Journal of Alloys and Compounds 262–263 (1997) 129–133

A representation of the Sm–Co–Zr–Cu–Fe quinary system: a tool for optimisation of 2/17 permanent magnets

A. Lefèvre[a,*], L. Cataldo[a], M.Th. Cohen-Adad[a], B.F. Mentzen[b]

[a] *Laboratoire de Physico-Chimie des Matériaux Luminescents (UMR No. 5620), Université Claude-Bernard Lyon I, 69 622 Villeurbanne Cedex, France*

[b] *Laboratoire des Multimatériaux et Interfaces (UMR No. 5615), Université Claude-Bernard, Lyon I 69 622, Villeurbanne Cedex, France*

Abstract

In order to optimise the elaboration process of Sm_2Co_{17} type magnets, the boundary of the single-phase domain at 1150°C and of the two-phase domain involving the 1/5 and the 2/17 at 850°C must be known. The knowledge of solid–liquid equilibria is also needed in order to avoid formation of other phases during sintering. It was then necessary to investigate phase equilibria in the Sm–Co–Zr–Cu–Fe system. However, since the variability of a such system under isobaric and isothermal conditions is four, the classic graphical representation can not be used. The presented part of the work concerns the region of interest near 1150°C. A specific approach of the quinary system is developed. It starts from the Sm–Co binary system, then the Sm–Co–Zr ternary system has been investigated: 1150°C isothermal section has been drawn for high Co contents and special attention has been paid to in the structural modification induced by Zr addition. Based on our knowledge of the ternary system, the Sm–Co–Zr–Cu quaternary one has been studied; an isothermal section has been drawn for a Cu concentration of 4 at.%. Finally a representation of the 1150°C single-phase domain in the quinary system Sm–Co–Zr–Cu–Fe is proposed. For this purpose, a method consisting of a two-dimensional projection of the domain coupled with a three-dimensional one is applied. This representation makes possible to predict if a quinary alloy is single-phased at 1150°C or not. Magnetic behaviour of alloys is shown. This easy to read, easy to use representation appears a good tool to optimise the 2/17-type permanent magnets.

Keywords: Sm_2Co_{17} type magnets; Solid–liquid equilibria; Phase equilibria; Sm–Co–Zr–Cu–Fe system

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 [1].

The 2/17 magnets, composed of Sm, Co, Zr, Cu and Fe, are obtained by a complex process. The purpose is to get a cellular microstructure associated with high coercitivity and high energy products. This microstructure is formed by cells composed of 2/17 R phase surrounded by boundaries composed of 1/5 phase.

The metallurgical process can be described by three successive steps.

- A powder with specific composition is sintered near 1200°C.
- A homogenisation annealing is performed to obtain a single disordered $SmCo_7$ state at 1150°C ($TbCu_7$ type structure).
- A precipitation treatment at 850°C is then per-

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[*] Corresponding author.

PII S0925-8388(97)00368-X

formed to obtain a specific microstructure constituted of a mixture of 2/17 R and 1/5 phases, called cellular microstructure.

But many problems of reproducibility and optimisation remain due to the poor knowledge of phase relationship in the involved quinary system.

Our purpose was to achieve better control of the process to obtain the magnets required by industry. Therefore it has been necessary to investigate phase equilibria in the Sm–Co–Zr–Cu–Fe system. The boundary of the single-phase domain at 1150°C and of the two-phase domain involving the 1/5 and the 2/17 R at 850°C had to be known. Knowledge of the solid–liquid equilibria was also necessary in order to avoid formation of other phases during sintering. So three regions of interest were defined; near 1150°C, near 850°C and in the solid–liquid equilibria range.

Only a part of the work concerning the first region of interest near 1150°C is presented in this paper.

2. Experimental method

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

Samples were annealed at 1150°C for 96 h and quenched in water. This procedure has been sufficient to obtain thermodynamic equilibrium [2].

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. Accurate lattice parameters were calculated by least-squares refinement. The diffraction data were collected on an automated Philips device. The powder profile collected at room temperature have been analysed using the Rietveld method.

3. Results and discussion

The investigation of any quinary system is difficult so a strict methodology is required to obtain sufficient results in a reasonable time. The study starts from the investigation of the different sub-systems. However, with five elements, 10 binary systems, 10 ternary systems, and five quaternary systems are involved, so only the most important of them for the behaviour of alloys were selected and studied.

The second problem concerns representation of the phase diagram. Under isobaric and isothermal conditions, the system exhibits four levels of freedom and classical graphical representation can not be used.

Two approaches to the Sm–Co–Zr–Cu–Fe quinary system have been applied. After a brief analysis of the first one, the second will be developed.

The first approach [3] relates closely to the historical development of the Sm–Co based permanent magnets. It begins from the Sm–Co binary system [4]. Most of the different phases observed in the quinary alloys derive from this system: they are $SmCo_5$ (noted 1/5); the rhombohedral Sm_2Co_{17} (noted 2/17 R); and some phases which belong to the $(n+1)/(5n-1)$ series [5], such as the Sm_5Co_{19} (noted 5/19), Sm_2Co_7 (noted 2/7), $SmCo_3$ (noted 1/3) and the $SmCo_2$ (noted 1/2). It appears that only the rhombohedral form of the Sm_2Co_{17} phase can exist in this system [4,6,7].

The Sm–Co–Cu system [3] has been studied. Complete solubility of Cu in the 1/5 and low solubility in the 2/17 R (20 at.% of Cu at 1150°C) have been observed. Copper could only be substituted for Co.

Schneider et al. [8] have studied the Sm–Co–Fe system: they report high solubility of Fe in the 2/17 R and low solubility in the 1/5. Iron can only substitute for Co. From neutron [9] diffraction experiments on $Nd_2(Co_xFe_{1-x})_{17}$, it occurs that iron has a strong preference for the dumbbell site in the 2/17 structure.

The results of our study of the Sm–Co–Cu–Fe quaternary system [3], confirm that Cu and Fe atoms could only substitute for Co without structural modification. Copper is preferentially dissolved in the 1/5 while Fe has a greater affinity for 2/17 R.

Both elements Cu and Fe induce strong modification of magnetic properties in the 1/5 and 2/17 R phases but they involve only very little structural modification. These type of atoms could only substitute on Co sites, these elements are 3*d* type and their atomic radii are quite similar.

Finally, a slide with a constant 4 at.% content of Cu has been drawn in the Sm–Co–Cu–Fe–Zr quinary system. It gives major results but has a great limitation since it could be useful only at constant composition of Cu.

A second approach to the quinary system has then been developed. Some results were achieved by study of the Sm–Co–Zr ternary system (Fig. 1). The atomic size of Zr is intermediate between those of Co and

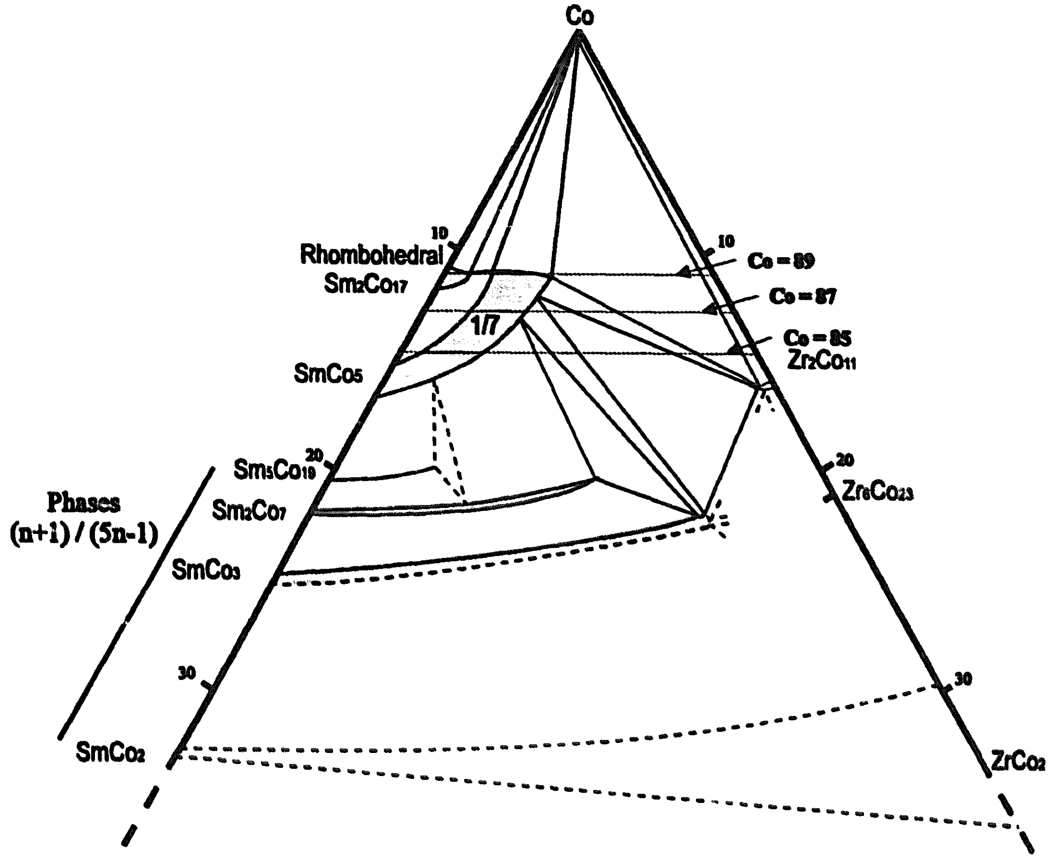

Fig. 1. Sm–Co–Zr ternary system: isothermal section at 1150°C (Co rich part). The indicated number are in at.%.

Sm and great structural modifications are involved by Zr substitution.

At high temperature (1150°C) Zr is responsible for formation of an hexagonal (Sm, Zr)$_2$Co$_{17}$ structure [2,10,11]. There is a small solubility of Zr in the 2/17 R phase while it is quite important in the 1/5 phase. This solubility is coupled with Co$_2$ dumbbell for Sm substitution and structural modifications are observed. A continuous evolution is observed from the 1/5 to the 2/17 R structure through a SmCo$_7$ disordered structure (TbCu$_7$ type). This domain is noted 1/7 and this phase is different from the 2/17 R, a two-phase domain is observed between them.

It should be noted that all magnetic alloys belong to the 1/7 domain. Zirconium is necessary to create the 1/7 structure and the decomposition of this structure is responsible of the cellular microstructure creation.

The quaternary system Sm–Co–Zr–Cu system has been studied. A slide for constant copper content of 4 at.% has been settled. A representation of the single-phase 1/7 and 2/17 R domains has been deduced (Fig. 2). Their shapes are nearly the same as in the ternary Sm–Co–Zr system. In the investigated range 0–4 at.%, Cu substitutes for Co and does not modify the phase equilibria.

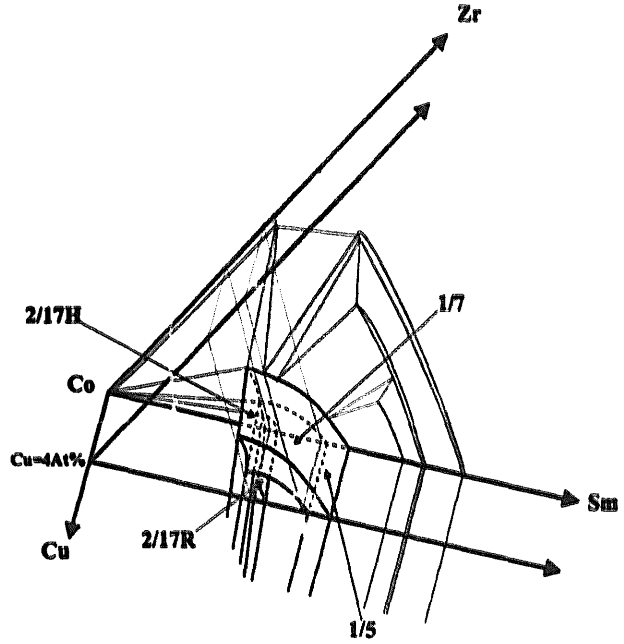

Fig. 2. Sm–Co–Zr–Cu quaternary system: isothermal section at 1150°C (Co rich part).

From the study of the different sub-systems it appears that these five elements could be grouped in two sets: 3*d* elements Co, Cu and Fe form a first

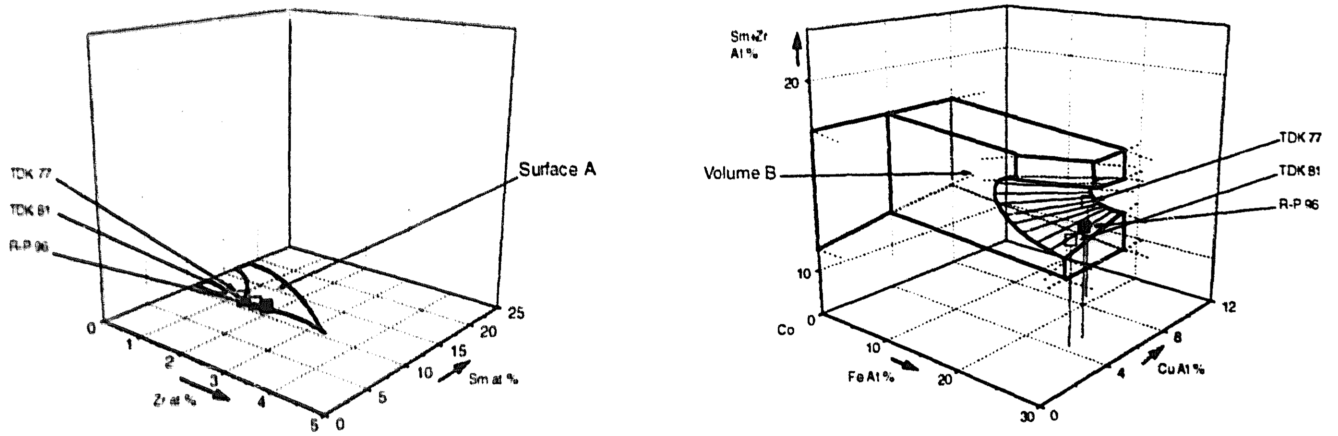

Fig. 3. Sm–Co–Zr–Cu–Fe quinary system in 'optimal projections': isothermal section at 1150°C. A system of two projections is used. In part A, Co, Cu and Fe contents are added. In part B, Sm and Zr contents are added.

class, Sm and Zr form the second. Each member of a class can be located in one type of site (Co or Sm site).

The method used to draw the quinary system is derived from the 'optimal projection' method [12] developed in high-order salt systems. A two-dimensional projection of the domain is used, coupled with a three-dimensional one.

In the first projection, Co, Cu and Fe contents are added so the single-phase domain is described in a plane (surface A). In the second projection, Sm and Zr contents are added so the single-phase domain is described in a three-dimensional space (volume B).

Five series of samples were prepared, each one of a given compositional content of Cu and Fe, and of different contents of Co, Sm and Zr:

Cu = 4 at.% and Fe = 12 at.%
Cu = 4 at.% and Fe = 24 at.%
Cu = 6 at.% and Fe = 24 at.%
Cu = 8 at.% and Fe = 12 at.%
Cu = 8 at.% and Fe = 24 at.%

From the characterisation of these samples, two projections of the 1/7 single-phase domain have been drawn for 4 at.% < Cu < 8 at.% and for 0 at.% < Fe < 24 at.%.

This easy to read, easy to use representation appears a good tool to optimise the 2/17 type permanent magnet. It makes it possible to predict when a quinary alloy is single-phased at 1150°C. The investigated compositions are projected in the two parts of the diagram (Figs. 3a,b).

If at least one of the projections is not located in A and/or B, the alloy is not single phase at 1150°C. If the projections are located in both surface A and volume B, then the alloy has the best chance to be single-phased at 1150°C.

Some bibliographical data are shown in Figs. 3a,b:

- The white square represents the first 2/17 magnet ($Sm_{11.8}Zr_{1.2}Co_{59.4}Cu_{8.8}Fe_{18.8}$) from TDK, prepared in 1977 [13] the energetic product is equal to 30 MGOs.
- The grey square represents a second composition ($Sm_{11.5}Zr_{1.5}Co_{57.7}Cu_{4.4}Fe_{24.9}$) with 33 MGOs from TDK prepared in 1983 [14].
- The black square represent a third composition ($Sm_{11.6}Zr_{1.8}Co_{56.6}Cu_{5.3}Fe_{24.7}$) with 33.5 MGOs obtained by Rhone Poulenc USA in 1996 [15].

In the planar projection A (Fig. 3a), the three compositions are very close, all of them belong to the 1/7 domain. Only small differences on the Sm and the Zr contents of the alloys are observed.

In the second projection B (Fig. 3b) more important changes can be observed. The best magnetic properties are obtained with samples with low Cu and high Fe contents. But in this case the single-phase domain is very narrow and reproducibility problems are increased.

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