves. This compound precipitates only in the second stage of the DSC thermogram. This second stage of crystallization does not seem to be seriously influenced by the previous ball milling process.

For both milled alloys the sharp crystallization peak is preceded by a smeared uprise of magnetization which is not observed in the corresponding heating curve for the as quenched sample. A similar gradual heat evolution is also observed in the DSC measurements (Fig.2a and 2b). To test this process the Fe$_{86}$Zr$_7$B$_6$Cu$_4$ alloy milled for 107 h was heated in the DSC to 770 K (i.e., lower than that of the sharp crystallization). Mössbauer spectroscopy confirms that the bcc fraction is significantly increased in this process.

The fact, that a significant magnetization is observed for the milled samples even above the $T_c$ of the amorphous phase indicates that partial crystallization occurs in the milling process. The effect is more pronounced for Zr based alloy (where it amounts about 40 % of the total magnetization) than for Finemet alloy (where it is below 8%). The mechanical crystallization of Finemet was recently reported by Giri et al.[3] and the rapid mechanical crystallization of the Fe-Zr based amorphous alloys are also known [7,12]. The role of the metallic contaminations and the effect of the milling atmosphere in the ball milling process is still under intensive investigations [13]. The present results show that in contrast to the Finemet alloy which can be comminuted to the small grain size necessary for consolidation with only a small amount of bcc fraction, the Fe-Zr-B-Cu alloy is more susceptible to mechanical crystallization during the comminution process.

The accomplishment of partial crystallization during the ball milling is evidenced by DSC (Fig.2a and 2b) and Mössbauer (Fig.3a and 3b) measurements as well.

![Graphs showing DSC curves for Finemet (a) and Fe$_{86}$Zr$_7$B$_6$Cu$_4$ (b) alloys after different milling times](image_url)
The DSC curves of the Fe$_{86}$Zr$_7$B$_6$Cu$_1$ and FINEMET amorphous ribbons and of the milled powders are shown in Fig. 2a and 2b. Despite the complicated behavior observed for the Fe$_{86}$Zr$_7$B$_6$Cu$_1$ alloy the sharp crystallization peak of the untreated ribbon is evidently reduced. In contrast to this the FINEMET ribbon shows only a somewhat modified relaxation behavior and the crystallization is essentially unchanged in agreement with the small crystallized fraction detected by magnetic measurements.

![DSC curves of Fe$_{86}$Zr$_7$B$_6$Cu$_1$ and FINEMET](image)

**Fig. 3: Mössbauer spectra of the ball milled powders**

Fig. 3 shows the Mössbauer spectra of the milled Fe$_{86}$Zr$_7$B$_6$Cu$_1$ and FINEMET powders. It is in good agreement with the DSC results. While the spectrum of the FINEMET alloy shows hardly any changes in comparison with the unmilled ribbon, the spectrum of the Fe$_{86}$Zr$_7$B$_6$Cu$_1$ alloy is significantly changed. After milling for 107 hours 17 percent of the Fe atoms is found in crystalline environments.

To overcome the problem of the mechanical crystallization that is evidently more severe for the Fe$_{86}$Zr$_7$B$_6$Cu$_1$ alloy a different route was also attempted. This alloy was embrittled before milling at 450 °C for 20 minutes in protecting atmosphere. It makes possible to enhance the rate of comminution: in contrast to the 107 hours needed to achieve the 100 μm particle size for untreated alloys, 8 h grinding of the embrittled pieces yields an amorphous powder of the above particle size with a negligible crystalline content.

Consolidation experiments by cold pressing at room temperature have shown that a densification approaching 100% could not be obtained. The relative density was 70, 82 and 86 % for the applied pressure of 2, 3.5 and 4.5 GPa respectively. No further consolidation was possible by subsequent heat treatment at 430 °C for 1.5 h in 10$^{-2}$ Pa vacuum. A subsequent hot pressing however was effective: a relative density of 90 and 91.5 % could be obtained by applying for 15 minutes 0.9 GPa at 400 °C and 0.8 GPa at 500 °C respectively.

In Table 1 the results of magnetic measurements performed on small toroids prepared by spark erosion from the consolidated pellets are presented. The coercive force and the technical saturation at 800 A/m saturating field have been determined using a dc B-H hysteresis loop tracer. The initial permeability was measured at 1kHz and the amplitude of exciting field was 0.8 A/m.

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Table I: Magnetic properties of Fe$_{86}$Zr$_7$B$_6$Cu$_1$ cores produced by hot pressing the amorphous powder

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Structure</th>
<th>$H_c$ (A/m)</th>
<th>$\mu_i$</th>
<th>$B_s$(T) at $H_{max}=800$ A/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>ribbon as received</td>
<td>amorphous</td>
<td>26.4</td>
<td>2304</td>
<td>0.48</td>
</tr>
<tr>
<td>ribbon H.T.630/1h</td>
<td>nanocryst.</td>
<td>28</td>
<td>12000</td>
<td>1.56</td>
</tr>
<tr>
<td>as compacted 0.9 GPa/400 °C</td>
<td>amorphous</td>
<td>285</td>
<td>385</td>
<td>0.12</td>
</tr>
<tr>
<td>0.9 GPa/400 °C</td>
<td>nanocryst.</td>
<td>128</td>
<td>351</td>
<td>0.46</td>
</tr>
<tr>
<td>as compacted H.T. 630 °C/1h</td>
<td>amorphous</td>
<td>136</td>
<td>347</td>
<td>0.15</td>
</tr>
<tr>
<td>H.T. 630 °C/1h</td>
<td>nanocryst.</td>
<td>119</td>
<td>321</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The nanocrystallized ribbon achieved only moderate soft magnetic properties. It is mainly due to the reduced width (1 mm) of the ribbon used in this test. 10 mm wide nanocrystalline ribbons with the same composition have shown an initial permeability above 40000 and coercivity as low as 3 A/m. The soft magnetic characteristics of the consolidated cores are inferior to those obtained by Kawamura et al. [1] because of the lower densification (91.5 %) obtainable in our consolidation facilities (0.8 GPa at 500 °C, instead of 1.5 GPa at 575 °C used in [1]). At relatively low densities one has to consider a distributed gap between the particles. The effective permeability for such a compact can be expressed as

$$\mu_e = \frac{\mu_d}{d + 2\mu_d}$$

(1)

where $d$ is the particle size, $\mu$ is the permeability of the bulk ribbon and $\delta$ is the average gap between the particles [14]. This gap include both the porosity and the oxide surface layer.

For the less dense cold pressed samples good bulk magnetic properties are not expected as can be inferred from eq.(1). Instead, powder cores applicable at high frequencies was prepared. The initial permeability of the cold pressed and subsequently nanocrystallized sample was around 110-120 and the induction at $H=800$ A/m was about 0.02-0.03 T for both types of material, which are the typical values for a metallic powder core [15]. Such a core shows an almost frequency independent effective permeability up to 100 kHz. To push the frequency limit above 1 MHz the effective insulation of the particles must be improved. In the case of the Zr containing alloys the insulation layer can be formed by controlled oxidation, annealing the as received powder in air below the first crystallization peak. It is expected that improving the particle insulation and compaction a nanoscale structure controlled bulk core material can be developed based on the high permeability, high resistivity and low power loss properties of the nanocrystalline materials.

Conclusions

The Fe$_{86}$Zr$_7$B$_6$Cu$_1$ amorphous alloy shows a much higher affinity towards mechanical crystallization than the Fe$_{73.5}$Cu$_{16}$Nb$_{5}$Si$_{13.5}$B$_{9}$ alloy. Hot consolidation at 500 °C and 0.8 GPa is not suitable to achieve the densification necessary for bulk soft magnetic properties. However the powders of both alloys are promising materials for manufacturing insulator coated powder cores for high frequency applications.

Acknowledgments

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