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A Revision of the Al-Rich Region of the Sm-Al Phase Diagram: The Sm_3Al_{11} Phase

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Phase equilibria in the Al-rich region of the Sm-Al binary system has been revised and updated: it has been confirmed that Sm_3Al_{11} is a congruently melting phase which, on cooling, undergoes catatectic decomposition $Sm_3Al_{11} \leftrightarrow$ liquid + $SmAl_3$.

Keywords Al-Sm system, Al-Sm phase diagram, experimental phase equilibria, rare earth intermetallics

1. Introduction

While most of the R-Al systems are quite well established, the Sm-Al still needs investigation because of some uncertainties emerging from a comparison of literature data.

A comprehensive examination of R-Al diagrams formed by the trivalent rare earth elements with Al shows progressive and systematic variations in the constitutional properties.[1,2] Light rare earth R-Al diagrams present the Al-richest R_3Al_{11} phase,which is absent in the heavy rare earth R-Al diagrams.

The first partial phase diagram for the Sm-Al system is reported in literature by Buschow and Van Vucht[3] and Casteels,[4] where only the Al-rich region (~66-100 at.% Al) was investigated. The Al-richest part (96-100 at.% Al) of the diagram was subsequently studied by Kononenko and Golubev.[5] The diagram shows four intermetallic line compounds stable at room temperature and the Sm_3Al_{11} phase with a congruent melting and a catatectic decomposition at 1066 °C. This part of the phase diagram is significantly different from the corresponding regions of other R-Al systems, wherein the R_3Al_{11} phases have been described as stable down to room temperature with an $\alpha \leftrightarrow \beta$ transformation in the solid state. In all the R-Al systems the Al-richest congruent melting compounds are RAl_2 and the other Al-richer phases have a peritectic or peritectoidal formation. The peritectoidal formation of $SmAl_3$ is characteristic of the light rare-earths (La, Ce, Pr, Nd).

Owing to a lack of data and the thermodynamically improbable shape of the liquidus curve in this diagram, a series of thermal analyses was performed by Saccone et al.[6] and thermodynamic investigations by Borzone et al.[7]; this has made it possible to re-define and calculate the Sm-Al phase diagram. In the paper by Saccone et al.[6] the congruent melting of Sm_3Al_{11} was confirmed, however, suggesting a melting temperature of 1380 °C, lower than the value ~1450 °C as earlier reported in literature.[3,4] A thermal effect was observed around the Sm_3Al_{11} composition at about 1070 °C. Nevertheless, it was not possible to definitely attribute this effect either to a catatectic reaction or to an allotropic transformation (as observed in the alloys of other light rare earths).

In the same paper a thermodynamic optimization was performed by alternatively considering the two hypotheses described above, catatectic reaction or allotropic transformation, and also by using several thermodynamic data relevant to the Ce-Al liquid alloys.[6] It was not possible to decide between the two alternatives because the available experimental information on this point was uncertain and both solutions were thermodynamically consistent.

Considering that the remaining part of the phase diagram seemed to be well defined, we decided to review the Al-rich part of the diagram, giving special attention to microscopic techniques.

This seemed to be useful also on the basis of the preliminary results we had obtained in the investigation of the Sm-Ni-Al system.[8,9] New experimental information on the Sm-Al system may also be useful in obtaining the best CALPHAD optimization.

2. Experimental Details

The samples were prepared by induction-melting of a mixture of weighed and polished small pieces of pure metals in alumina-sintered crucibles. The samples were examined as cast or after annealing in alumina containers sealed in steel cylinders or in quartz tubes at different temperatures and then quenched in cold water. The handling, synthesis and thermal treatment of the samples were performed under argon atmosphere. The metals used are: aluminum (WAV AG "Kryal") 99.999 and samarium (JM Alfa Aesar®) 99.9 minimum mass% purity.

Microstructures of the alloys were systematically investigated by light optical microscopy (LOM), and a scanning electron microscope (SEM), and quantitative data were

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Table 1 Selected Sm-Al binary alloys investigated in this work

No.	Sm at.%	Al at.%	Thermal treatments	Phase observed (EPMA and XRD) and microstructure notes
1	5.0	95.0	As cast	Sm_3Al_{11} primary crystals and fine eutectic structure
2	5.0	95.0	Annealed 10 days at 500 °C, quenched	Sm_3Al_{11} primary dendritic crystals and eutectic structure
3	5.0	95.0	Annealed 35 days at 580 °C, quenched	Primary crystals showing a catatectic decomposition formed by a mixture of $SmAl_3$ and (Al) surrounded by eutectic structure
4	11.0	89.0	As cast	Sm_3Al_{11} primary dendritic crystals and fine eutectic structure
5	11.0	89.0	Annealed 10 days at 600 °C, quenched	Primary crystals of Sm_3Al_{11}, catatectic decomposition surrounded by eutectic structure
6	11.0	89.0	Annealed 15 days at 750 °C, quenched	Non-uniform sample: large $SmAl_3$ crystals and small amount of catatectic liquid, surrounded by eutectic mixture
7	21.4	78.6	As cast	Homogeneous sample: polygonal Sm_3Al_{11} crystals
8	21.4	78.6	Annealed 10 days at 500 °C, quenched	Primary crystals showing an uncompleted catatectic reaction and eutectic structure
9	21.4	78.6	Annealed 30 days at 800 °C, quenched	Large $SmAl_3$ crystals surrounded by a fine eutectic structure. See Fig. 2 and 3. Notice the small quantities of Sm_3Al_{11} crystals with catatectic droplets showing the structure corresponding to the subsequent eutectic reaction

collected by electron probe microanalysis (EPMA). Samples for X-ray diffraction were powdered and analyzed by means of a Debye-Scherrer camera with Cu-Kα filtered radiation. Values of the lattice parameters were processed and refined through a least-squares interpolation, by using the Nelson-Riley function.[10]

3. Results and Discussion

Table 1 summarizes the data obtained in the examination of some Al-rich alloys. On the basis of these results, it may be concluded that the Sm_3Al_{11} from the liquid easily forms as primary crystals, and its catatectic decomposition is confirmed. Sm_3Al_{11} monophasic-polycrystalline as cast samples, after annealing, showed indeed the characteristic catatectic morphology[11] and a gradual decomposition corresponding to the reaction $Sm_3Al_{11} \rightarrow$ liquid + $SmAl_3$, in agreement with the papers by Buschow[3,12] and by Casteels.[4] This reaction however is very sluggish: after annealing at 800 °C for 1 month, some unreacted Sm_3Al_{11} may still be observed. The version of the phase diagram in Fig. 1, is drawn on the basis of the present results and the literature data,[3-6] where, for the catatectic reaction, an average value of ~1070 °C is reported, as suggested by different authors.[3,4,6]

Figures 2 and 3 show the typical metallographic appearance of a sample which underwent a catatectic reaction (sample alloy No. 9 in Table 1).

The cell parameters obtained for the phases observed in our samples are:

Sm_3Al_{11} tI10(Al def)-$BaAl_4$ type, a = 428.1(1) pm, c = 990.6(2) pm (literature data: a = 428.7 pm, c = 990.5 pm[13]; a = 428 pm, c = 990 pm[4])

$SmAl_3$ hP8-Ni_3Sn type, a = 638.8(1) pm, c = 460.7(1) pm (literature data: a = 638.0 pm, c = 459.7 pm[13]; a = 638.0(3) pm, c = 459.7(4) pm[12])

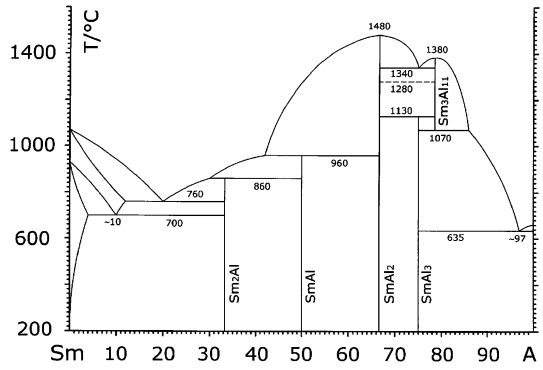

Fig. 1 Sm-Al phase diagram proposed on the basis of present results and literature data[3,4,6]

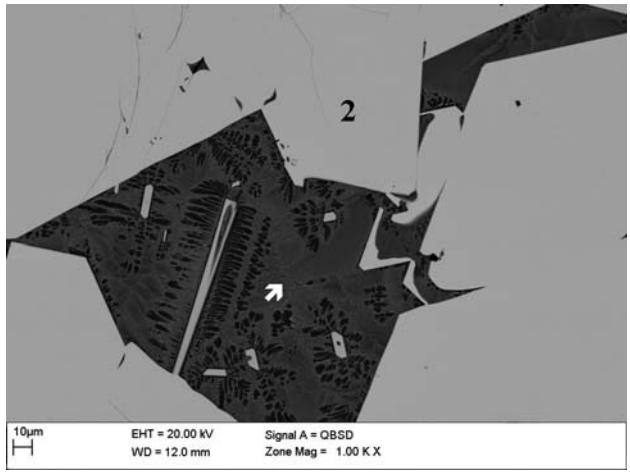

Fig. 2 BSE micrograph of a $Sm_{21.4}Al_{78.6}$ sample (No. 9 in Table 1). Large grown crystals of $SmAl_3$ (2) surrounded by fine eutectic structure (indicated by the arrow). Notice the small quantities of Sm_3Al_{11} crystals with catatectic droplets showing the structure corresponding to the subsequent eutectic reaction

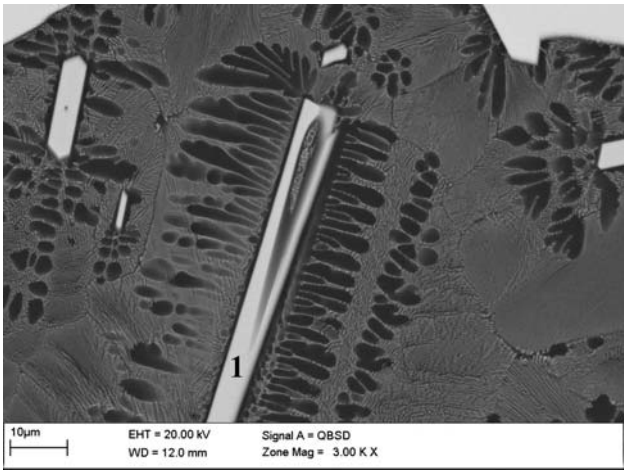

Fig. 3 Detail of the Fig. 2 with greater magnification. Sm_3Al_{11} (1) crystals with catatectic droplets showing the structure corresponding to the subsequent eutectic reaction

For the Sm_3Al_{11} we may observe a good agreement with the literature data while for the $SmAl_3$ a small discrepancy may be noticed, similar to that reported in literature for the $GdAl_3$ phase.[14]

The metastable oI28-Sm_3Al_{11} phase was not observed as reported also in Ref[6] and Ref[7].

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