ELSEVIER

Journal of Alloys and Compounds 229 (1995) 283-286

Journal of ALLOYS AND COMPOUNDS

The scandium–rhodium phase diagram

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Received 13 February 1995; in final form 18 April 1995

Abstract

As a result of an investigation of the alloys of the Sc–Rh system using metallography, X-ray diffraction, microprobe and differential thermal analysis and melting point determination according to the method of Pirani and Alterthum, the constitutional diagram of the Sc–Rh system has been constructed. Two intermediate phases, Sc_2Rh and Sc_3Rh, were observed. The existence of three other phases in this system, namely $ScRh_3$ (Cu_3Au-type structure), ScRh (CsCl) and $Sc_{57}Rh_{13}$ (a proper type of structure), has been confirmed. The phases ScRh, Sc_3Rh and $Sc_{57}Rh_{13}$ melt congruently at 1990 °C, 1110 °C and 1150 °C respectively. The phases $ScRh_3$ and Sc_2Rh form by peritectic reactions at 1650 °C and 1080 °C respectively. The phases Sc_2Rh and Sc_3Rh decompose by the solid state reactions at 980 °C and 930 °C respectively. The coordinates of four eutectic points and one eutectoid point are determined.

Keywords: Scandium; Rhodium; Phase diagrams

1. Introduction

The phase diagram of the Sc–Rh system has not been investigated previously. Data on crystal structures of some scandium–rhodium intermediate phases are present in the literature. However, information on preparation and temperatures of formation, and also on solid solubility regions, is completely absent. It is only known that the phase based on $ScRh_3$ has the cubic Cu_3Au-type structure with lattice period $a = 3.900$ Å [1], $a = 3.898$ Å [2] and $a = 3.909$ Å [3]. According to the data of Refs. [4,5], the equiatomic compound ScRh with the CsCl-type structure and lattice period $a = 3.206$ Å [4] and $a = 3.204$ Å [5] also exists. It is known [6] that the thermodynamic stability of the phase based on ScRh is higher than that of $ScRh_3$ (standard enthalpies $\Delta_f H^0_{298.15}$ of formation of -94.5 ± 1.5 kJ mol^{-1} and -51.7 ± 1.4 kJ mol^{-1} respectively). A compound of the stoichiometry $Sc_{57}Rh_{13}$ with a proper cubic type of structure and $a = 14.4051(7)$ Å was reported in Ref. [7]. In studies devoted to superconductivity of the alloys, assumptions were made as to the existence of Sc_3Rh [2] as well as $ScRh_2$, Sc_2Rh and Sc_4Rh [8], but no data on structure and lattice periods have been reported.

2. Experimental methods

As starting material rhodium powder was used with a nominal purity of 99.96%, preliminarily sintered in vacuum at 1200 °C and then arc remelted. We used also scandium metal of which the metal impurity content did not exceed 0.15 wt.%, the oxygen impurity content being 1.3 wt.%. The alloys for the investigation were prepared by arc melting with a non-consumable tungsten electrode on a water-cooled copper hearth in an atmosphere of purified argon. The weight losses during melting were on the average up to 1.15 wt.% and were attributed to losses of the more volatile component scandium. After preliminary measurements of the melting points of the as-cast samples by the method of Pirani and Alterthum [9], the homogenizing annealings, depending on the compositions, were conducted at 1400 °C (100 h) or at 800 °C (300 h). After annealing at 1400 °C with a view to revealing the solubility changes of the alloys with

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0925-8388/95/$09.50
SSDI 0925-8388(95)01694-5

decreasing temperature, further annealing at 800 °C was carried out.

The investigation of cast and annealed alloys was carried out by a metallography, X-ray diffraction, microprobe analysis and differential thermal analysis.

The microstructural examination of the scandium-rich alloys was conducted after chemical etching in a solution containing nitric acid and glycerine in a volume ratio of 1:3. The other alloys were electrochemically etched by a glycerine solution of aqua regia ($HCl:HNO_3$:glycerine = 3:1:2). X-ray diffraction studies of the alloys were conducted using a Debye camera with a diameter of 57.3 mm and an Ni-filter with Cu Kα radiation as well as with a diffractometer for planar sections. The calculation of the lattice parameters was carried out by means of a program based on the method of Cohen [10] and Hess [11]. Microprobe analyses were conducted using a JEOL Superprobe-733 instrument, which gave an accuracy of ±1 at.%. For thermographic studies a W-(W-20%Re) wire thermocouple served as a pick-up.

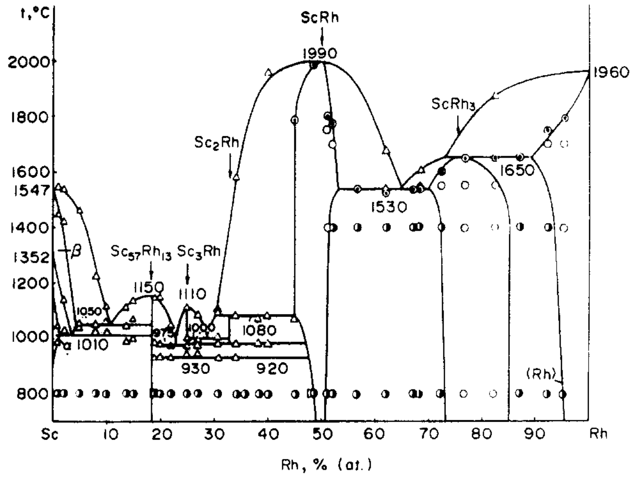

Fig. 1. The Sc–Rh phase diagram: ○, single phase; ◑, two phases; ⊙, solidus; □, microprobe; △, thermal analysis.

3. Results and discussion

The results of the investigation made it possible for the first time to construct the Sc–Rh phase diagram (Fig. 1). The accuracy is equal to ±1 at.% and ±20 °C. It has been established that intermediate phases based on five compounds form in this system (Table 1): $ScRh_3$, ScRh, Sc_2Rh, Sc_3Rh and $Sc_{57}Rh_{13}$. The phase based on ScRh forms congruently at 1990 °C. This phase has an extensive homogeneity region, extending at subsolidus temperatures from 45 to 53 at.% Rh. With decreasing temperature this region becomes narrower and at 800 °C extends between 48.5 and 50.7 at.% Rh. The crystalline lattice of the ScRh phase, in accordance with literature information, belongs to the CsCl structure type. Its lattice period within the limits of measuring error (±0.02 Å) correlates with literature data and in the alloy with 48.5 at.% Rh amounts to 3.20 Å.

The second intermediate phase existing in the system, the $ScRh_3$ phase, forms by the peritectic reaction $L + \langle Rh \rangle \rightleftharpoons ScRh_3$ at 1650 °C. The incongruent nature of its formation has been derived on the basis of the typical peritectic microstructures of the cast alloys within the composition field 76.4-86.5 at.% Rh (Fig. 2(a)). The peritectic point is placed at nearly 73 at.% Rh, which results from the difference in microstructures of the cast alloys with 76.4 and 72.2 at.% Rh. In the latter alloy the primary $ScRh_3$ phase crystallizes already on solidification of the melt and contains a small amount of the non-equilibrium eutectic. The $ScRh_3$ phase has an extensive homogeneity region of about 15 at.% (microstructures of the alloys with 72.2, 76.4 and 81.5 at.% Rh at 1560 °C are single phase). With decreasing temperature, according to the metallography data, the homogeneity region of $ScRh_3$ at the lower end of the rhodium content becomes somewhat narrower and expands at the upper end. The lattice period of this phase within the homogeneity region changes within the limits of measuring error of the

Table 1
Crystallographic data for Sc–Rh intermediate phases

Intermediate phase	Space group	Structure type	Lattice parameter *a* (Å)	
			Determined by us	Literature data
$ScRh_3$	*Pm*3*m*	Cu_3Au	3.89	3.900 [1] 3.898 [2] 3.909 [3]
ScRh	*Pm*3*m*	CsCl	3.20	3.206 [4] 3.204 [5]
Sc_2Rh		Not determined		
Sc_3Rh		Not determined		
$Sc_{57}Rh_{13}$	*Pm*$\bar{3}$	$Sc_{57}Rh_{13}$	14.40	14.4051(7) [6]

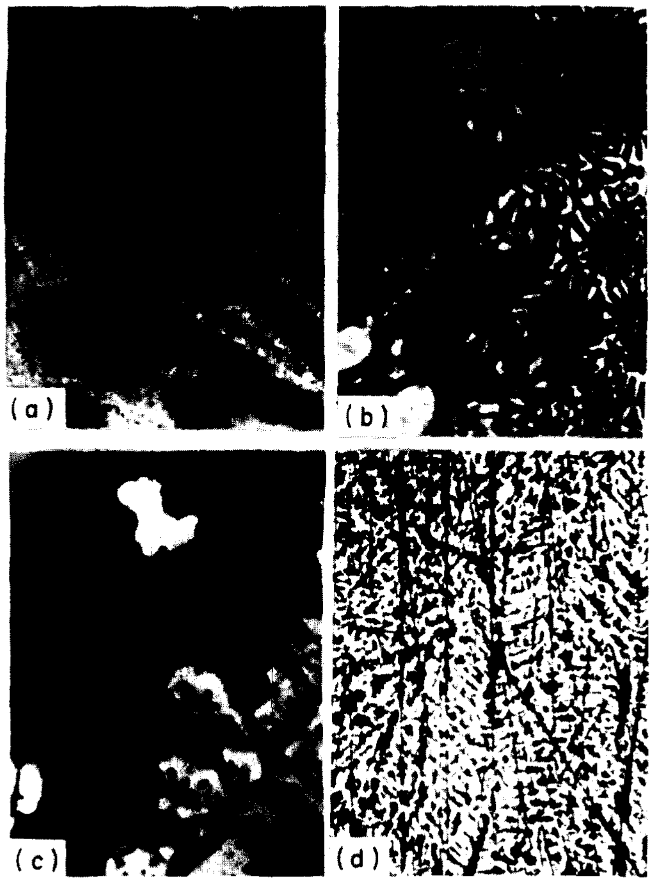

Fig. 2. Microstructures of the alloys of the Sc–Rh system: (a) 81.5 at.% Rh, cast, $\langle Rh \rangle + ScRh_3$; (b) 66.3 at.% Rh, cast, $ScRh_3$ + eutectic ($ScRh + ScRh_3$); (c) 34.1 at.% Rh, cast, $ScRh + Sc_2Rh$ + eutectic ($Sc_2Rh + Sc_3Rh$); (d) 5 at.% Rh, cast, eutectoid $\langle \beta\text{-}Sc \rangle \rightleftharpoons \langle \alpha\text{-}Sc \rangle + Sc_{57}Rh_{13}$. (Magnifications: (a) 340×; (b), (c) 1000×; (d) 120×.)

Debye–Scherrer method and coincides with the values summarized in Refs. [1–3].

The maximum solubility of scandium in rhodium was determined by the composition determined as the intersection point of the peritectic horizontal line with the solidus curve of the rhodium solid solution. It amounts to 12 at.% Sc and decreases with decreasing temperature (to about 4.5 at.% Sc at 800 °C). This is confirmed by the single-phase nature of the alloy with 91.2 at.% Rh after annealing at 1700 °C, whereas the alloy with 95.5 at.% Rh, annealed at 800 °C, contained the rhodium solid solution and a small amount of $ScRh_3$.

Our results show the existence of the eutectic equilibrium $L \rightleftharpoons ScRh + ScRh_3$ in the Sc–Rh system (Fig. 2(b)). The eutectic temperature has been determined by the method of Pirani and Alterthum on alloys containing 56.9–68.3 at.% Rh and amounts to 1530 °C. The position of the eutectic point (about 65 at.% Rh) has been established from microstructural data. X-ray diffraction studies of the alloys cast and annealed at 1400 and 800 °C within the composition field 56.9–72.2 at.% Rh, indicate that ScRh and $ScRh_3$ coexist in these alloys. Thus, the existence of the intermediate phase of stoichiometry $ScRh_2$, reported in Ref. [8], is not confirmed by us.

Within the range of compositions 50–100 at.% Sc we observed the existence of the intermediate phases based on Sc_2Rh and Sc_3Rh, and the existence of $Sc_{57}Rh_{13}$. The Sc_4Rh phase was not found by us.

Differential thermal analysis data of the alloys containing from 30.7 to 45.2 at.% Rh showed that the Sc_2Rh phase was formed by the peritectic reaction $L + ScRh \rightleftharpoons Sc_2Rh$ at 1080 °C. Metallography of the cast alloys of the present compositions indicates the occurrence of the primary phase ScRh (light dendrites), and then Sc_2Rh (grey) and the non-equilibrium eutectic ($Sc_2Rh + Sc_3Rh$), which appears as dark (Fig. 2(c)). No visible homogeneity region of the Sc_2Rh phase is found. The structure type was not determined because of difficulties of preparing the single-phase Sc_2Rh. This may be the result of a narrow homogeneity region. However, on the X-ray diagrams of the cast and annealed (at 800 °C) alloys, within the range 34.1–40 at.% Rh, we observed separate and independent lines. These were attributed to a phase of Ti_2Ni structure type by analogy with similar compounds of the same stoichiometry in the related systems Sc_2Ru and Sc_2Ir.

The stoichiometry, character and temperature of formation of the Sc_3Rh phase have been determined by us on the basis of the shape of the Sc_3Rh phase liquidus curve, derived from differential thermal analysis data of alloys containing from 22 to 27.2 at.% Rh. The alloy with 25.4 at.% Rh possesses the highest liquidus temperature (1110 °C), which indicates a congruent nature of crystallization of the phase based on Sc_3Rh. No visible homogeneity region of the Sc_3Rh phase is found. The structure type of its lattice is also not established because we have not obtained a single-phase Sc_3Rh alloy. From the shape of the liquidus curves it may be concluded that the Sc_2Rh and Sc_3Rh phases take part in the eutectic equilibrium $L \rightleftharpoons Sc_2Rh + Sc_3Rh$, which occurs, according to differential thermal analysis data, at 1000 °C. It can be seen that the eutectic mixture metallographically appears degenerate. The position of the eutectic point is established at about 29 at.% Rh, on the intersection of the Sc_2Rh and Sc_3Rh phase liquidus curves with the invariant eutectic horizontal line.

The existence of the phase $Sc_{57}Rh_{13}$ has been confirmed. From the shape of its liquidus curve, derived from differential thermal analysis data of alloys containing from 13.9 to 22 at.% Rh, we determined that this phase forms congruently at about 1150 °C. No visible homogeneity region of $Sc_{57}Rh_{13}$ is found. The crystalline lattice belongs to a cubic structure type with the period value $a = 14.40$ Å, as reported in Ref. [7]. Heating curves of the annealed alloys containing 19, 20 and 22 at.% Rh indicate the occurrence of the reaction $L \rightleftharpoons Sc_{57}Rh_{13} + Sc_3Rh$ at 975 °C. In the cast alloys of these compositions, according to the metallography data, the $Sc_{57}Rh_{13}$ crystallizes as the primary phase, followed by the degenerate eutectic ($Sc_{57}Rh_{13} + Sc_3Rh$).

The microstructural investigation of the alloys annealed at 800 °C, within the range of compositions 19–45.2 at.% Rh, reveals the presence of three phases, formed by both crystallization and solid state transformation. The thermal effects in the heating curves of these alloys in the temperature range 930–1000 °C substantiate the existence of solid phase transformation within the investigated range of compositions. With a view to establishing the compositions of the phases participating in the solid phase transformations, we performed microprobe analyses of the alloys annealed at 800 °C. The results showed that the phases based on ScRh, Sc_2Rh and $Sc_{57}Rh_{13}$ coexisted in the alloys after annealing. Comparing differential thermal analysis data and microprobe analysis data we concluded that at 980 °C decomposition of the Sc_2Rh phase ($Sc_2Rh \rightleftharpoons Sc_3Rh + ScRh$) takes place. The Sc_3Rh phase, in turn, is not stable, decomposing at 930 °C ($Sc_3Rh \rightleftharpoons ScRh + Sc_{57}Rh_{13}$). However, the disintegration rate of the Sc_2Rh phase appears to be lower than that of the Sc_3Rh phase, because the Sc_2Rh phase appears to be lower than that of the Sc_3Rh phase, because the Sc_2Rh phase is still present at 800 °C in the alloys, in addition to $Sc_{57}Rh_{13}$ and ScRh.

The shape of the liquidus curve of the $Sc_{57}Rh_{13}$ phase also points to the possible existence of a eutectic of the type $L \rightleftharpoons \langle \beta\text{-Sc} \rangle + Sc_{57}Rh_{13}$. However, in the cast alloys containing 5–15 at.% Rh, according to the metallography data, a eutectic mixture is not observed. It may be a consequence of its degeneracy, provoked by different steepnesses of the liquidus curves of $\langle \beta\text{-Sc} \rangle$ and $Sc_{57}Rh_{13}$. The eutectic point composition at about 11 at.% Rh is determined as the intersection of the liquidus curves of these phases with the invariant horizontal line. The temperature of the reaction $L \rightleftharpoons \langle \beta\text{-Sc} \rangle + Sc_{57}Rh_{13}$, 1050 °C, was determined on the basis of two independent methods, differential thermal analysis and melting points measuring according to Pirani and Alterthum. In the heating curves of the alloys of 2–15 at.% Rh we observed at temperatures from 990 to 1020 °C thermal effects that were attributed by us to the eutectoid reaction $\langle \beta\text{-Sc} \rangle \rightleftharpoons \langle \alpha\text{-Sc} \rangle + Sc_{57}Rh_{13}$ (the temperature of which is assumed to be 1010 °C). The data spread may be explained as being due to the presence of scandium with different degrees of oxygen contamination in our alloys (not more than 1.3 wt.%). The eutectoid composition, about 4 at.% Rh, is determined as the point of intersection of the solubility curves $\langle \beta\text{-Sc} \rangle - \langle \beta\text{-Sc} \rangle + \langle \alpha\text{-Sc} \rangle$ and $\langle \beta\text{-Sc} \rangle - \langle \beta\text{-Sc} \rangle + Sc_{57}Rh_{13}$ (plotted from the differential thermal analysis data) with the invariant horizontal line. This agrees with the typical eutectoid microstructures of the cast and annealed (at 800 °C) alloys with 5 at.% Rh (Fig. 2(d)).

The solubility of rhodium in β-scandium, according to our results, reaches 4.5 at.%. This is determined on the basis of the position of the alloy with 5 at.% Rh at 1050 °C, according to differential thermal analysis data, at the end of the eutectic horizontal line, corresponding to the reaction $L \rightleftharpoons \langle \beta\text{-Sc} \rangle + Sc_{57}Rh_{13}$. The solubility of rhodium in α-scandium amounts to about 1.5 at.%. This result follows from the occurrence of the thermal effect in the heating curve of the alloy with 2 at.% Rh at 1030 °C and from the heating curve of the alloy with 1 at.% Rh, which exhibits two effects (at 990 and 1045 °C). Therefore, the first alloy lies on the invariant eutectoid horizontal line, whereas the alloy with 1 at.% Rh lies outside it.

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