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Optimisation of 2/17 permanent magnets using the quinary Sm–Co–Cu–Fe–Zr phase diagram

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Abstract

The combination of high magnetisation and high Curie temperature of the Sm_2Co_{17} type magnets makes them attractive for a number of applications requiring high-energy products and long term stability for continuous operating up to 300°C. In order to optimise the elaboration process, it was necessary to investigate phase equilibria in the Sm–Co–Zr–Cu–Fe system. The presented part of the work concerns two regions of interest near 1150°C and 850°C. A specific method is proposed to represent the diagram where a two dimension projection of the different domains is coupled with a three dimensional one. This representation appears as a tool to understand the metallurgical process and to obtain better reproducibility of the alloys magnetic properties. Then an optimisation could be made. Magnetic behaviour of alloys is discussed.

Keywords: Permanent magnets; Sm–Co–Cu–Fe–Zr compounds; Phases equilibria

1. Introduction

The combination of high magnetisation and high Curie temperature of Sm_2Co_{17} type magnets makes them attractive for a number of applications requiring high energy products and long term stability for continuous operating up to 300°C. These magnets are composed of Sm, Co, Zr, Cu and Fe, and they present hard magnet properties when their microstructure is constituted by a network of cells based on 2/17R phase surrounded by boundaries based on 1/5 phase [1–3]. Respectively 2/17R and 1/5 phases derive from Sm_2Co_{17} and $SmCo_5$ compounds where Sm and Co are substituted by Fe, Cu and Zr. Sm_2Co_{17} is rhomboedral (Th_2Zn_{17} type structure) and the substituted 2/17R has the same structure. $SmCo_5$ is hexagonal ($CaCu_5$ type structure) like 1/5 phase. In $SmCo_5$ the substitution of Sm and Co by Cu, Fe and Zr produces structural modifications toward an hexagonal phase with the 2/17 stoichiometry (Th_2Ni_{17} type structure) through a disordered phase called 1/7 ($TbCu_7$ type structure) [4–6].

This microstructure is obtained by a complex metallurgical process, including sintering, homogenisation treatment near 1150°C and annealing near 850°C.

The homogenisation treatment leads to a monophased state 1/7 and the microstructure is formed during the annealing at 850°C by nucleation-growth of ordered 2/17R cells in the 1/5 matrix. Often nucleation of 1/3 or 2/7 platelets is observed on the twin boundaries [1–3].

So the best magnetic properties are obtained when the material meets both of these conditions:

– monophasic 1/7 at high temperature.
– biphasic 2/17R+1/5 at lower temperatures in order to obtain the decomposition.

Phase diagram appears to be a good tool to predict whether the material fills the conditions and to optimise the magnetic properties.

2. Experimental method

Samples were prepared by weighing appropriate amounts of the pure components (99.9 mass%). They were placed in a water-cooled copper sample holder and melted in an arc furnace under argon. A multi-melting procedure with intermediate crushing and blending was necessary to secure adequately homogeneous alloys.

Samples were annealed at 1150°C for 96 h and quenched in water. This procedure is sufficient to obtain

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thermodynamic equilibrium. After quenching, samples were annealed at 850°C during 400 and 800 h.

The bulk composition was checked by plasma emission spectroscopy. The observed phases were characterised by X-ray diffraction of ground samples and by metallographic investigations. Phase compositions were determined by beam microprobe analysis (Cameca), and analyses were conducted at 25 kV using PROZA correction. The phase diagram was studied by Differential Thermal Analysis and Thermal Gravimetry coupled techniques using a Setaram TAG 24 device. The structure was investigated by X-ray powder diffractometry. Precise lattice parameters were obtained by least-squares refinement.

3. Results and discussion

The Sm–Co–Zr–Cu–Fe system has been investigated at 1150°C and 850°C in the Co rich region. In such system monophasic and biphasic domains belong to a hyperspace. In order to reduce the dimensions of the representation space we proposed [7] to use two projections:

- One is a three-dimensional projection where three axes are assigned to the variables [Sm]+[Zr], [Cu] and [Fe] content. [Co] contents can be calculated from the balance.
- The second is a two dimensional projection where composition [Sm], [Zr] and [Co]+[Cu]+[Fe] are represented in a classical composition triangle.

The monophasic field 1/5–1/7–2/17H at 1150°C is represented in Fig. 1a and b.

At 1150°C a continuous domain is observed from the 1/5 structure up to the 2/17H superstructure through the 1/7 disordered one. The composition of the magnets must be located inside this domain and it is represented in Fig.

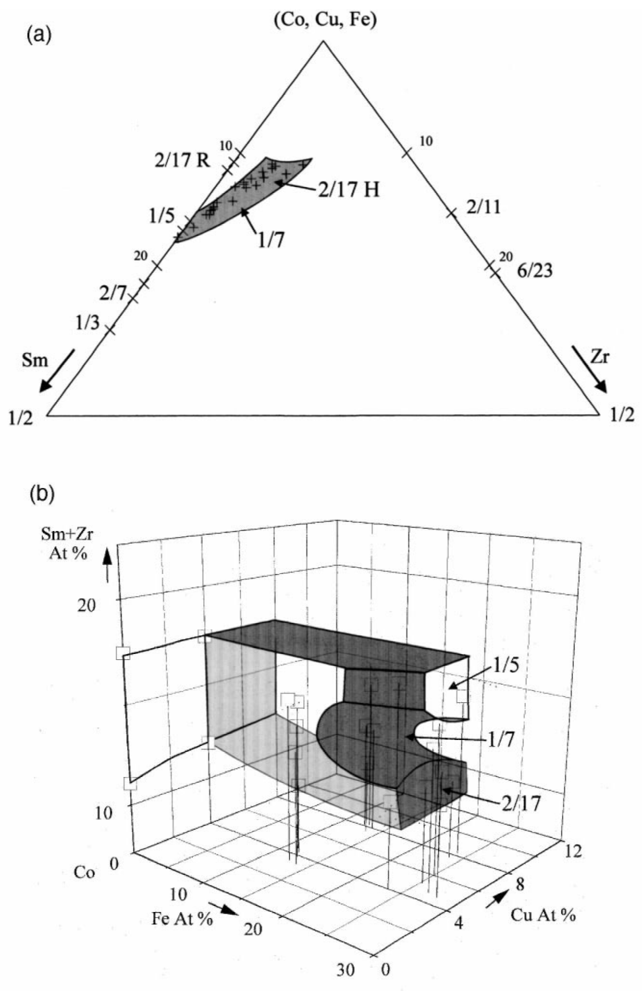

Fig. 1. Sm–Co–Zr–Cu–Fe quinary system: A system of two projections is used to represent the 1/5–1/7–2/17H monophasic field at 1150°C. (A) Co,Cu and Fe contents are added and the grey surface represents the single phase domain. (B) Sm and Zr contents are added and the grey surfaces describe the limits of the equilibrium field. Experimental data are represented in the two projections.

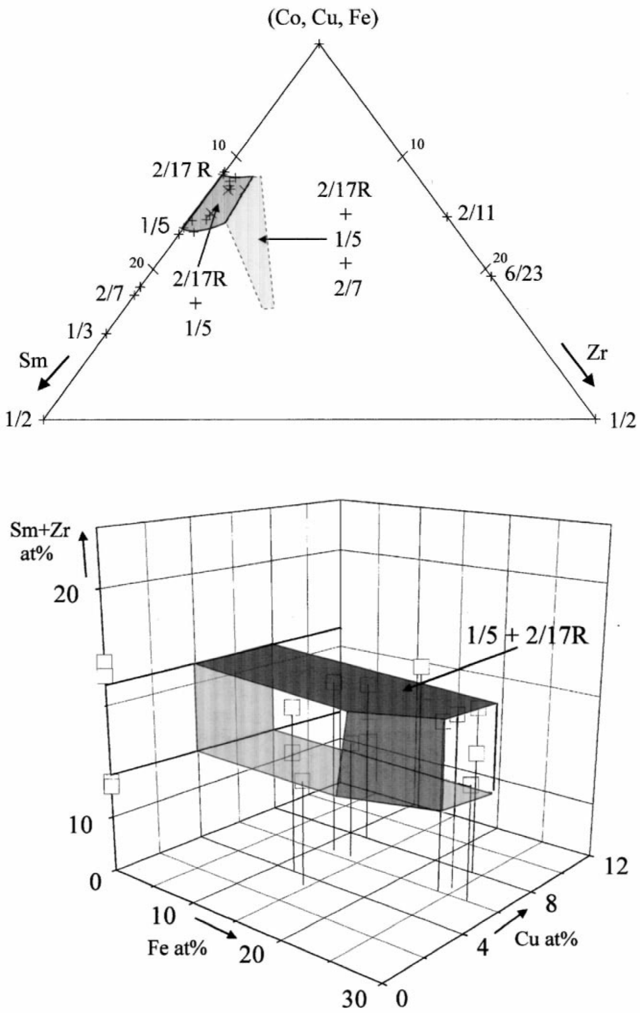

Fig. 2. Sm–Co–Zr–Cu–Fe quinary system: A system of two projections is used to represent the 1/5+2/17R biphased domain at 850°C. (A) Co,Cu and Fe contents are added and the grey surfaces represent the 2/17R+1/5 biphasic domain and the adjacent 2/17R+1/5+2/7 three phases domain. (B) Sm and Zr contents are added and the grey surfaces describe the limits of the equilibrium fields. Experimental data are represented in the two projections.

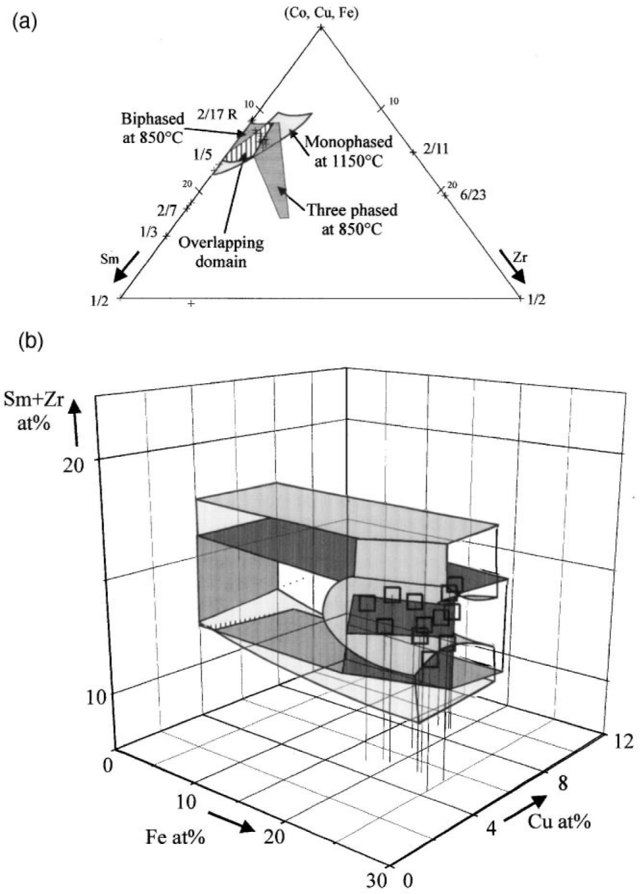

Fig. 3. Sm–Co–Zr–Cu–Fe quinary system: A system of two projections is used to represent the superposition of: the 1/5–1/7–2/17H monophasic domain at 1150°C and the 1/5+2/17R biphasic domain at 850°C. Composition of alloys with the best magnetic properties are represented in the two projections. In part A the hatched surface describes the overlapping domain.

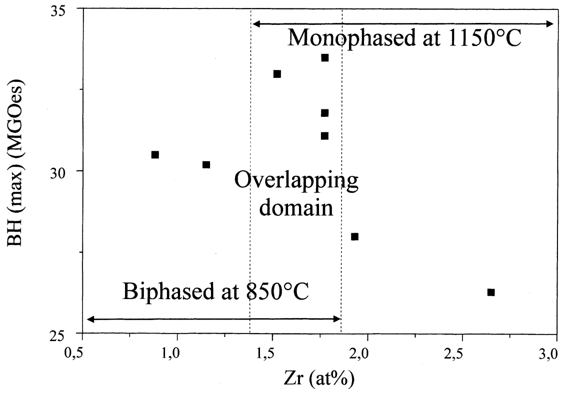

Fig. 4. The energy product $BH_{(\max)}$ is better when the composition of the alloys is located in the overlapping domain (bibliographical data).

1a and b. The grey surfaces correspond to the limits of the equilibrium field. In the Fig. 1b only a part of the monophasic field is represented. The domain is extended outside the vertical planes. It can be seen (Fig. 1b) that at high Fe content, the structural evolution from 1/5 up to 2/17H is not continuous due to the disappearance of the 1/7 bridge. This disappearance does not concern a demixing phenomenon but is due to the shape of the hyperdomain.

The biphasic field 1/5+2/17R at 850°C, is given in Fig. 2a and b. In Fig. 2b the adjacent domain is relative to the three phases 1/5+2/17R+2/7.

At 850°C the solubility of Zr in the 1/5 phase is small. The 1/7 disordered structure is destroyed and the 2/17R phase nucleates and grows in the 1/5 matrix. If Zr content is too important, 2/7 or 1/3 phase is formed as shown in Fig. 2b.

When projections are superimposed, the common field describes the composition domain that meets the two constraints (Fig. 3a and b).

The representative points of the different compositions proposed in bibliographical data [8–15] are projected in the two parts of the representation (Table 1). Analysis of the bibliographical data shows that the best magnets are located in common field in the two projections (Fig. 4).

For the specimens which meet the two constraints (monophasic 1/7 at 1150°C and biphasic 1/5+2/17R at

Table 1
Compositions and magnetic properties of alloys (bibliographical data)

Ref.	Composition (at%)					Magnetic properties	
	Sm	Zr	Co	Cu	Fe	Br	BH_{max}
[8]	11.87	1.15	59.37	8.81	18.8	11.2 kG	30.2 MGOes
[9]	11.76	0.88	60.88	8.82	17.65	11,3 kG	30.5 MGOes
[10]	11.54	1.52	57.71	4.37	24.86	12 kG	33 MGOes
[10]	12.17	1.93	60.33	6.65	18.91	10.5 kG	28 MGOes
[11]	11.94	2.32	57.95	8.87	18.91	??	??
[12]	11.61	2.28	58.78	8.72	18.61	??	??
[13]	11.77	2.65	63.09	4.85	17.65	10.5kG	26.3 MGOes
[14]	12.2	2.63	60.59	5.27	19.31	??	??
[3]	11.5	2.4	58.4	5.3	22.5	??	??
[15]	11.63	1.77	56.56	5.30	24.74	11.9 kG	33.5 MGOes
[15]	11.63	1.77	59.21	5.30	22.09	11.5 kG	31.8 MGOes
[15]	11.63	1.77	62.74	5.30	18.56	11.3 kG	31.1 MGOes

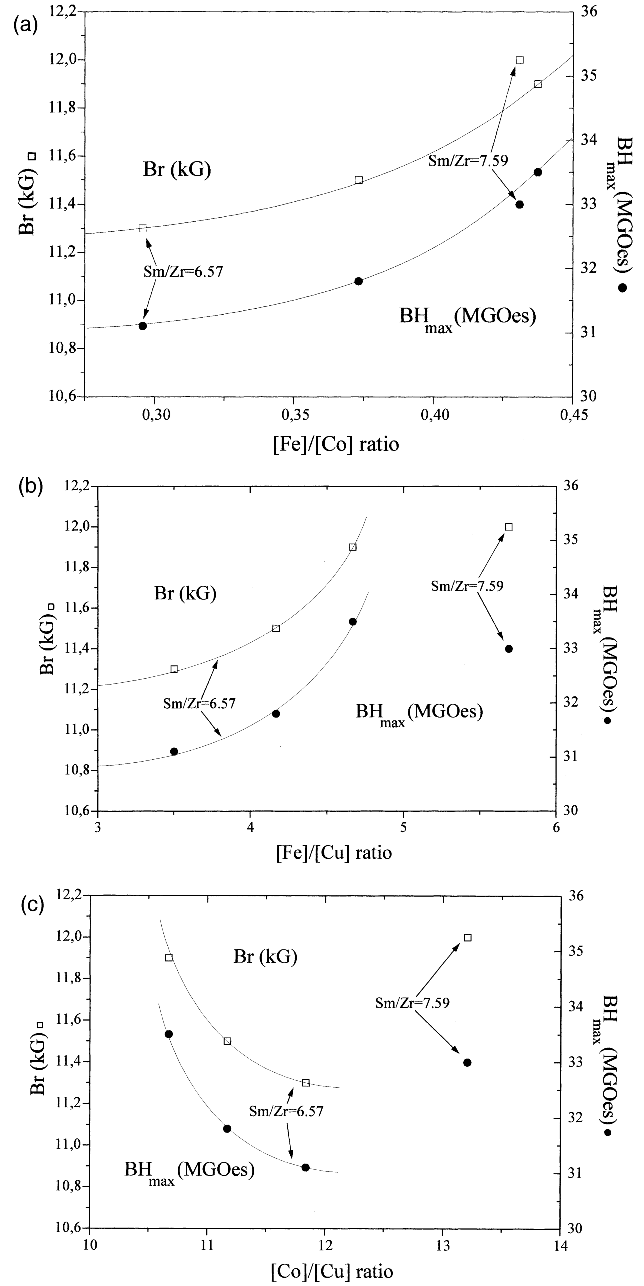

Fig. 5. (a) When the composition of the alloys is located in the overlapping domain (bibliographical data), the magnetic properties increase with the [Fe]/[Co] ratio. (b) When the composition of the alloys is located in the overlapping domain (bibliographical data), the magnetic properties increase with the [Fe]/[Cu] ratio. (c) When the composition of the alloys is located in the overlapping domain (bibliographical data), the magnetic properties decrease with the [Co]/[Cu] ratio.

850°C), it is possible to define the compositional effect of each element. Unfortunately, regarding the overlapping domain, literature data is scarce. Nevertheless, a comparison between the bibliographical data shows that the energetic product, BH_{max} and remanent magnetisation, Br, increase with [Fe]/[Cu] and [Fe]/[Co] ratios (Fig. 5a and b) and decrease when the [Co]/[Cu] ratio increases (Fig. 5c). The influence of Sm/Zr substitution could be derived in the same conditions. For an optimisation of the element contents, the limit will be imposed by the boundaries of the overlapping domain. A rational optimisation of the element contents needs also the knowledge of the temperature effect on the equilibrium field limits.

4. Conclusion

The evolution of the alloys during the different stages of the metallurgical process can be described as a pathway though a non-isothermal quinary system. The knowledge of the limits of the equilibrium fields is a good tool in the determination of the composition of the alloys that meet the both constraints imposed, to generate the expected cellular microstructure. However, it is also a help in obtaining a rational optimisation of the magnetic properties.

References

[1] L. Rabenberg^2, R.K. Mishra, G. Thomas, IEEE Trans. Magn. 19/6 (1983) 2723–2724.
[2] A.E. Ray, S. Liu, J. Mater. Eng. Perform. 1–2 (1992) 183–192.
[3] C. Maurry, L. Rabenberg, C.H. Allibert, Phys. Status Solidi 140-57 (1993) 57–72.
[4] A. Lefevre, L. Cataldo, M.-Th. Cohen-Adad, C.H. Allibert, N. Valignat, J. Alloys Comp. 232 (1996) 296–301.
[5] A. Lefevre, L. Cataldo, M.-Th. Cohen-Adad, B.F. Mentzen, J. Alloys Comp. 255 (1997) 161.
[6] A. Lefevre, M.-Th. Cohen-Adad, B.F. Mentzen, J. Alloys Comp. 256 (1997) 207.
[7] A. Lefevre, L. Cataldo, M.-Th. Cohen-Adad, B.F. Mentzen, in preparation.
[8] T. Ojima, S. Tomizawa, T. Yoneyama, T. Hori, IEEE Trans. Magn. 13/5 (1977) 1317–1319.
[9] Sun Daki, Liu Yjin, Paper N° IX-7 at the Fifth Internationnal Workshop on Rare Earth-cobalt Permanent Magnets and their Applications; Roanoke, Virgina, 7–10 June, 1981.
[10] R.J. Mishra, G. Thomas, T. Yoneyama, A. Fukuno, T. Ojima, J. Appl. Phys. 52/3 (1981) 2517–2519.
[11] G.V. Ivanova, L.M. Magat, A.G. Popov, V.G. Maykov, V.I. Khrabrov, YA.S. Shur, Phys. Met. Metallogr. 53/4 (1982) 57–64.
[12] L. Rabenberg, R.K. Mishra, G. Thomas, J. Appl. Phys. 53/3 (1982) 2389–2391.
[13] G.C. Hadjipanayis, J. Appl. Phys. 55/6 (1984) 2091–2093.
[14] S. Derkaoui, C.H. Allibert, F. Delannay, J. Laforest, J. Less-Common Met. 136 (1987) 75–86.
[15] B.M. Ma, Y.L. Liang, J. Patel, D. Scott, C.O. Bounds, IEEE Trans. Magn. 32/5 (1996) 4377–4379.