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Structure evolution and changes in magnetic properties of severe plastic deformed Nd(Pr)–Fe–B alloys during annealing

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Abstract

Structural changes and hysteresis properties of Nd(Pr)–Fe–B alloys of various compositions were studied after severe torsion straining under high pressure and following annealing. It was shown that in all the alloys studied, severe plastic deformation leads to formation of ultrafine-grained non-equilibrium structure and, at extremely large strains, even to formation of an amorphous structure. Annealing resulted in crystallization of alloys, formation of stable magnetic and non-magnetic phases and in marked improvements in hard magnetic properties. Homogenization of alloys is responsible for an increase in coercivity of the deformed samples.

1. Introduction

In recent years materials with ultrafine-grained (UFG) structures have attracted much interest among researchers. These materials are characterized by unusual physical and mechanical properties as compared to their coarse-grained counterparts. One can fabricate materials with high hard magnetic properties via formation of UFG structure. As a rule, traditional methods of processing of an IJFG structures [1,2] usually relate to powders and ribbons and require a subsequent additional step — consolidation. An advanced method of processing an UFG structure in a monolithic sample is severe plastic deformation (SPD) [3].

In the works [4–6], influence of SPD and annealing on the structure and magnetic properties of R–Fe–B (R is rare earth) alloys was studied. The present work continues this investigation.

2. Experimental method and materials

The chemical and phase constitution as well as the structural and magnetic characteristics of the non-homogenized alloys of sub-stoichiometric composition $Nd_9Fe_{84}B_7$ and super-stoichiometric composition $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ are given in Table 1. In addition, the alloy $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ was examined in a homogenized state. The SPD method is described in detail in [3] and involves conducting torsion straining under high pressure on Bridgnan anvils. The produced samples were 5 mm in diameter and 0.15 mm in thickness. The degree of strain was varied by changing the angle of rotation φ. Annealing of samples was conducted in vacuum. Structural studies were made by X-ray diffraction and transmission electron microscopy analyses. The magnetic hysteresis characteristics were measured in the plane of the disc sample using a vibromagnetometer. The specific magnetization σ_m was measured in a magnetic field of 1300 kA m^{-1}. Prior to measurements of hysteresis characteristics each sample was subjected to magnetization in an impulse field of 5600 kA m^{-1}.

3. Results and discussion

The TEM studies of alloy 1 in the deformed state showed that severe plastic deformation at $\varphi=5\ \pi$ led to formation of a granular type structure with a mean grain size of about 0.3 μm and a high density of dislocations exceeding 10^{10} cm^{-2}. According to the X-ray diffraction data alloy 1 deformed at $\varphi=5\ \pi$ contains $Pr_2Fe_{14}B$, α-Fe and Pr-rich phases. The diffraction peaks for the main phase $Pr_2Fe_{14}B$ of the deformed samples are significantly broadened. This broadening testifies to the formation of an UFG structure, an increase of defect concentrations and to increased internal stresses due to severe plastic deformation. The X-ray examination of samples of alloy 1 de-

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Table 1
Phase composition and magnetic properties of studied alloys in the initial state

	Alloy	State	Phase Composition			Magnetic properties		
			$R_2Fe_{14}B$ vol. %	R-rich vol. %	α-Fe vol. %	*jHc* kA m^{-1}	σ_r Am^2 kg^{-1}	σ_m Am^2 kg^{-1}
1	$Pr_{20}Fe_{73.5}B_5Cu_{1.5}$	Cast	65	28	7	40	17	90
2	$Pr_{20}Fe_{73.5}B_5Cu_{1.5}$	Cast+ 1000°C–10h	75	25	no	344	63	79
3	$Nd_9Fe_{84}B_7$	Cast	80	no	20	8	5	131

formed at a higher strains ($\varphi > 10\ \pi$) shows the presence of an amorphous phase distributed within the whole sample volume. However along with the amorphous phase α-Fe phase is also present in strongly deformed alloy 1.

The structural changes on SPD of homogenized alloy 2 are similar to those described above. The X-ray diffraction pattern testifies that the main $Pr_2Fe_{14}B$ phase and the R-rich phase become amorphous due to SPD. Distinct diffraction peaks of the α-Fe phase are not present on an X-ray pattern of alloy 2 deformed at $\varphi = 16\ \pi$. The X-ray structural analysis of alloy 3 after SPD at $\varphi = 16\ \pi$ shows the presence of crystalline peaks of the α-Fe phase only. The absence of crystalline peaks for the $Nd_2Fe_{14}B$ phase also testifies that it has become amorphised.

In Tables 2–4 the *jHc*, σ_m, σ_r data for alloys 1, 2, 3, deformed at various φ and subjected to subsequent annealing are presented.

As shown in the Tables, the dependencies of *jHc* and σ_r on degree of strain have a common tendency in all alloys. Up to a specific degree of SPD (approximately $\varphi = 5\ \pi$) *jHc* increases, but with further increase in strain, *jHc* drops. The initial increase of *jHc* is explained by structural refinement. The subsequent decrease of *jHc* is caused by amorphisation of the alloys and by an increase of defects density. Some primary increase in *jHc* due to SPD is observed even in homogenized alloy 2 which, in the initial state, has a high value of *jHc*. Evidently, in alloy 2 it is structural refinement that mainly influences *jHc* in the

Table 2
Magnetic properties of samples produced from cast alloy 1

φ, π	SPD			SPD+600°C–0.3 h		
	jHc kA m^{-1}	σ_m Am^2 kg^{-1}	σ_r Am^2 kg^{-1}	*jHc* kA m^{-1}	σ_m Am^2 kg^{-1}	σ_r Am^2 kg^{-1}
0	40	90	17	137	–	31
2	384	83,5	48	1554	76,5	60
5	268	85	51,5	1680	74	58
10	160	91	50	1680	78	61
16	72	86	40	1680	82	64

Table 3
Magnetic properties of samples produced from homogenized alloy 2

φ, π	SPD			SPD+600°C–0.3 h		
	jHc kA m^{-1}	σ_m Am^2 kg^{-1}	σ_r Am^2 kg^{-1}	*jHc* kA m^{-1}	σ_m Am^2 kg^{-1}	σ_r Am^2 kg^{-1}
0	344	79	58	–	–	–
2	510	80	56	1360	80	64
5	558	81	60	2000	82	68,5
10	296	82	51	2240	86,5	72,5
16	230	86	50	2240	88	72.5

Table 4
Magnetic properties of samples produced from cast alloy 3

φ, π	SPD		SPD+600°C–0.3 h		
	jHc kA m^{-1}	σ_m Am^2 kg^{-1}	*jHc* kA m^{-1}	σ_m Am^2 kg^{-1}	σ_r Am^2 kg^{-1}
0	8	131	–	–	–
2	58	140,5	89	141	70
5	40	142,5	130	142	73
10	30	139,5	151	148	89
16	27	139	140	141	79

primary stage of SPD and this influence is more significant than accumulation of defects within the grains of the main phase.

Annealing of alloy 1 at $T=6000$°C leads to a structural recovery and a decrease in dislocation density. The TEM studies of samples with $\varphi=5\ \pi$ showed that the mean grain size of the main phase remains almost the same as in the deformed state. A number of fine circular grains, less than 0.1 μm in diameter, appear on the boundaries of coarse grains. According to the X-ray diffraction data the annealed sample contains only two phases: Pr-rich and $Pr_2Fe_{14}B$ phases. The diffraction peaks are not substantially broadening. During the anneal amorphous soft magnetic phase disappear. Evidently, the α-Fe phase partially reacts with the excess Pr and transforms to the $Pr_2Fe_{14}B$ phase. However, according to thermomagnetic data [5] small fraction of α-Fe phase remains even in annealed samples of alloy 1.

Changes in the phase composition and microstructure led to a sharp increase in the *jHc* values for the annealed samples. The maximum levels of coercivity for the chosen processing regimes were as follows: for alloy 1 - 1674 kA m^{-1}, for alloy 2 - 2233 kA m^{-1}, for alloy 3 - 151 kA m^{-1}. With increasing p from 0 to 10 π a distinct increase in *jHc* is observed in all annealed alloys. Further increases in φ have little influence on *jHc* and σ_r, of the annealed samples. This indicates the formation of UIFG structures at $\varphi=10\ \pi$.

Comparing the data for cast and homogenized $Pr_{20}Fe_{7.35}B_5Cu_{1.5}$ alloys, one can note that *jHc* and σ_r for the deformed and annealed alloy 2 are higher than the corresponding values for samples of alloy 1. These higher values for alloy 2, as compared to alloy 1, can be explained by the absence of the α-Fe phase in the alloy 2 in the initial and the deformed states.

In the case of uniaxial ferromagnetic material, having a random grain orientation, σ_r must be equal to $\sigma_s/2$. The predicted value of σ_r should be about 64 Am^2 kg^{-1} for the isotropic $Pr_{20}Fe_{7.35}B_5Cu_{1.5}$ alloy, containing no less than 25% of the non-magnetic Pr-rich phase. However, σ_r for the deformed and annealed alloy 2 is 72.5 Am^2 kg^{-1}. This indicates that an anisotropic state is formed within the sample plane. The increase of σ_r in annealed samples of alloys 1 and 2 is explained by an increasing degree of magnetic anisotropy with increasing SPD. The X-ray structural studies also indicate the appearance of crystallographic texture which is a cause of magnetic anisotropy.

A large fraction of excess Fe in alloy 3 reduces its coercivity in the UFG state processed by SPD. The value of σ_r achieved, 89 Am^2 kg^{-1}, is also higher than that calculated for the isotropic state of the main phase of the given alloy (70 Am^2 kg^{-1}). An elevated level of σ_r can be explained by the occurrence of crystallographic texture and by intergrain exchange interaction resulting from the formation of an UFG structure. In rapidly quenched nanocrystalline alloys of similar compositions, the latter effect is also observed [6].

4. Conclusion

1. In the R–Fe–B alloys of various composition a non-equilibrium UFG structure is formed due to SPD. At high strains of SPD the alloys become largely amorphous, and the X-ray diffraction analysis shows the presence of the α-Fe crystalline phase only.
2. Annealing of the deformed alloys leads to crystallization of the main phase $R_2Fe_{14}B$ with a UFG structure. This results in a marked improvement of magnetic properties. The coercivity for samples of homogenized alloy $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ subjected to SPD with subsequent annealing achieves a value as big as 2232 kA m^{-1}.
3. Enhanced values σ_r of the deformed and annealed alloys testifies to the appearance of magnetic anisotropy within the sample plane that rises with increasing degree of strain. High value of σ_r (0.89 Am^2 kg^{-1}) in the substoichiometric alloy $Nd_9Fe_{84}B_7$ after deformation and annealing can be attributed to the intergrain exchange interaction.

References

[1] J.J. Becker, J. Appl. Phys. 55(6) (1984) 2067–2072.
[2] P.A.I. Smith, P.G. McCormick, K. Street, Mater. Sci. Forum 179–181 (1995) 527–532.
[3] R.Z. Valiev, A.V. Korznikov, R.R. Mulyukov, Mater. Sci. Eng. A168 (1993) 141.
[4] A.G. Popov, D.V. Gunderov, V.V. Stolyarov, JMMM 156–157 (1996) 33–34.
[5] V.V. Stolyarov, A.G. Popov, D.V. Gynderov, V.S. Gaviko, G.F. Korznikova, A.S. Ermolenko, R.Z. Valiev, Phys. Met. Metallogr. 83(2) (1997) 173–179.
[6] A. Manaf, R.A. Buckley, H.A. Davies, JMMM 128 (1993) 302–306.