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The influence of M = Mo, Nb in $Fe_{80}(B,M,Cu)_{20}$-type alloys on the crystallization behaviour and on the magnetic properties

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Abstract

In amorphous $Fe_{80}(B,Mo,Cu)_{20}$-type alloys the crystallization behaviour and the magnetic properties, Curie temperature T_C, coercivity H_C, saturation polarization J_S, and magnetostriction λ_S in the as-quenched state and annealed in vacuum for 1 h were investigated in dependence on the Mo content (5–7–9 at.%) with and without 1 at.% Cu and at a constant B content of 12 at.%. With increasing Mo content, T_{X1} and T_{X2} are increasing. Addition of 1 at.% Cu decreases T_{X1} and increases T_{X2}. After optimal annealing of the alloys with 7 and 9 at.% Mo and 1 at.% Cu low coercivity $H_C \approx 20$ A/m is established. Nearly one magnitude smaller H_C values are observed at the alloy $Fe_{80}B_{12}Mo_3Nb_4Cu_1$, $H_C = 3$ A/m. Decreasing magnetostriction λ_S and nanocrystal grain size with increasing Mo content are lowering the coercivity. The partial substitution of Mo by Nb reduces significantly the grain size and consequently H_C. The decreasing Curie temperature with increasing Mo content of the alloys in the as-quenched state affects their magnetic properties.

Keywords: Rapidly quenched and nanocrystalline alloys; Crystallization behaviour; Structure; Grain size; Magnetic properties

1. Introduction

In nanocrystalline soft magnetic FeSiBCuNb-type alloys, the development of Fe_3Si nuclei is enhanced by Cu and the growth of it is hindered by Nb. In [1] it is shown how the nanocrystal grain size depends on the atomic diameter due to the addition of elements like V, Mo, W, Ta, Nb: with increasing atomic diameter of these elements the grain size is reduced. According to [2] 6 at.% Nb affects grain sizes of about 10 nm in FeBNb-base alloys.

The aim of this paper is to investigate the influence of Mo (5–7–9 at.%) and 1 at.% Cu in Fe_{80}(B, M, Cu)$_{20}$-type alloys and the partial substitution of Mo by Nb in the combination of Mo_3 and Nb_4 on the crystallization behaviour, structure and magnetic properties. The B content was kept constant at 12 at.%.

2. Experimental

Amorphous ribbons (width 10 mm, thickness about 25 μm) were produced by single roller melt spinning technique. For H_C measurement pieces of these ribbons were annealed for 1 h at different temperatures T_a under vacuum. As the Cu-free alloys have a very small difference between the crystallization temperatures T_{X1} and T_{X2}, all samples for structure characterization and measurements of the magnetic properties magnetostriction λ and saturation polarization J_S were annealed at the onset temperature of T_{X1} for 1 h.

The chemical composition of the investigated alloys in atomic percent is

$Fe_{83}B_{12}Mo_5$	$Fe_{82}B_{12}Mo_5Cu_1$
$Fe_{81}B_{12}Mo_7$	$Fe_{80}B_{12}Mo_7Cu_1$
$Fe_{79}B_{12}Mo_9$	$Fe_{78}B_{12}Mo_9Cu_1$
$Fe_{81}B_{12}Mo_3Nb_4$	$Fe_{80}B_{12}Mo_3Nb_4Cu_1$

DSC measurements and Curie temperature determinations were performed by a Netzsch DSC 404 and by a magnetic balance, respectively, with $v = 20\,\mathrm{K\,min^{-1}}$. X-ray diffraction (Philips PW 1820) was used for phase and structure analysis. The magnetic properties were measured at room temperature by a Förster Koerzimat (coercivity H_C) by the small angle rotation method after Narita (magnetostriction λ, measured at $H = 150$ A/cm) and by a magnetometer (saturation polarization J_S).

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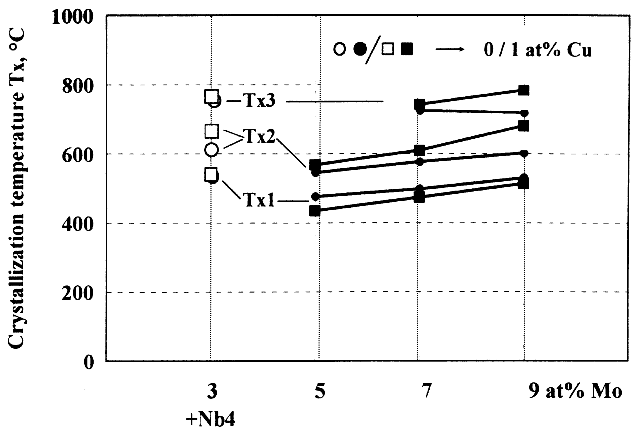

Fig. 1. Crystallization temperatures T_X in dependence on the composition of the alloys: $Fe_{rest}Mo_{(5–7–9)}B_{12}Cu_{(0–1)}$ and $Fe_{rest}Mo_3Nb_4B_{12}Cu_{(0–1)}$.

3. Results and discussion

3.1. Structure

A two- and three-steps crystallization is observed. Fig. 1 summarizes the crystallization steps in dependence on the composition. At the first one α-Fe crystallizes at T_{X1} surrounded with an amorphous residual phase. At T_{X2} the boride phases Fe_3B and Mo_2B appear. Above T_{X3} further unknown phases appear.

With increasing Mo content T_{X1} and T_{X2} are increased; whereas 1 at.% Cu decreases T_{X1} and increases T_{X2} and thus broadens the annealing field for the formation of nanocrystalline α-Fe and amorphous residual phase enabling optimal soft magnetic properties by the variation of the volume parts. The same behaviour is observed for Mo_3Nb_4-containing alloys; in this connection Nb is more effective than Mo because of its larger atomic diameter. Concerning the crystal structure and the grain size after annealing at the onset temperature of T_{X1} (1 h), Table 1 gives information.

It is to state that in all alloys primary crystallization of α-Fe occurs, except in the alloy $Fe_{81}B_{12}Mo_9$. Here simultaneous formation of α-Fe, Fe_3B and Mo_2B is observed. The Cu-free alloys are very critical of their annealing temperature because of their narrow existence area for α-Fe and the amorphous residual phase. The grain size of α-Fe with increasing Mo content is reduced. Because of the larger atomic diameter of Nb the substitution of Mo by Nb leads to very small grain sizes of about 5 nm. The influence of Cu results altogether in a smaller grain size as a consequence of its enhancing the number of α-Fe nuclei.

Table 1
Structure and grain size in dependence on the composition after annealing at the onset temperature T_a of T_{X1} (1 h, vacuum)

Alloy composition (at.%)	T_a (°C)	Structure	Grain size (nm)
$Fe_{83}B_{12}Mo_5$	450	α-Fe + am.[a]	≈100
$Fe_{81}B_{12}Mo_7$	475	α-Fe + am.	20
$Fe_{79}B_{12}Mo_9$	500	α-Fe + am. + Fe_3B + Mo_2B	≈100
$Fe_{81}B_{12}Mo_3Nb_4$	500	α-Fe + am.	10
$Fe_{82}B_{12}Mo_5Cu_1$	425	α-Fe + am.	15
$Fe_{80}B_{12}Mo_7Cu_1$	450	α-Fe + am.	13
$Fe_{78}B_{12}Mo_9Cu_1$	475	α-Fe + am.	8
$Fe_{80}B_{12}Mo_3Nb_4Cu_1$	500	α-Fe + am.	5

[a] Amorphous residual phase.

3.2. Magnetic properties

3.2.1. Curie temperature T_C

The magnetic properties of the amorphous state of the investigated alloys are significantly influenced by low Curie temperatures T_C (Fig. 2). The Cu-free alloys show lower values than the Cu-containing alloys. The Cu-free Mo_9 alloy has a Curie temperature at about room temperature. The

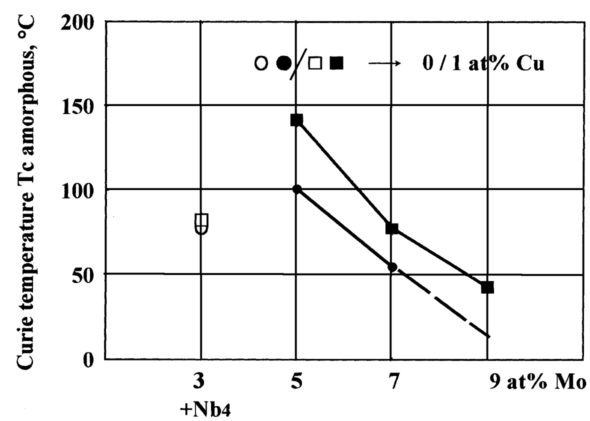

Fig. 2. Curie temperature T_C of the amorphous state in dependence on the composition of $Fe_{rest}Mo_{(5–7–9)}B_{12}Cu_{(0–1)}$ and $Fe_{rest}Mo_3Nb_4B_{12}Cu_{(0–1)}$ alloys.

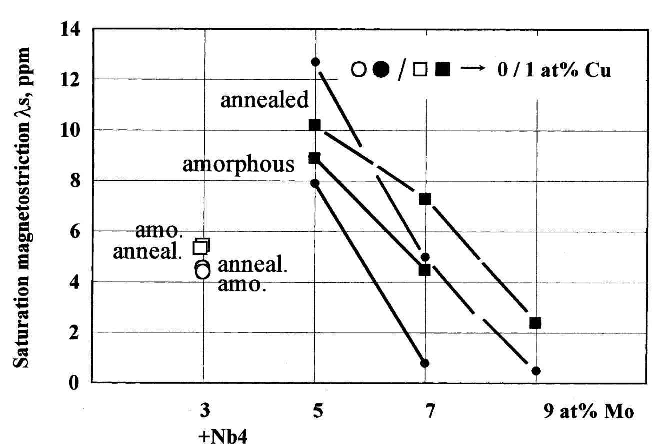

Fig. 3. Saturation magnetostriction λ_S in dependence on the composition of the alloys: $Fe_{rest}Mo_{(5–7–9)}B_{12}Cu_{(0–1)}$ and $Fe_{rest}Mo_3Nb_4B_{12}Cu_{(0–1)}$ in the amorphous state and after annealing at the onset temperature T_a of T_{X1}.

Curie temperature of the Nb substituted alloys is about 80°C with minor influence of Cu.

3.2.2. Saturation magnetostriction λ_S

The saturation magnetostriction λ_S in dependence on the Mo content (Fig. 3) of the alloys in the amorphous state decreases for compositions with and without Cu content, whereas the Cu-free alloys show smaller values. Because of its low Curie temperature near room temperature, the Mo_9-containing alloys give no signal. The annealing at the onset temperature of T_{X1} (1 h) in principle increases the magnetostriction. The Cu-free alloys again show a smaller magnetostriction. The Mo_5 alloy behaviour is inverse owing to the annealing temperature sensitivity of the Cu-free alloy. The Mo_3Nb_4 alloys show an analogous λ behaviour in the amorphous and annealed state at a level of about 5×10^{-6}.

3.2.3. Saturation polarization J_S

The saturation polarization J_S in the amorphous state shows the same trend in dependence on the Mo content like the Curie temperature dependency (Fig. 4). It ranges between 1.15 T and about zero for the Mo_9-containing alloy ($T_C \approx$ room temperature). The Cu-free alloys show a smaller saturation polarization.

After annealing, the saturation polarization absolutely increases but decreases with growing Mo content, whereas the Cu-free alloys again have smaller values. The saturation polarization is determined by the structure and the volume part of the α-Fe phase. As Cu enhances the α-Fe nuclei development, a larger α-Fe volume part is effective for the saturation polarization, nevertheless the onset temperature for T_{X1} of Cu-containing alloys is lower. The drop of J_S for the alloy Mo_9 without Cu is attributed to the additional crystallization of Fe_3B and Mo_2B phases.

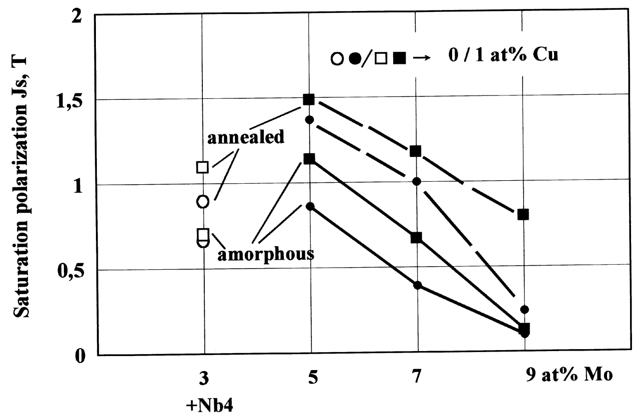

Fig. 4. Saturation polarization J_S in dependence on the composition of the alloys: $Fe_{rest}Mo_{(5-7-9)}B_{12}Cu_{(0-1)}$ and $Fe_{rest}Mo_3Nb_4B_{12}Cu_{(0-1)}$ in the amorphous state and after annealing at the onset temperature of T_{X1}.

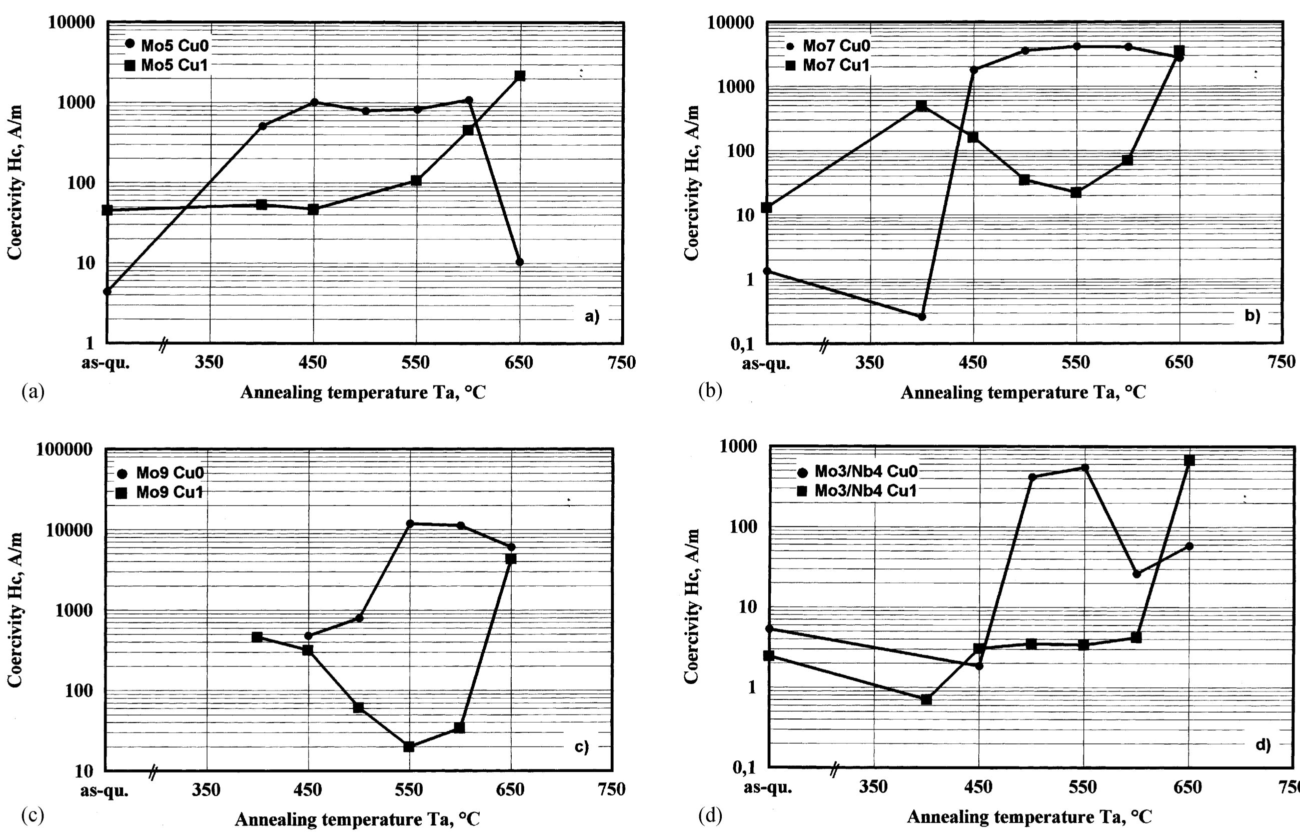

Fig. 5. (a–d) Coercivity H_C in dependence on the annealing temperature T_a (1 h, vacuum) of the alloys: $Fe_{rest}Mo_{(5-7-9)}B_{12}Cu_{(0-1)}$ and $Fe_{rest}Mo_3Nb_4B_{12}Cu_{(0-1)}$.

The $Mo_3Nb_4Cu_1$ alloy after annealing gives 1.1 T in saturation polarization. Note that this behaviour is valid for annealing at onset temperature of T_{X1} (1 h).

3.2.4. Coercivity H_C

The coercivity in dependence on different annealing temperatures T_a (1 h) and on the Mo content (Fig. 5a–d) responds very sensitively to the developing phase components, to the grain size of the α-Fe nanocrystals and to the magnetostriction. Considering the lowest coercivity after annealing with increasing Mo content for Cu-containing alloys, H_C is decreasing because of the lowering of their grain size and their magnetostriction with increasing Mo content. But with the Cu-free alloys an increasing behaviour is observed owing to the earlier occurrence of boride phases in these alloys. The smallest coercivity is obtained for the $Mo_3Nb_4Cu_1$ alloy. The very small grain size of 5 nm and the low magnetostriction are the causes for this behaviour.

4. Conclusions

A partial substitution of B and Fe, respectively, by 7 up to 9 at.% Mo in combination with 1 at.% Cu distinctly improves the soft magnetic behaviour of $Fe_{80}B_{20}$-type alloys. The reasons are lower magnetostriction and very small nanocrystal grain size. The best soft magnetic properties are obtained when Mo is partially replaced by Nb. At the annealing temperature for lowest coercivity ($T_a = 550°C$ per hour), a $Fe_{81}B_{12}Mo_3Nb_4Cu_1$ alloy shows at α-Fe grain size of 5 nm a saturation magnetostriction $\lambda_S = 5 \times 10^{-6}$, a saturation polarisation $J_S = 1.22$ T and a coercivity $H_C = 3$ A/m.

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