Effect of Al and Cu Additions on Microstructure and Magnetic Properties of NdTb–FeCo–B Magnets

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With the addition of Al and/or Cu into the NdFeB based magnet, the soft free iron phase was not observed in the cast alloys while it exists in the microstructure of the undoped NdFeB ingots. For the undoped sample, free iron disappeared after hot deformation process. Grain orientation is not good and there are deviations in the growth direction of the lamellar grains which are not perpendicular to the pressing direction. On the other hand, there is a striking change that the intergranular chemistry of Al added ingot separated into Nd-rich phase and a ternary FeNdAl composition most probably formed at the pressing temperature of 750 °C. The highest remanent magnetization of 7.47 kG obtained for this sample, it might be due to the hard magnetic properties of this ternary composition. For the Al–Cu added sample, the high H_c and B_r values of 7.71 kOe and 7.33 kG, respectively, can be attributed to the homogeneous distribution of the intergranular composition and good orientation of the magnetic grains by hot deformation process.

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1. Introduction

Hot deformation technique is used to obtain anisotropic RE–Fe–B (RE = rare earth) magnets from cast ingots or hot pressed powder samples. The grain alignment is achieved by the presence of Nd-rich intergranular phase which is liquid at deformation temperature. The main advantage of this process is to produce anisotropic magnets from cast ingots with the elimination of the handling of magnetic powders which can be easily oxidized in the production route [1–3]. It was found that low melting additives such as Al, Cu, Ga, or Zn were found effective in increasing coercivity due to the better wetting behavour and seperation of magnetic $Nd_2Fe_{14}B$ grains in hot deformed or sintered RE–Fe–B magnets [4–10].

However, the addition of the high melting Zr addition inhibited the grain rotation during hot deformation process resulted in poor texture and a decrease in Br value [11]. In Ga, Al, and Cu doped magnets different intergranular phases were detected such as NdCu, NdGa, $Al_3Fe_{11}Nd$ or FeNdAl [12, 13].

The composition of intergranular region is crucial to obtain magnets which have good oriented grains resulting in improved magnetic properties. Therefore, we purposed to investigate the effects of Al and Cu additions on chemistry of the intergranular composition and magnetic properties of the hot deformed NdFeB magnets in this study.

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2. Experimental

The alloy compositions with $Nd_{18}Tb_1Fe_{68}Co_5B_8$, $Nd_{18}Tb_1Fe_{66.5}Co_5B_8Cu_{1.5}$, $Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$ and $Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{0.75}Cu_{0.75}$ were prepared by induction melting in a quartz tube under vacuum about 10^{-3} mbar and solidified in water to achieve fine microstructure. Hot deformed magnets were produced by hot-pressing of the as-cast ingots in an open die at 750 °C under high purity argon atmosphere. The pressure during the hot pressing was 2.55 ton/cm^2. Hot pressed samples were heat treated at between 560–580 °C for 1 h. Scanning electron microscope (SEM) equiped by an energy dispersive spectrometer (EDS) was utilized to investigate microstructure of the specimens. $2 \times 2 \times 2$ mm^3 specimens were cut from the hot pressed magnets. Magnetic measurements of the cubic samples were performed under a maximum magnetizing field of 20 kOe with a vibrating sample magnetometer (VSM).

3. Results and discussions

Figure 1 displays the microstructures of the three samples before hot deformation process. In Fig. 1a the region *c* corresponds to free iron in the microstructure of the as cast $Nd_{18}Tb_1Fe_{68}Co_5B_8$ alloy in addition to hard magnetic $Nd_2Fe_{14}B$ and Nd-rich phases indicated as region *a* and *b*, respectively. On the other hand, Fig. 1b and c shows that free iron phase was not observed in microstructures of the Al or Cu added cast ingots analysed by EDS system (neglecting the B-content which could not be detected with the EDS system).This surprising change can be attributed that Al or Cu additions enhanced the peritectic formation of the magnetic $Nd_2Fe_{14}B$ phase. In the Al or Cu doped ingots the magnetic $Nd_2Fe_{14}B$ grains are good-separated by Nd-rich phase.

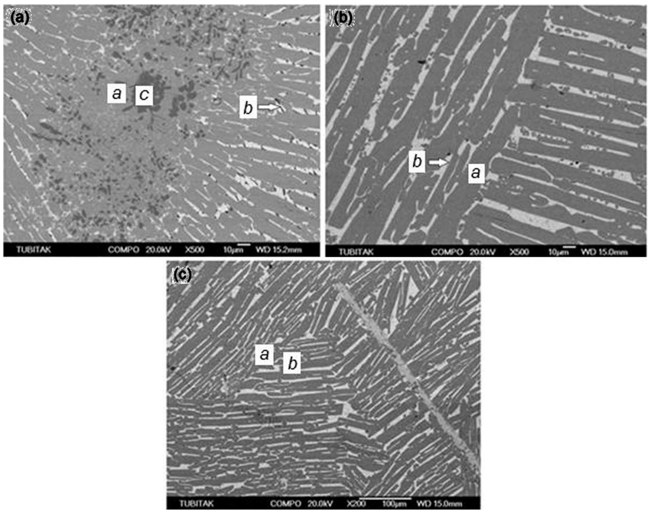

Fig. 1. SEM micrographs of the cast ingots of undoped (a), Al added, (b) and Cu substituted (c) samples. *a*: $Nd_2Fe_{14}B$ magnetic phase, *b*: Nd-rich phase and *c*: Fe.

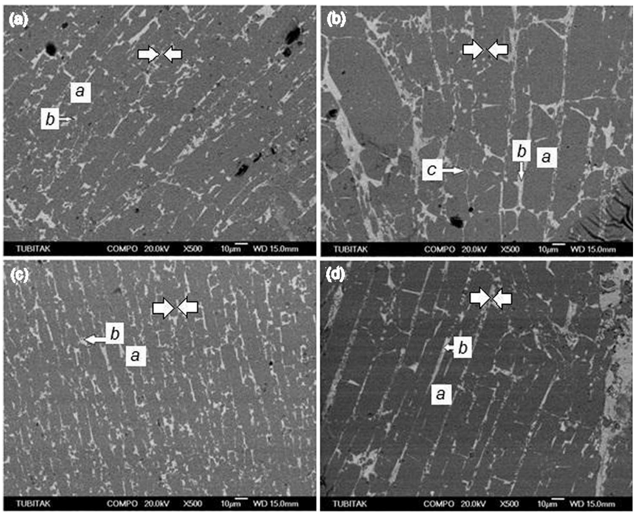

Fig. 2. SEM micrographs of the undoped (a), Al added (b), Al–Cu added (c), and Cu substituted (d) samples hot deformed at 750 °C. All samples are annealed at temperatures between 550–600 °C for 1 h after hot pressing. *a*: $Nd_2Fe_{14}B$ magnetic phase, *b*: Nd-rich phase and *c*: FeNdAl composition. Arrows show pressing directions.

For the Al added ingot, the composition is given by EDS as Nd_3(Fe,Co,Al) in the region *b* (Table I). A small amount of Al took place in the structure of the magnetic phase most probably due to its small ionic radius while Cu remained in the intergranular composition. For the Cu doped ingot intergranular Nd rich composition is given as Nd_3(Co,Cu), all of the iron content remained in the hard magnetic phase. Melting temperature of Nd-rich intergranular phase decreased when Co substituted iron in the composition. Fe–Nd and Co–Nd eutectic temperatures are about 685 °C and 566 °C, respectively [14, 15]. In Fig. 2a EDS analysis showed that the free iron existing in the undoped ingot (Fig. 1a) disappeared by the hot deformation process. The removal of free iron surrounded by the $Nd_2Fe_{14}B$ grains after pressing at 750 °C can be explained by the heavily cracking of the magnetic matrix grains and penetration of the Nd-rich liquid phase into the grains through the cracks to make direct contact with the free iron. The peritectic reaction between the free iron and Nd-rich phase at 750 °C resulted in the formation of $Nd_2Fe_{14}B$ phase [16]. For the undoped cast ingot, in the intergranular region *b* Nd:TM (transition metal) ratio is about 4, after hot deformation process it decreased to 2.06 because Nd was consumed to form tetragonal $Nd_2Fe_{14}B$ structure. The soft ferromagnetic iron is surrounded by magnetic $Nd_2Fe_{14}B$ grains in contact with each other mostly in those regions. Under this circumstance, the larger hard magnetic $Nd_2Fe_{14}B$ grains are expected to be broken rather than the rotation of that during hot deformation process.

For the cast Al added ingot region *b* is $Nd_{2.6}$(Fe,Co,Al), after hot deforming this phase separated into Nd-rich $Nd_{2.7}$(Fe,Co) and ternary Nd(Fe,Co)$_{1.3}$Al$_{0.1}$ phases. The forming ternary FeNdAl composition has a higher melting temperature after the pressing process (Table II). This high melting Nd-poor composition inhibits the rotation of the magnetic grains in the liquid phase as a result, it prevents preferential alignment of the grains.

In Fig. 2a and b the black spots correspond to pores in the microstructure of the samples. The pores deteriorate magnetic properties of the material because they create self-demagnetization fields which are opposite to the magnetization direction in the magnetic material, therefore, coercivity and remanent magnetization values decreased [17].

In Table II EDS results show that ferromagnetic transition metal (Fe and Co) content decreased by about 1.38% in tetragonal $Nd_2Fe_{14}B$ structure by the addition of a small amount of nonmagnetic Al. For the Al doped ingot, the significant amount of iron in the Nd-rich phase was consumed to form NdFeAl composition during hot deformation process. The region *c* has a Nd poor composition reported that in Al added NdFeB magnets hard ferromagnetic μ phase was observed at the $Nd_2Fe_{14}B$ grain boundaries. μ phase ($Nd_{33}Fe_{67-x}Al_x$, $2.5 < x < 5$) forms by peritectic reactions at 750 °C and has a large anisotropy field ($\mu_0 H_A > 8$ T) [13, 18]. This magnetic phase most probably formed at the pressing temperature of 750 °C, this composition was idendified in EDS analysis and detected in the DTA analysis after pressing at 800 °C in a report [19].

Al–Cu added sample has the oriented grains in the microstructure (Fig. 2c) and intergranular region has the homogeneously distributed Nd-rich composition. Nd-rich phase consists of mainly iron with small amounts of Al, Co, and Cu. This sample has the highest density among other samples resulting in good magnetic properties (Table III).

TABLE I

Atomic compositions (at.%) determined by EDS in the various phases of the ingots.

Sample	Region	Fe	Nd	Tb	Co	Al	Cu	O	Chemical composition
		[at.%]							
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	*a*	82.05	11.69	1.29	4.98	–	–	–	$(Nd,Tb)_{2.1}(Fe,Co)_{13.9}$
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	*b*	13.52	75.23	–	5.48	–	–	8 5.77	Nd-(Fe,Co)
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	*c*	100	–	-	–	–	–	–	Fe
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$	*a*	80.24	11.21	2.39	5.01	1.16	–	–	$(NdTb)_{2.2}(Fe,Co,Al)_{13.8}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$	*b*	4.66	66.94	–	17.61	3.68	–	7.11	$Nd_{2.6}(Fe,Co,Al)$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Cu_{1.5}$	*a*	82.2	10.85	2.3	4.64	–	–	–	$(NdTb)_{2.1}(Fe,Co)_{13.9}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Cu_{1.5}$	*b*	–	70.27	–	15.81	–	7.1	6.82	$Nd_3(Co,Cu)$

TABLE II

Atomic compositions (at.%) determined by EDS in the various phases of the hot deformed samples.

Sample	Region	Fe	Nd	Tb	Co	Al	Cu	O	Chemical composition
		[at.%]							
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	*a*	82.49	10.71	2.49	4.31	–	–	–	$(NdTb)_{2.1}(Fe,Co)_{13.9}$
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	*b*	11.78	61.86	–	18.25	–	–	8.1	Nd-(Fe,Co)
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$	*a*	86.12	10.67	1.74	–	1.48	–	–	$(NdTb)_2(Fe,Al)_{14}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$	*b*	7.43	68.74	–	17.97	–	–	5.86	$Nd_{2.7}(Fe,Co)$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{1.5}$	*c*	45.38	39.72		5.24	3.98	–	5.68	$Nd(Fe,Co)_{1.3}Al_{0.1}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{0.75}Cu_{0.75}$	*a*	80.74	10.77	2.42	5.00	1.06	–	–	$(NdTb)_{2.1}(Fe,Co)_{13.9}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Al_{0.75}Cu_{0.75}$	*b*	20.35	62.69	–	3.81	3.67	9.48	–	Nd-(Fe,Co,Al,Cu)
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Cu_{1.5}$	*a*	83.27	10.88	1.73	4.39	–	–	–	$(NdTb)_2(Fe,Co)_{14}$
$Nd_{18}Tb_1Fe_{66.5}Co_5B_8Cu_{1.5}$	*b*	–	70.22		18.67	–	5.62	5.48	$Nd_{2.9}(Co,Cu)$

TABLE III

Density, height reduction ratio and magnetic properties of the samples after hot deformation process.

Sample	D [g/cm^3]	H_C [kOe]	B_r [kG]	$(BH)_{max}$ [MG Oe]	Height reduction ratio
$Nd_{18}Tb_1Fe_{68}Co_5B_8$	6.77	5.18	6.29	8.80	85
$Nd_{18}Tb_1Fe_{66.5}Co_5Al_{1.5}B_8$	6.98	5.94	7.47	13.07	76
$Nd_{18}Tb_1Fe_{66.5}Co_5Al_{0.75}Cu_{0.75}B_8$	7.32	7.31	7.33	14.88	82
$Nd_{18}Tb_1Fe_{66.5}Co_5Cu_{1.5}B_8$	7.25	5.89	6.32	10.10	79

In Fig. 3 good magnetic properties are obtained for the Al and Cu added sample which also have the highest density. The high values of H_c and B_r for the Al–Cu added sample can be attributed to the homogeneous distribution of the low melting intergranular composition and the well-oriented magnetic grains by hot deformation process. For the undoped sample H_c and B_r decrease although its height reduction ratio has the highest value, this might be due to the cracking of the large magnetic grains instead of rotation during pressing process. The lower density is most probably due to the viscosity of the Nd-rich phase in the undoped sample (low melting additives such as Cu, Ga, or Al are added to increase the fluidity of the liquid phase to penetrate homogeneously into the holes during hot deformation or sintering processes) [4–10].

For the Al added sample, remanent magnetization has the highest value in spite of the relatively lower density and height reduction ratio. It may be due to the formation of hard magnetic μ composition in the intergranular region during hot deformation process.

4. Conclusions

In this study, we observed that Al or Cu additions to the NdFeB permanent magnet affect significantly the magnetic properties depending on the microstructural changes. Al and Cu additions enhanced the peritectic formation of the magnetic $Nd_2Fe_{14}B$ phase in the casting process. The density of the NdFeB magnet increased by Al and Cu additives resulted in better magnetic properties. For the Al doped sample, the ternary FeNdAl composition was formed during pressing process and the highest remanent magnetization was obtained most probably due to the hard magnetic properties of this ternary composition. For the undoped, Al–Cu, and Cu added samples, intergranular region contained only Nd-rich phase after hot deformation process. The high coercivity and

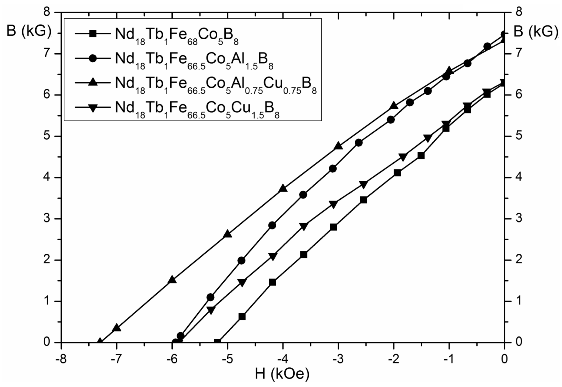

Fig. 3. Demagnetization curves of the hot deformed samples.

remanent magnetization obtained for the Al–Cu added sample can be attributed to the oriented grains, high density and homogeneously distributed intergranular Nd--rich composition. As a result, Al or Cu additions enhanced the magnetic properties of the NdFeB magnets by chemical changes in the composition of the intergranular region and affect substitutionally on the magnetic properties of the magnetic material.

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