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The ternary system Sm–Co–Zr isoplethic section at Co = 89 at.%

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Abstract

A knowledge of solid–liquid equilibria is necessary to optimise sintering temperature in industrial Sm_2Co_{17}-type magnets. A single-phase state is reported as precursor of the cellular microstructure of the Sm_2Co_{17} permanent magnets. The formation of this phase at high temperature seems for a large part to be governed by Zr addition. In order to understand the behaviour of 2:17-type magnets, phase relationships have been investigated in the Co-rich field of the Sm–Co–Zr system.

The 1150°C isothermal section has been reinvestigated. A two-phase region was observed involving hexagonal and rhombohedral Sm_2Co_{17}. An isoplethic section has been drawn for temperatures between 1150°C and the melting points of the alloy with Co = 89 at.%, (Sm + Zr) = 11 at.%. Two four-phase equilibria have been observed. A tentative polythermal representation of the Sm–Co–Zr system in the Co-rich field has been drawn.

Keywords: Ternary phase diagram; Samarium–cobalt–zirconium compounds; Solid solubility; Permanent magnet materials

1. Introduction

The combination of high magnetisation and high Curie temperature of Sm_2Co_{17}-type permanent magnets makes them attractive for a number of applications requiring high energy products and long term stability for continuous operation up to 300°C.

A specific cellular microstructure must be obtained to increase the coercivity [1], and the best magnetic behaviour of Sm_2Co_{17}-type magnets is obtained by addition of Fe, Cu and Zr coupled with heat treatments.

In order to optimise the magnetic properties and preparation conditions it is necessary to investigate the phase relationships associated with these compounds.

Among the three elements commonly added to the Sm_2Co_{17}, zirconium seems to be the most important in the modification of phase relationships, but it is not easy to derive the specific influence of Zr from the bibliographical data concerning quinary alloys [2–7].

Following a study of the Sm–Co binary system in the Co-rich field [8], we have investigated the Sm–Co–Zr ternary phase diagram and the influence of Zr on the Sm_2Co_{17} phase.

The effect of Zr on the Sm_2Co_{17} phase was studied by Fujii et al. [9]. In this paper, samples were prepared along the $Sm_2Co_{(17-x)}Zr_x$ line and annealed at 1000°C for 1 week. From the X-ray diffraction pattern it was found that rhombohedral Sm_2Co_{17} (denoted Sm_2Co_{17}(R): Th_2Zn_{17}-type structure) can be obtained for $0.0 \leq x \leq 0.6$. From $x = 0.6$ to $x = 1.0$ the samples showed a mixture of rhombohedral and hexagonal forms of Sm_2Co_{17} (Th_2Ni_{17}-type structure). The unit cell volume was increased by addition of Zr, suggesting that Zr substitutes for Co in the Sm_2Co_{17} cell.

Another study was made by Nishio et al. [10]. The 1200°C isothermal section of the Sm–Co–Zr phase diagram was established in the Co-rich field. Zr was slightly soluble in the Sm_2Co_{17}(R) phase. It extends the $SmCo_5$ stability range up to the hexagonal Sm_2Co_{17} structure (denoted Sm_2Co_{17}(H)): disordered $SmCo_7$ ($TbCu_7$-type structure) should form a bridge between these two regions. The stabilisation by Zr of the Sm_2Co_{17}(H) form was confirmed and the transformation between the two forms of Sm_2Co_{17} ap-

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peared to be first order; a two-phase region was detected.

More recently, Allibert and coworkers [11–13] have studied the 1150°C isothermal section of the Sm–Co–Zr phase diagram. The existence of a two-phase region between Sm_2Co_{17} and $SmCo_7$ was assumed, but it was not observed.

In order to determine the effect of Zr on the Sm_2Co_{17} phase, we have investigated an isoplethic slab corresponding to a constant concentration of cobalt (89 at%).

2. Experimental procedure

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.

As-cast samples show small phase segregation and exhibit a disordered $TbCu_7$-type structure. After annealing at a high enough temperature for a sufficiently long time segregation disappears and the structure is no longer disordered.

In order to check if thermodynamic equilibrium was reached, samples were annealed in different ways. One part was annealed at 1150°C for 96 h and quenched in water. The other was annealed at 1240°C for 12 h and then at 1150°C for 10 h. As described later, the same results were obtained in both cases.

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 the coupled techniques of differential thermal analysis (DTA) and thermal gravimetry using a Setaram TAG 24 device.

3. Results and discussion

Samples along the $Co_{89}Sm_{(11-x)}Zr_x$ line, with $x = 0$, 1, 2, 3, 4, 6 and 8 at.%, were prepared and annealed at 1150°C for 96 h. Samples with $x = 1$, 2 and 3 at.% were annealed at 1240°C for 12 h and 1150°C for 10 h.

Two more samples, $Sm_8Co_{90}Zr_2$ and $Sm_{7.5}Co_{91}Zr_{1.5}$, not located on the section were prepared and annealed at 1150°C for 96 h.

As a first stage we have studied the isoplethic section AB (Fig. 1) at constant temperature (1150°C).

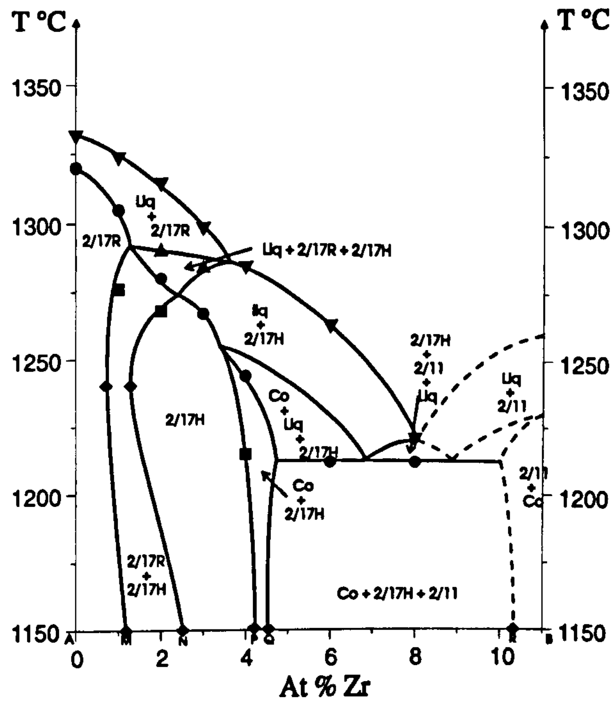

Fig. 1. Sm–Co–Zr ternary system: isoplethic section with 89 at.% Co.

In the second stage the section has been studied at various temperatures, and in order to confirm the results samples not located on the section have been investigated.

Finally, a tentative polythermal representation of Sm–Co–Zr in the Co-rich range has been drawn.

3.1. Isothermal results (1150°C)

Two samples (Zr = 0 and 1 at.% annealed for 96 h at 1150°C) were prepared between A and M; a single phase is observed by metallographic investigation. X-ray diffraction patterns show only the Sm_2Co_{17}(R) form (Fig. 2(a)).

Between N and P, samples with Zr = 3 and 4 at.% (annealed for 96 h at 1150°C) appear to be single phase by metallographic investigation. Only the Sm_2Co_{17}(H) form is observed on X-ray diffraction patterns (Fig. 2(b)).

Between M and N a two-phase region has been observed on sample Zr = 2 at.% annealed 96 h at 1150°C. The X-ray diffraction pattern of this sample showed a mixture of rhombohedral and hexagonal forms of Sm_2Co_{17} (Fig. 2(c)). Some peaks are common to the two forms of Sm_2Co_{17}; they correspond to the $SmCo_7$ substructure. This two-phase domain has also been observed by metallographic investigation (Fig. 3) and the boundaries have been determined by microprobe analysis (Table 1).

All these results have been confirmed with samples

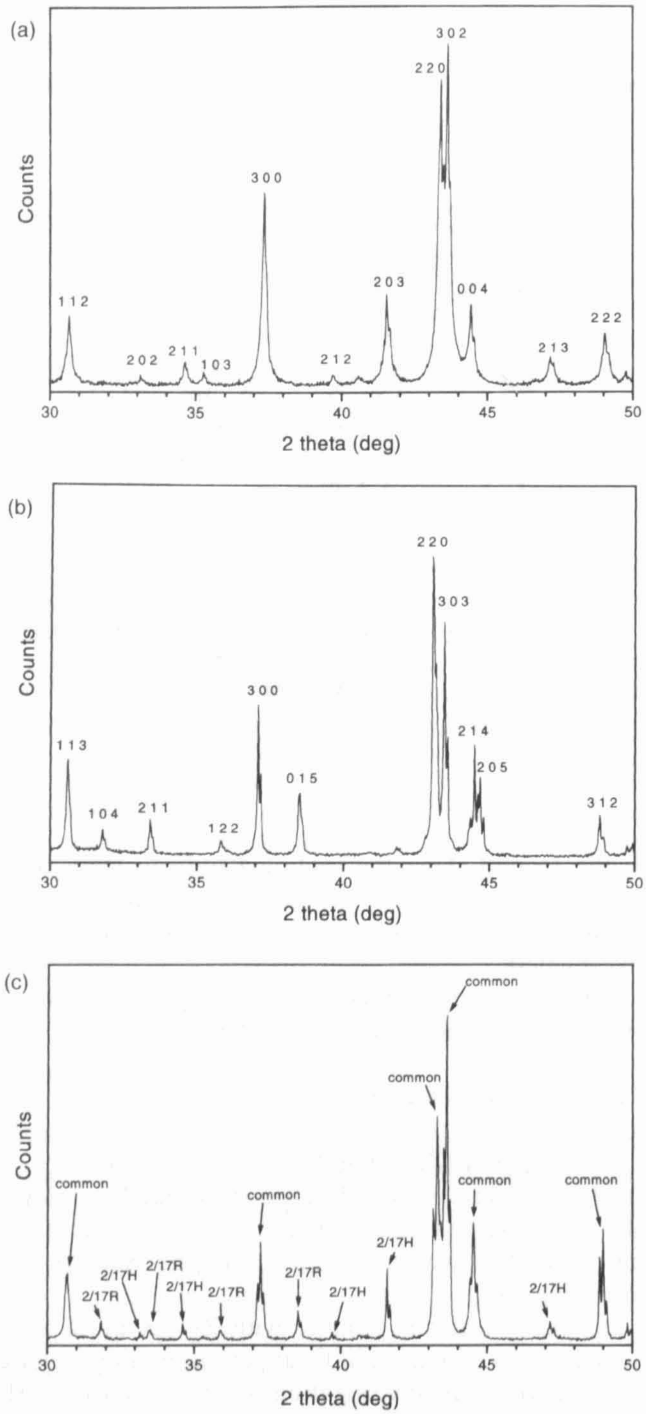

Fig. 2. X-ray diffraction pattern of sample: (a) $Sm_{11}Co_{89}Zr_0$ annealed at 1150°C for 96 h (the peaks correspond to the rhombohedral Sm_2Co_{17} structure); (b) $Sm_7Co_{89}Zr_4$ annealed at 1150°C for 96 h (the peaks correspond to the Sm_2Co_{17}(H) structure); (c) with 9 at.% Sm, 89 at.% Co, 2 at.% Zr annealed at 1150°C for 96 h showing a mixture of the rhombohedral (2:17(R)) and hexagonal (2:17(H)) forms of Sm_2Co_{17}. Common peaks correspond to the substructure ($TbCu_7$).

annealed at 1240°C for 12 h and then at 1150°C for 10 h. For Zr = 1 at.% a single rhombohedral phase is observed by X-ray diffraction and metallographic analysis. For Zr = 3 at.% the hexagonal structure is

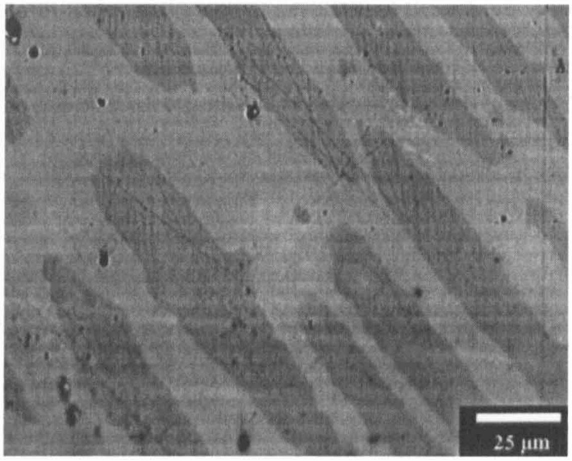

Fig. 3. Micrograph of sample with 9 at.% Sm, 89 at.% Co, 2 at.% Zr, annealed at 1150°C for 96 h. Micrograph of sample etched by 1% nital. Sm_2Co_{17}(R) appears in light grey, the hexagonal phase appears as a darker grey.

observed. For the sample Zr = 2 at.% a two-phase region has been observed.

Between Q and R a three-phase region has been observed for samples with Zr = 6 at.% and Zr = 8 at.% (Fig. 4), Sm_2Co_{17}(H) being in equilibrium with cobalt and Zr_2Co_{11}. The boundaries of this region have been determined by microprobe analysis (Table 1). This result is fully consistent with the results of Nishio et al. [10] and Derkaoui et al. [13].

Between P and Q a two-phase region containing Sm_2Co_{17}(H) and cobalt must exist. This was observed by Nishio et al. [10] and Derkaoui et al. [13].

Between R and B a two-phase region exists containing cobalt and Zr_2Co_{11}. This has already been observed in the Co–Zr binary phase diagram.

3.2. Isoplethic section (Co = 89 at.%)

In order to determine the isoplethic section, some samples were quenched and analysed after annealing at 1240°C. A DTA investigation has also been performed on samples annealed at 1150°C for 96 h having compositions between 0 and 8 at.% Zr.

Investigations on samples annealed at 1240°C show the evolution of the rhombohedral–hexagonal two-phase region. Samples with Zr = 2 and 3 at.% appear to be single-phase by metallographic investigation and the hexagonal structure is observed by X-ray diffraction. The hexagonal–rhombohedral two-phase region was observed by metallographical investigations in the sample with Zr = 1 at.% (Fig. 5). The boundaries have been determined by microprobe analysis (Table 1).

The rhombohedral Sm_2Co_{17} single-phase region extends up to 1320°C. At higher temperature the liquid phase is observed. This is in good agreement

Table 1
Microprobe analyses of samples annealed at 1150 and 1240°C (at.%)

Samples			Sm_2Co_{17}(R)			Sm_2Co_{17}(H)			Cobalt			Zr_2Co_{11}		
Sm	Co	Zr	Sm	Co	Zr	Sm	Co	Zr	Sm	Co	Zr	Sm	Co	Zr
1150 °C														
9	89	2	10.4	88.5	1.1	8.9	88.5	2.6						
8	90	2	10.8	88.4	0.8	9.7	88.7	1.9	0.2	99.8	0.0			
3	89	8				6.7	88.9	4.4	0.2	99.7	0.1	0.5	83.4	16.1
1240 °C														
10	89	1	88.6	10.7	0.7	88.6	10.3	1.1						

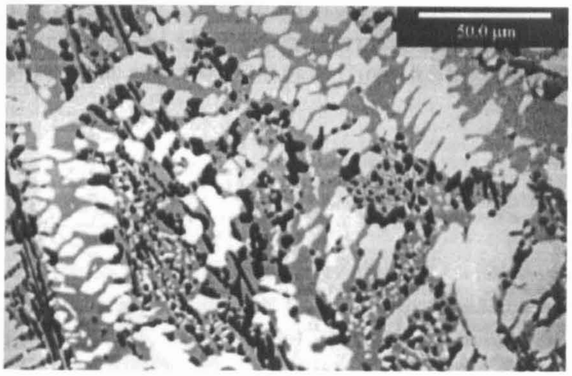

Fig. 4. Micrograph of a sample with 9 at.% Sm, 89 at.% Co, 2 at.% Zr (as-cast). Backscattered electron scanning microscopy (15 kV). Sm_2Co_{17}(H) primary phase appears in light grey. A precipitation of Sm_2Co_{17} and cobalt (black) appears in a Zr_2Co_{11} matrix (medium grey).

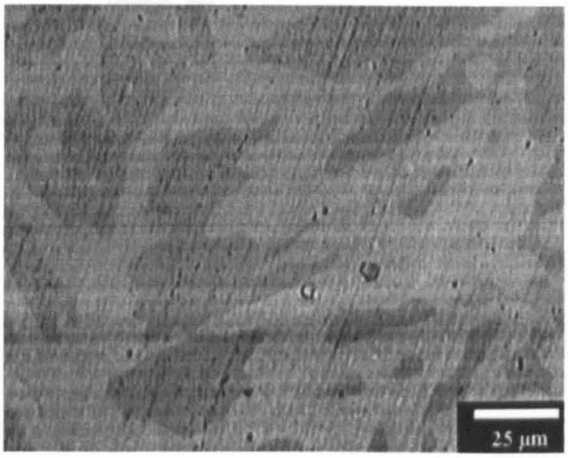

Fig. 5. Micrograph of a sample with 9 at.% Sm, 89 at.% Co, 2 at.% Zr, annealed at 1240°C for 12 h and at 1150°C for 10 h. Micrograph of sample etched by 1% nital. Sm_2Co_{17}(R) appears in light grey, the hexagonal phase appears as a darker grey.

with our previous work [8]. The Sm_2Co_{17}(H) form is not observed in the Sm–Co binary phase diagram.

The rhombohedral + hexagonal Sm_2Co_{17} region has been observed for the sample with Zr = 1 at.% annealed at 1240°C. The phase boundaries at this temperature have been determined by microprobe analysis (Table 1).

The single-phase field of Sm_2Co_{17}(H) is distinct from the rhombohedral one and it is probably obtained by deformation of the $SmCo_5$ structure through the disordered $SmCo_7$ structure, as reported by Nishio et al. [10].

A three-phase region of Sm_2Co_{17}(R) + Sm_2Co_{17}(H) + liquid is observed in the DTA curves (Table 2).

The three-phase Sm_2Co_{17}(H) + Zr_2Co_{11} + cobalt region extends up to a four-phase equilibrium, clearly observed at 1212°C in the DTA curves (samples Zr = 6 and 8 at.%). The specific microstructure of the Zr = 8 at.% (Fig. 4) sample indicates that there is a eutectic plateau, where the liquid is in equilibrium with Sm_2Co_{17}(H), Zr_2Co_{11} and cobalt.

Originating from this four-phase plateau, several three-phase regions are observed:

— Sm_2Co_{17}(H), cobalt and liquid;
— Sm_2Co_{17}(H), Zr_2Co_{11} and liquid;
— Zr_2Co_{11}, cobalt and liquid.

3.3. Samples not located on the isoplethic slide

The Sm_2Co_{17} rhombohedral + hexagonal two-phase region must be adjacent to a three-phase region containing cobalt + Sm_2Co_{17}(R) + Sm_2Co_{17}(H). In

Table 2
Results of DTA analyses

Samples		Solidus (°C)		Liquidus (°C)
Sm–Co89at.%–Zr0at.%		1320		1332
Sm–Co89at.%–Zr1at.%	1276	1305		1324
Sm–Co89at.%–Zr2at.%	1368	1280	1290	1315
Sm–Co89at.%–Zr3at.%	1267	1284		1299
Sm–Co89at.%–Zr4at.%	1215	1244		1285
Sm–Co89at.%–Zr6at.%		1212		1263
Sm–Co89at.%–Zr8at.%		1212		1221
Sm–Co90at.%–Zr2at.%		1275		1306
Sm–Co91at.%–Zr1.5at.%		1275		1310

order to confirm the existence of this region, the samples $Sm_8Co_{90}Zr_2$ and $Sm_{7.5}Co_{91}Zr_{1.5}$ were prepared and annealed at 1150°C for 96 h.

The three-phase region has been observed for these samples by metallographic investigation, X-ray diffraction and microprobe analysis (Table 1). DTA curves show a four-phase plateau at 1275°C (Table 2). At this temperature liquid, cobalt, and rhombohedral and hexagonal forms of Sm_2Co_{17} are in a transitory equilibrium.

3.4. Polythermic representation in the Co-rich range

Based on this result and on the isoplethic section, a tentative polythermic representation has been drawn (Fig. 6).

4. Conclusion

A knowledge of solid–liquid equilibria is very important to optimise sintering temperature in industrial 2:17-type permanent magnets.

The isoplethic section at Co = 89 at.% has been investigated and the solid–liquid equilibrium determined.

Two four phase equilibria are observed:

– one involving Co, Sm_2Co_{17}(H), Zr_2Co_{11} and liquid occurs at 1212°C;

– one involving Sm_2Co_{17}(H), Sm_2Co_{17}(R), Co and liquid occurs at 1275°C.

Two single-phase regions have been observed: one for Sm_2Co_{17}(R), and one for Sm_2Co_{17}(H). A two-

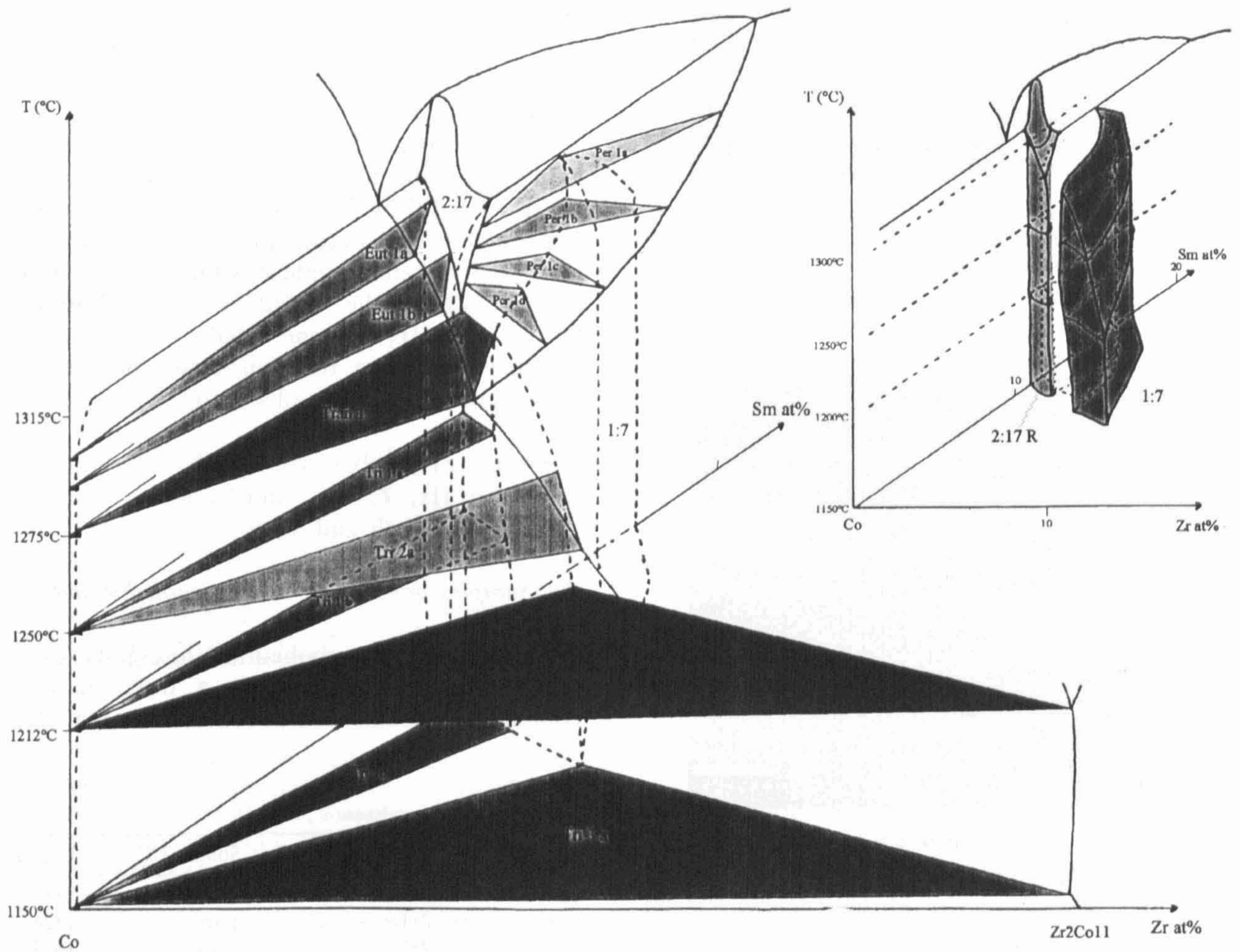

Fig. 6. Sm–Co–Zr ternary system: polythermic representation in the Co-rich range. (Inset: Sm_2Co_{17}(R) and Sm_1Co_7 (from Sm_1Co_5 to Sm_2Co_{17}(H)) single-phase fields shown by dashed lines on the main diagram.) The right-hand side represents equilibria with the liquid. The three-phase region Sm_2Co_{17}(R) + Co + liquid is denoted by Eut 1a and Eut 1b. The three-phase region Sm_2Co_{17}(R) + Sm_1Co_7 + liquid is denoted by Per 1a, Per 1b, Per 1c and Per 1d. The four-phase transitory equilibrium between Sm_2Co_{17}(R) + Sm_1Co_7 + Co + liquid is denoted by Tran 1. The three-phase region Sm_2Co_{17}(R) + Sm_1Co_7 + Co is denoted by Tri 1a, Tri 1b, Tri 1c. The three-phase domain Sm_1Co_7 + Co + liquid is denoted by Tri 2a. The four-phase eutectic equilibrium between Sm_1Co_7 + Zr_2Co_{11} + Co + liquid is denoted by Qua 1. The three-phase region Sm_1Co_7 + Zr_2Co_{11} + Co is denoted by Tri 3a.

phase field has been observed between them, and it confirms that $Sm_2Co_{17}(H)$ is not observed in the Sm–Co binary phase diagram.

As suggested by Nishio et al. [10], the $Sm_2Co_{17}(H)$ structure is probably obtained by deformation of the $SmCo_5$ structure through the disordered $SmCo_7$ structure.

This result is just a point of departure and will be completed by a second isoplethic section with Co = 85 at.% before performing further investigations on quaternary and quinary alloys corresponding to the permanent magnet composition.

The single-phase state obtained at high temperature near 1150°C in 2:17-type permanent magnets is a precursor of the cellular microstructure [1–11]. At this point of investigation, the formation of this single-phase state seems for a large part to be controlled by Zr addition.

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References

[1] A.E. Ray and S. Liu, *J. Mater. Eng. Perform.*, *1* (1992) 183.
[2] G.V. Ivanova, L.M. Magat, A.G. Popov, V.G. Maykov, V.I. Khrabrov and Ya.S. Zhur, *Fiz. Met. Metalloved.*, *53* (1982) 687.
[3] A.E. Ray, *J. Appl. Phys.*, *55* (1984) 2094.
[4] D. Li and K.J. Strnat, *J. Appl. Phys.*, *55* (1984) 2103.
[5] G.V. Ivanova, A.G. Popov, L.M. Magat, V.G. Maykov, T.Z. Puzanova, Ya.S. Shur and N.V. Nikolayeva, *Fiz. Met. Metalloved.*, *59* (1985) 1114.
[6] Y. Morita, T. Umeda and Y. Kimura, *IEEE Trans. Magn.*, *23* (1987) 2702.
[7] T.S. Chin, W.C. Chang, R.T. Chang, M.P. Hung and H.T. Lee, *IEEE Trans. Magn.*, *25* (1989) 3782.
[8] L. Cataldo, A. Lefevre, F. Ducret, M.Th. Cohen-Adad, C.H. Allibert and N. Valignat, in preparation.
[9] H. Fujii, M.V. Satyanarayana and W.E. Wallace, *Solid State Commun.*, *41* (1982) 445.
[10] T. Nishio, Y. Fukui and Y. Iwana. *J. Jpn. Inst. Met.*, *52* (1988) 502.
[11] S. Derkaoui, C.H. Allibert, F. Delannay and J. Laforest. *J. Less-Common Met.*, *136* (1987) 75.
[12] C. Maurry, L. Rabenberg and C.H. Allibert, *J. Less-Common Met.*, *140* (1993) 57.
[13] S. Derkaoui, N. Vallignat and C.H. Allibert, in preparation.