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A Contribution to the Sm–Co Phase Diagram

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The Co-rich part of the Sm–Co system has been investigated by X-ray diffraction, metallographic and thermoanalytic methods. The existence of five closely related compounds (Sm_2Co_7 , SmCo_{5-x} , SmCo_5 , SmCo_{5+x} and $\text{Sm}_2\text{Co}_{17}$) has been confirmed. A tentative phase diagram of the Co-rich part of the Sm–Co system is presented. The practical difficulties encountered in the construction of this phase diagram are discussed.

Introduction

Since the discovery that permanent magnets with large coercivity, remanence and energy-product can be prepared on the basis of the SmCo_5 intermetallic compounds, many versions of the phase diagram of the binary Sm–Co system have been presented (Lihl, Ehdal, Kirchmayr & Wolf, 1969; Buschow & Van der Goot, 1968; Naastepad, Den Broeder & Klein-Wassink, 1973). Recently, however, two new phases, SmCo_{5-x} (a phase variant of the CaCu_5 -type structure) (Khan & Feldmann, 1973) and SmCo_{5+x} (of the TbCu_7 -type structure) (Khan, 1974), have been reported to exist in this binary system. Even in the most recent phase diagram of the Sm–Co system (Buschow & Den Broeder, 1973), these two phases are missing. Investigations were therefore carried out in order to amend the Sm–Co phase diagram.

Experimental

The alloys in the composition-range Sm_2Co_7 to $\text{Sm}_2\text{Co}_{17}$ were prepared in two series. For the first series, the alloys (1–3 g) were arc-melted on a water-cooled copper hearth under an atmosphere of specially purified argon gas (10–15 ppm oxygen). The elements were supplied by HEK (Lübeck) and had the reported purity 99.9 and 99.999 wt.% for Sm and Co respectively. The second series of alloys was prepared by casting the Sm–Co alloys (weighting about 100–150 g) in copper dies cooled by liquid nitrogen in a Balzer's medium frequency induction oven. The elements for this series were supplied by Th. Goldschmidt (Essen) and had the purity of 99.9 wt.% for both the elements.

The alloys were investigated in the as-cast state as well as after annealing at temperatures between 500 and 1400°C (depending upon the composition of the alloy)

for $\frac{1}{2}$ hour to three weeks (depending upon the annealing temperature) and subsequent quenching in liquid nitrogen.

In order to avoid oxidation of alloys during heat-treatment, the specimens, wrapped in tantalum foil, were encapsulated in quartz ampoules filled with specially purified argon gas (Khan & Qureshi, 1973).

The final composition of the alloy specimens was determined, before and after annealing, with a Philips X-ray fluorescence spectrometer with an accuracy of better than 1 wt. %.

For X-ray diffraction analysis, an Enraf-Nonius Guinier camera and a Philips horizontal goniometer, both provided with a Philips Co anode fine-focus X-ray tube (of 1 kW power) were used. Metallography was carried out with a Leitz polarization microscope. Differential thermal analysis was carried out in recrystallized alumina crucibles with a Linseis 'DTA-Anlage'. The temperatures were measured with an accuracy of $\pm 5^\circ\text{C}$.

Results and discussion

The intermetallic compounds found in the Co-rich part of the binary Sm-Co system are listed in Table 1. The compounds having composition close to Sm_2Co_7 and $\text{Sm}_2\text{Co}_{17}$ were found to be single phase, the former melting peritectically and the latter congruently. Both these compounds exhibit polymorphism. The high-temperature phase modification of Sm_2Co_7 [$\text{Sm}_2\text{Co}_7(h)$] is hexagonal of the Ce_2Ni_7 -type structure, whereas the low-temperature phase modification [$\text{Sm}_2\text{Co}_7(L)$] crystallizes in a rhombohedral structure of the Gd_2Co_7 -type. The transformation of $\text{Sm}_2\text{Co}_7(L)$ into $\text{Sm}_2\text{Co}_7(h)$ takes place at $1080 \pm 20^\circ\text{C}$. Our results on Sm_2Co_7 contradict, therefore, those of Buschow (1970). Fig. 1(a) shows the Guinier X-ray pattern of $\text{Sm}_2\text{Co}_7(h)$. It is seen that the reflexions are quite sharp contrary to previous findings (Buschow, 1970). The structural data for this modification of Sm_2Co_7 are given in Table 2. The agreement between the calculated and observed intensities is satisfactory with the exception that the reflexions 002, 208 and 1,0,16 are not observed, whereas the calculation shows that they should be observable. Point defects or small deviations in the atomic positions from those given in Table 2 may be responsible for this discrepancy. Similar discrepancies were also found in the structural data for $\text{Sm}_2\text{Co}_7(L)$. X-ray

diffraction analysis on the single crystals of $\text{Sm}_2\text{Co}_7(h)$ and $\text{Sm}_2\text{Co}_7(L)$ is still being carried out in order to explain these discrepancies. The results will be presented in a separate paper.

The $\text{Sm}_2\text{Co}_{17}$ compound crystallizes in a hexagonal high-temperature modification [$\text{Sm}_2\text{Co}_{17}(h)$] of the disordered TbCu_7 -type and a rhombohedral low-temperature modification [$\text{Sm}_2\text{Co}_{17}(L)$] of the $\text{Th}_2\text{Zn}_{17}$ -type (Khan, 1973). The crystal structure of $\text{Sm}_2\text{Co}_{17}(h)$ is therefore neither of the $\text{Th}_2\text{Ni}_{17}$ -type [reported by Buschow & Van der Goot (1968)] nor of the CaCu_5 -type [reported by Khan & Müller (1973)]. The discrepancy in the observed and calculated intensities for $\text{Sm}_2\text{Co}_{17}(h)$ on the basis of the CaCu_5 -type structure [as pointed out by Khan & Müller (1973)] can be removed on the basis of the TbCu_7 -type structure with disordered substitutions (Khan, 1973). $\text{Sm}_2\text{Co}_{17}(h)$ transforms into $\text{Sm}_2\text{Co}_{17}(L)$ at about 1310°C .

The investigations of the compounds SmCo_{5+x} ($-0.3 \leq x \leq 1$) were found to be very difficult. The overall impression was that in this composition range only one compound existed, *i.e.* of the CaCu_5 -type. The Guinier X-ray diffraction patterns of the as-cast alloys showed, however, extraordinary broadening of most of the diffraction lines [Fig. 1(b)]. The broadening of powder X-ray diffraction lines is usually due to the following causes:

(a) the average crystallite size is very small ($< 1000 \text{ \AA}$); the density of stacking or layer faults is very high.

(b) Microstrain is introduced in the crystal structure owing to cold work (*i.e.* grinding) or quenching from the melt in a similar way as in the case of the σ - and β -tungsten phases, since the structure of these compounds is very brittle.

However, if we neglect, for the time being, the broadening of the diffraction lines due to the above-mentioned effects, the X-ray diffraction pattern of these compounds, which is shown in Fig. 1(b), can be indexed on the basis of the CaCu_5 -type structure. The photomicrographs of these compounds (Fig. 2) show the distinct presence of three phases. Another way of explaining this broadening of X-ray powder diffraction lines of Fig. 1(b) would then be that these compounds solidify in a composite of phases, the lattice parameters of which are very close to one another. Two of them (SmCo_{5-x} and SmCo_5) have already been reported by Khan (Khan & Feldmann, 1973; Khan & Qureshi, 1973). A third phase (SmCo_{5+x} , $0.2 \leq x \leq 0.6$)

Table 1. *Intermetallic compounds in the Co-rich part of the Sm-Co system*

Compound	Lattice parameters			Structure	Remarks
	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>		
Sm_2Co_7 ; $\text{Sm}_2\text{Co}_7(h)$	5.043 ₃	24.311 ₇	0.8033	hexagonal, Ce_2Ni_7 -type	peritectic; <i>c/a</i> for sub-structure of the CaCu_5 -type
$\text{Sm}_2\text{Co}_7(L)$	5.06 ₁	36.50 ₄	0.801 ₄	rhombohedral, Gd_2Co_7 -type	
SmCo_{5-x} $x \leq 0.2$	5.00 ₄	3.97 ₄	0.794 ₂	hexagonal	CaCu_5 -type with stacking faults
SmCo_5	4.99 ₇	3.97 ₈	0.796	hexagonal, CaCu_5 -type	congruently melting
SmCo_{5+x} $0.2 \leq x \leq 0.6$	4.96 ₇	4.00 ₁	0.805 ₃	hexagonal, TbCu_7 -type	disordered
$\text{Sm}_2\text{Co}_{17}$; $\text{Sm}_2\text{Co}_{17}(h)$	4.85 ₆	4.08 ₁	0.840 ₄	hexagonal, TbCu_7 -type	congruently melting disordered
$\text{Sm}_2\text{Co}_{17}(L)$	8.40 ₂	12.23 ₁	1.455 ₇	rhombohedral, $\text{Th}_2\text{Zn}_{17}$ -type	

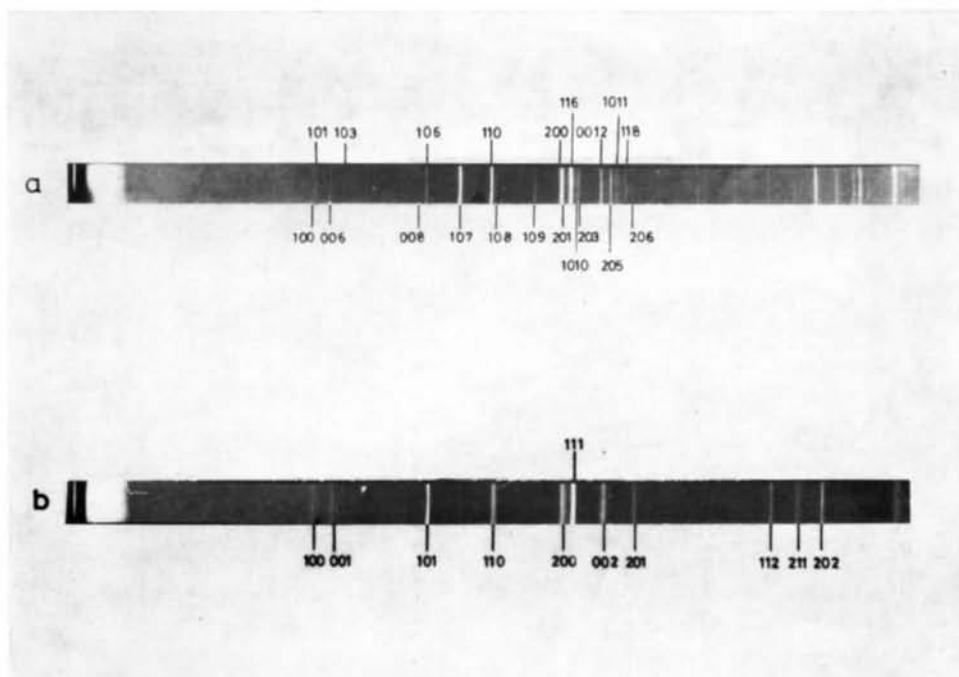


Fig. 1. Guinier X-ray diffraction photographs (5 h Co K α ; 30 kV, 30 mA) of (a) Sm_2Co_7 , annealed at 1200°C for 12 h and quenched in liquid N_2 (b) $\text{SmCo}_{5.2}$ (as-cast). The broadening of the reflexions 110, 200, 002, 201 and 211 is noteworthy. The weak satellite to the right of the reflexion 100 (marked at the bottom) belongs to SmCo_{5-x} .

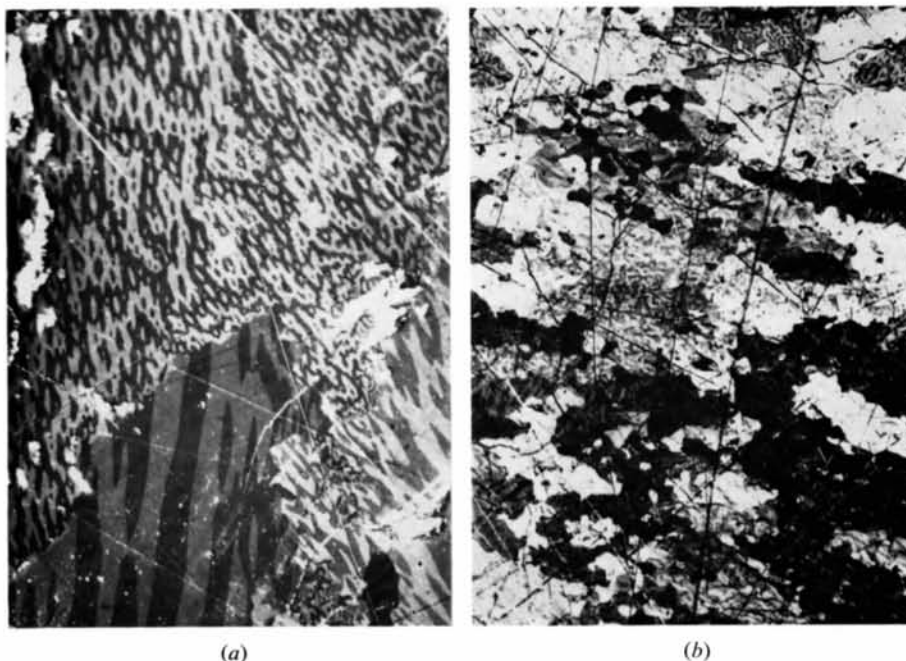


Fig. 2. Photomicrographs of $\text{SmCo}_{5.2}$ (as-cast), (a) Kerr-effect, $200\times$; (b) etched with 1% alcoholic nitric acid for 10 s, $200\times$. Dark, gray and white islands represent SmCo_{5-x} , SmCo_5 and SmCo_{5+x} phases respectively.

Table 2. Crystal structure of $\text{Sm}_2\text{Co}_7(h)$

Experiment: Sm_2Co_7 alloy annealed at 1200°C for 24 h and quenched in liquid nitrogen; Guinier X-ray photograph, 5h Co $K\alpha$ (30 kV, 30 mA).

Structure: Ce_2Ni_7 -type, $p6_3/mmc$ (D_{6h}^{14}),
 $a = 5.043$ Å, $c = 24.311$ Å
 c/a (sub-structure of the CaCu_5 -type) = 0.8033

4Sm (f) $\frac{1}{3}, \frac{2}{3}, z$ ($z = 0.0302$)
 4Sm (f) $\frac{1}{3}, \frac{2}{3}, z$ ($z = 0.1747$)
 2Co (a) 0, 0, 0
 4Co (e) 0, 0, z ($z = 0.1670$)
 4Co (f) $\frac{1}{3}, \frac{2}{3}, z$ ($z = 0.8334$)
 6Co (h) $x, 2x, \frac{1}{2}$ ($x = 0.8351$)
 12Co (k) $x, 2x, z$ ($x = 0.8338, z = 0.0854$).

Remarks: Atom-parameters are taken from Cromer & Larson (1959).
 $I_c = 10^{-4} \text{HPLG} |F_c|^2$ (see Sagel, 1958).
 All reflexions permitted by the space group have been included.

<i>h</i>	<i>k</i>	<i>l</i>	$\sin^2 \theta_c$	$\sin^2 \theta_o$	I_o	I_c
0	0	2	0.0054	n.o.	0	7
0	0	4	0217	n.o.	0	3
1	0	0	0420	0.0419	13	15
1	0	1	0433	0433	35	31
1	0	2	0474	n.o.	0	3
0	0	6	0488	0488	18	20
1	0	3	0542	0540	10	9
1	0	4	0637	n.o.	0	3
1	0	5	0759	n.o.	0	1
0	0	8	0868	0868	30	26
1	0	6	0908	0908	80	74
1	0	7	1084	1084	490	523
1	1	0	1260	1260	415	407
1	0	8	1288	1287	15	33
1	1	2	1314	n.o.	0	3
0	0	10	1356	n.o.	0	4
1	1	4	1477	1477	5	6
1	0	9	1518	1519	50	47
2	0	0	1680	1680	100	112
2	0	1	1694	1693	290	281
2	0	2	1734	n.o.	0	0
1	1	6	1748	1749	841	841
1	0	10	1776	1775	6	8
2	0	3	1802	1802	70	67
2	0	4	1897	n.o.	0	0
0	0	12	1952	1954	130	121
2	0	5	2019	2019	125	148
1	0	11	2060	2060	50	69
1	1	8	2128	2128	75	73
2	0	6	2168	2168	30	26
2	0	7	2344	2342	4	6
1	0	12	2372	2371	20	25
2	0	8	2547	n.o.	0	10
1	1	10	2616	2617	20	20
0	0	14	2657	2658	55	48
1	0	13	2711	2713	25	30
2	0	9	2778	n.o.	0	0
2	1	0	2940	2950	8	6
2	1	1	2954			
2	1	2	2994	n.o.	0	0
2	0	10	3036	n.o.	0	2
2	1	3	3062	n.o.	0	3
1	0	14	3077	3077	30	46
2	1	4	3157	n.o.	0	1
1	1	12	3212	3211	30	15
2	1	5	3279	n.o.	0	0
2	0	11	3320	n.o.	0	3
2	1	6	3428	3429	25	28
1	0	15	3470	3465	8	11
0	0	16				

Table 2 (cont.)

2	1	7	3604	3605	265	266
2	0	12	3632	3633	7	13
3	0	0	3780	3777	116	115
3	0	1	3794	n.o.	0	0
2	1	8	3808	3810	8	18
3	0	2	3834	n.o.	0	1
1	0	16	3890	n.o.	0	8
3	0	3	3902	n.o.	0	0
1	1	14	3917	3922	145	151
2	0	13	3971	3972	200	195
3	0	4	3977	n.o.	0	2
2	1	9	4038	4040	30	31
3	0	5	4119	n.o.	0	0
3	0	6	4268	4272	300	307

has recently been found (Khan, 1974). More work is being carried out in order to derive the individual contributions of the above-mentioned effects to this X-ray diffraction line broadening.

Fig. 3 shows the equilibrium phase diagram of the Co-rich part of the Sm-Co system. In fact, it was not possible to obtain the compounds SmCo_5 , SmCo_{5-x} and SmCo_{5+x} as single phase either by compositional variation or by change of annealing temperature. In order to insert these phases in the phase diagram, use has been made of the following facts:

- (a) SmCo_5 and SmCo_{5+x} are unstable at low temperatures,
- (b) the c parameter of SmCo_{5+x} is larger than that of SmCo_5 ,
- (c) SmCo_{5-x} forms peritectically and contains a few additional, weak X-ray diffraction lines in its spectrum.

The alloys were therefore prepared in the composition range, SmCo_{5+x} ($-0.3 \leq x \leq 1$), in 0.1 steps and the above-mentioned changes were noted after an-

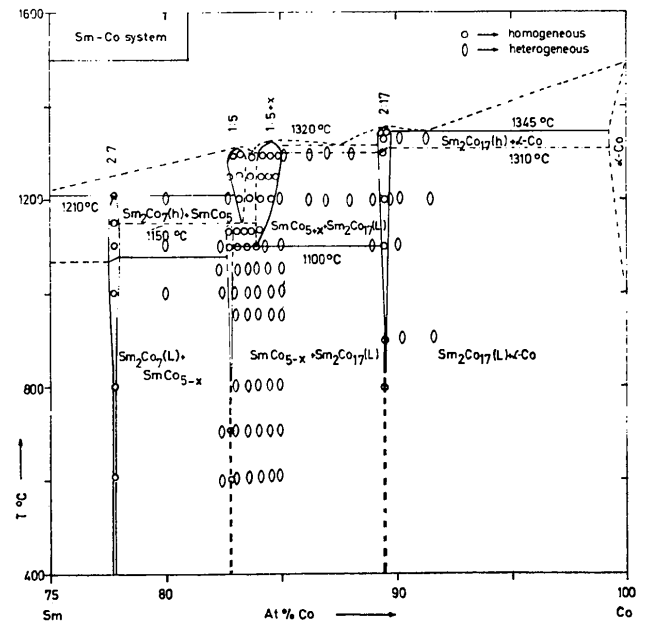


Fig. 3. Phase diagram of the Co-rich part of the Sm-Co system.

nealing at and quenching (LN₂) from different temperatures.

It should be mentioned that results obtained with differential thermal analysis (DTA) did not agree with those obtained by metallographic and X-ray diffraction methods. For example, with DTA, SmCo_{5±x} and Sm₂Co₁₇ compounds were found to be peritectically melting in agreement with the results of Lihl *et al.* (1969) and Buschow & Van der Goot (1968). However, with X-ray diffraction and metallographic methods, these compounds were found to be congruently melting. A shift in the composition of the alloys due to oxidation, evaporation of Sm and chemical reactivity of Sm with crucible materials at elevated temperatures may lead to this discrepancy. In the case of metallographic and X-ray diffraction methods, this compositional shift can be detected and interpreted directly, whereas in the case of DTA this is not possible since the change in composition occurs gradually. Even if oxidation of the samples can be avoided by taking special precautions, however, evaporation and reaction (with crucible materials) of Sm are practically unavoidable.

The Co-rich part of the Sm-Co phase diagram (Fig. 3) differs from that even very recently reported (Buschow & Den Broeder, 1973) in the following respects:

- (a) the two polymorphic forms of Sm₂Co₇ and Sm₂Co₁₇ have been inserted correctly,
- (b) no peritectic has been observed in the composition range SmCo_{5+x} ($-0.3 \leq x \leq 1$),
- (c) one peritectoid and two eutectics have been inserted,
- (d) the new phases SmCo_{5-x} and SmCo_{5+x} have been correctly inserted.

It should be noted that SmCo_{5+x} and Sm₂Co_{17(h)} are isostructural (*i.e.* of the TbCu₇-type with disordered substitutions). It means that we should obtain a homogeneous region from SmCo_{5+x} to Sm₂Co_{17(h)} in the phase diagram, at least, at temperatures near to the solidus. What we experimentally obtain is a eutectic in the neighbourhood of SmCo₇. An explanation for this discrepancy is still being sought.

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Crystal Structure of Monoclinic NaCaHSiO₄

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Monoclinic NaCaHSiO₄ has a structure based on Ca²⁺ and Na⁺ ions and HSiO₄³⁻ groups, which are linked into chains by strong hydrogen bonds. The structure is similar to that of an orthorhombic form, from which it differs in the orientation of the silicate tetrahedra and the arrangement of hydrogen bonds.

NaCaHSiO₄, first synthesized by Thilo, Funk & Wichmann (1951), is important in relation to processes for extracting alumina from aluminosilicate materials. From chemical and other evidence, these workers suggested that it contained separate HSiO₄³⁻ tetrahedra. This conclusion was supported by the spectroscopic studies of Stavitskaya, Ryskin & Mitropol'skii (1968),

who concluded also that the tetrahedra were linked by strong hydrogen bonds. Gard, Ramsay & Taylor (1973) reported crystal data; they found the crystals to be monoclinic. In contrast, Lyutin, Kazak, Ilyukhin & Belov (1972) reported a structure determination on crystals that they had found to be orthorhombic, with cell parameters closely related to those given by Gard.