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The binary system Re–Al ☆

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Abstract

The binary system rhenium–aluminium is characterized by the occurrence of seven intermediate phases and two eutectics. The intermediate phases are: Re_2Al, ReAl, Re_4Al_{11}, $ReAl_4(h)$, Re_8Al_{33-x}, $ReAl_6$, and $ReAl_{12}$. They form at 1494±4°C (peritectoid), 1060±10°C (peritectoid), 1665°C (congruent melting), 1404±4°C (incongruent melting), 1008±4°C (polymorphic transformation), 803±4°C (incongruent melting), and 750±4°C (incongruent melting), respectively. Crystal structure data and lattice parameters for all these phases are given. The two eutectics occur (1) at 1655±3°C and ~74 at%Al, and (2) at 658°C and >99 at%Al.

Keywords: Alloy system rhenium–aluminium; Phase diagram; Crystal structures

1. Introduction

Using metallography and XRD on arc melted but still heterogeneous samples, Cornish and Witcomb [1] recently modified the Re–Al phase diagram [2] with respect to the occurrence of a eutectic at ~35 at%Re and ~1000°C as well as a phase Re_3Al_2. The work of Schuster [2] in turn was an update of the early literature data [3,4] and was based on limited experimental data such as Debye Scherrer type XRD of alloys equilibrated at $1000°C \leq T \leq 1500°C$. Though in this diagram the existence of six intermediate Re–Al phases was established, several crystal structures as well as reaction temperatures remained not satisfactorily resolved. Since that work, however, single crystal structure analysis was performed on $ReAl_6$, Re_4Al_{11} [5,6] (labelled $ReAl_3$ in Ref. [2]), and $Re_{14}Al_{57-x}$ [7] (labelled $ReAl_4$ in Ref. [2]). The crystals for the latter phase were prepared at 1000°C from alloys coexisting with liquid aluminium. Using Guinier XRD techniques in the composition region near 80 at%Al, we observed in samples quenched from higher temperatures (1100°C) as well as from lower temperatures (820°C) apparently related, but distinctively different XRD powder patterns and prepared single crystals of these phases [8]. Since it seemed not obvious, how to include these phases in the constitution diagram and none of the invariant temperatures were ever corroborated, a detailed redetermination of the phase relations in the entire system was undertaken using DTA, XRD and metallography on Re–Al alloys arc melted and annealed, as well as rapidly quenched from the melt.

2. Experimental

The starting materials were high purity Al (rods, purity: 99.999%, from Koch Light Ltd., UK) and Re (powder, purity: 99.99%, from Chase Brass and Copper, USA). About 15 alloys were prepared by arc melting under pure argon and heat treatment at temperatures ranging from 600°C (670 h) to 1100°C (30 h) followed by water quenching. During the heat treatment the samples were in alumina crucibles sealed in evacuated quartz tubes. This arrangement permits moderate quenching rates sufficient for most samples of this system. However, for rapid argon quenching experiments the apparatus described by Perring [9] was used. It permits from a starting temperature of e.g. 1400°C a quenching rate of 4000 K/s.

All alloys were inspected by XRD using Guinier chambers (from Huber GmbH, Germany) and $CuK\alpha_1$–radiation. Phase analysis from these powder patterns was done using the computer program STRUKTUR [10]. These data indicated, that (1) in alloys containing ≥7 at% Re no equilibrium was obtained after annealing at 600°C

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and (2) on the average loss of 2 − 5 at%Al occured during sample preparation. For selected Re-rich alloys, detailed diffraction profiles were recorded on a Philips PW 1051/81 powder diffractometer (scanning range $5 \leq 2\theta \leq 140°$, step 0.02°, CuKα–radiation, width of the recording slit 0.1 mm, total measuring time 48 h, equivalent to 25.4 s per scan step) or in an image plate Guinier–Huber chamber ($CuK\alpha_1$–radiation, $5° \leq 2\theta \leq 100°$). Rietveld refinement was done using the FULLPROF software [11].

Differential thermal analysis (DTA) runs were performed on alloys annealed at 600°C (compositions ≥93 at%Al) and 800°C (compositions ≤90 at%Al) in Al_2O_3 crucibles under flow of pure argon using general heating rates of 5 K/min. Alloys consisting of Re_4Al_{11} and phases richer in Al were subjected to DTA analysis up to 1500°C using a 404S/3 thermal analyzer from Netsch, Germany. Alloys consisting of Re_4Al_{11} and phases richer in Re were investigated up to 1700°C using a DTA 9216-18 from Setaram, France. For calibration, the melting points of the pure metals Al (660.3°C), Ag (961.8°C), Au (1064.2°C), Ni (1455.2°C), and Pd (1554.8°C) were used. The accuracy of both instruments is estimated to be better than ±10 K.

Microstructures were inspected using a BH2 light optical microscope fitted with Nomarski prisms (from Olympus Optical Co. Ltd., Japan). SEM analysis was done on a DSM962 (from Zeiss, FRG) using the LINK eXII analysis system.

3. Results and discussion

3.1. The intermediate phases

Seven intermediate phases are observed and characterized by XRD and DTA in the present study:

Re_2Al is confirmed to have $MoSi_2$-type crystal structure (*tI6*, space group *I4/mmm*) with $a = 0.2981(1)$ nm and $c = 0.9582(1)$ nm corroborating earlier data [2,6] (the typing error regarding the value of the *c* parameter in Ref. [2] was corrected in the ASTM card #38-805). Re_2Al is found to coexist with Re at 820°C and 1100°C (this work), and at 1000°C [2]. On the aluminium rich side, Re_2Al coexists with ReAl up to 1050°C and with Re_4Al_{11} at 1070°C and above. Alloys containing Re_2Al show a DTA peak at 1494±4°C (onset upon heating). The specific signal (area/mg alloy) was strongest in the alloy containing pure Re_2Al (as determined by XRD). Annealing this alloy at 1550°C for 10 min followed by *rapid* quenching yielded the diffraction pattern of rhenium ($a = 0.2754(1)$ nm, $c = 0.4451(1)$ nm) and not of Re_2Al. Thus the decomposition of Re_2Al occurs peritectiodally at 1494±4°C.

ReAl has CuTi-type crystal structure (*tP4*, space group *P4/nmm*) with $a = 0.3084(1)$ nm and $c = 0.5957(1)$ nm. Satisfactory match between observed and calculated intensities of the powder diffractogram are obtained with the Re as well as the Al atoms in positions (2*c*) with $z = 0.638$ and $z = 0.178$, respectively. ReAl is found to decompose into Re_2Al and Re_4Al_{11}. As was reported earlier [2], this reaction could not be observed by DTA. Thus the decompositon temperature was determined by XRD of annealed and quenched samples: After heat treatment at 1050°C ReAl was still observed but after heat treatment at 1070°C the phase was not found but Re_2Al and Re_4Al_{11} instead. Thus, the peritectoid decomposition of ReAl must occur at 1060±10°C.

Re_4Al_{11} has Mn_4Al_{11}-type crystal structure (*aP15*, space group *P1*) [12] as confirmed by Niemann and Jeitschko [5,6], who reported the lattice parameters $a = 0.51599(6)$ nm, $b = 0.8963(1)$ nm, $c = 0.51693(6)$ nm, $\alpha = 90.44(1)°$, $\beta = 99.76(1)°$, and $\gamma = 105.17(1)°$. The XRD diffraction pattern calculated by using these structural data matches perfectly the pattern observed for the phase labelled $ReAl_3$ in Ref. [2]. Re_4Al_{11} coexists on the Re-rich side with ReAl and Re_2Al, and on the Al-rich side with liquid aluminium (at 1600°C and at 1500°C [6]), $ReAl_4(h)$ (at 1100°C) and Re_8Al_{33-x} (at 950°C and 820°C). Single phase Re_4Al_{11} alloys (annealed at 820°C or 1100°C) show no DTA signal up to the melting temperature at 1665°C.

A phase bundle consisting of two or more phases exists at the composition near 80 at%Al: $ReAl_4(h)$, Re_8Al_{33-x}, and potentially $Re_{14}Al_{57-x}$. Within the analytical accuracy of the methods employed so far, the nonstoichiometries of the latter two phases result in compositions $Re_{20}Al_{80}$. Thus, at present we treat the phases occurring at this composition as modifications having temperature dependent stabilities of one single phase.

The high temperature modification is labelled $ReAl_4(h)$. Structure determination was impeded by heavy twinning of the crystals isolated from alloy $Re_{10}Al_{90}$ annealed at and quenched from 1100°C. Thus, only part of the reflections measured on a four-circle diffractometer (STOE STADI4, MoKα radiation) could be indexed with a monoclinic *c*-centered unit cell with $a = 0.5132(2)$ nm, $b = 1.747(1)$ nm, $c = 0.5167(2)$ nm, and $\beta = 100{,}43(3)°$, which is very similar to that of WAl_4 (*mC30*, space group *Cm*) [13]. However, attempts to refine the structure with this model failed as well as attempts to interpret the whole diffraction pattern of the single crystal measured. The powder pattern of the alloy mentioned above ($Re_{10}Al_{90}$, 1100°C) can also only partly be indexed with the single crystal data. Remaining reflections cannot be attributed either to Re_8Al_{33-x} [8] or $Re_{14}Al_{57-x}$ found previously [7]. At 1100°C $ReAl_4(h)$ coexists with liquid aluminium. In alloys containing nominally 80, 81, 84, or 87 at%Al and annealed at 820°C, DTA signals are observed at 1404±4°C. These are interpreted to correspond to the reaction $ReAl_4(h) = L + Re_4Al_{11}$. In the same alloys DTA signals occurred at 1008±4°C assigned to the transformation between $ReAl_4(h)$ and the low temperature modification Re_8Al_{33-x}, since these were the only DTA signals observed in the

temperature interval between 950°C (stable modification: Re_8Al_{33-x}) and 1100°C (stable modification: $ReAl_4(h)$).

Re_8Al_{33-x} has a newly determined crystal structure (*aP41*, space group *P1*) [8]. The single crystals investigated were isolated from alloy Re10Al90 annealed at and quenched from 950°C. The lattice parameters refined from powder data are $a=0.51535(6)$ nm, $b=0.90782(8)$ nm, $c=1.3727(1)$ nm, $\alpha=96.852(7)°$, $\beta=95.521(9)°$, and $\gamma=92.392(9)°$. Re_8Al_{33-x} is found to coexist with liquid aluminium at 950°C as well as at 820°C.

The phase $Re_{14}Al_{57-x}$ [7], which is structurally closely related to Re_8Al_{33-x}, was not observed in the present study. The crystals of that phase were isolated from alloy $Re_{10}Al_{90}$ annealed at and quenched from 1000°C, a temperature remarkably close to the DTA signals at 1008±4°C the transformation temperature between Re_8Al_{33-x} and $ReAl_4(h)$. Thus, this alloy might have been cycled periodically through this transformation during the heat treatment, and the structure of $Re_{14}Al_{57-x}$ corresponds to a transient state between Re_8Al_{33-x} and $ReAl_4(h)$ frozen in upon quenching. This would explain the substantial defects observed for several Al atoms in this otherwise rigid and highly ordered structure [7]. Similar phenomena occur in other binary aluminide systems (e.g. Ti–Al [14], Mo–Al [15]). Alternatively, $Re_{14}Al_{57-x}$ could have a very narrow temperature range of stability around 1008±4°C and the DTA signals observed at this temperature are actually due to two thermal effects (transitions $Re_8Al_{33-x} \Rightarrow Re_{14}Al_{57-x}$ and $Re_{14}Al_{57-x} \Rightarrow ReAl_4(h)$) not resolved into two signals by our apparatus. More detailed studies are needed to resolve this issue.

$ReAl_6$ is isostructural with $MnAl_6$ (*oC28*, space group *Cmcm*) [16] as confirmed by Wilkinson [17] and others [5,6]. This is corroborated in the present study yielding the lattice parameters $a=0.7608$ nm, $b=0.6617$ nm, and $c=0.9046$ nm from alloy $Re_{10}Al_{90}$ annealed at 780°C. The alloys $Re_{16}Al_{84}$ and $Re_{13}Al_{87}$ annealed at this temperature showed DTA signals at 803±4°C interpreted as peritectic decomposition of $ReAl_6$ into $L+Re_8Al_{33-x}$.

$ReAl_{12}$ is isostructural with WAl_{12} (*cI26*, space group *Im3̄*) [3,16–20]. In excellent agreement we found a lattice parameter of $a=0.75261(5)$ nm in alloy Re_7Al_{93} annealed at 600°C. $ReAl_{12}$ coexists with $ReAl_6$ and Al. The DTA signals observed at 750±4°C in all alloys richer in aluminium than $ReAl_6$ are assigned to the incongruent melting of $ReAl_{12}$ into $L+ReAl_6$.

3.2. The phase diagram

In addition to the transformation and decomposition temperatures of the intermediate phases two eutectic reactions are observed by DTA:

Having observed melting of Re_4Al_{11} at 1665°C, it was at first surprising to record DTA signals scattering around 1655±3°C in alloys more rich in Re, since up to this point Re_4Al_{11} was assumed to melt incongruently. However, the microstructure of alloys $Re_{27}Al_{73}$ (Fig. 1) clearly establishes the occurrence of a eutectic $L=Re_4Al_{11}+Re$. The primary phase in Fig. 1 was analysed by SEM–EDX to contain 73.9±0.2 at%Al, which is close to the ideal value of 73.3 at%Al for Re_4Al_{11}. The composition of the eutectic is found to be virtually identical (73.9±0.8 at%Al). These findings match excellently with the recently reported observation of a eutectic in this composition range [1]. XRD on alloys rapidly quenched from 1550°C showed the Re-rich phase to be (Re) having a unit cell only 0.5% smaller than the value given in the literature for the pure metal [21]. Thus neither a phase Re_3Al_2 [1,3] nor the large solubility of Al in Re reported in Ref. [1] are corroborated.

Confirming d′Alte da Veiga [4], a second eutectic $L=ReAl_{12}+(Al)$ was observed at 658°C in the alloys Re_2Al_{98} and Re_5Al_{95}. The onset of the DTA signal indicating melting in these alloys occurred 2–3 K below the value measured for pure Al (starting material). The composition of this eutectic is assumed to be at ≥ 99 at%Al, but no specific effort was made to determine it exactly. In the literature the value of 0.26 at%Al (at 600°C) reported by Savitskii et al. [3] was corrected down to 0.015 at%Al (at 600°C) [22].

The intermetallic phases are assumed to be line compounds, as there were no systematic variations observed for the lattice parameters (up to $T=1500$°C), whether the phases were coexisting with the neighboring phase more rich in Re or more rich in Al. The phase diagram resulting

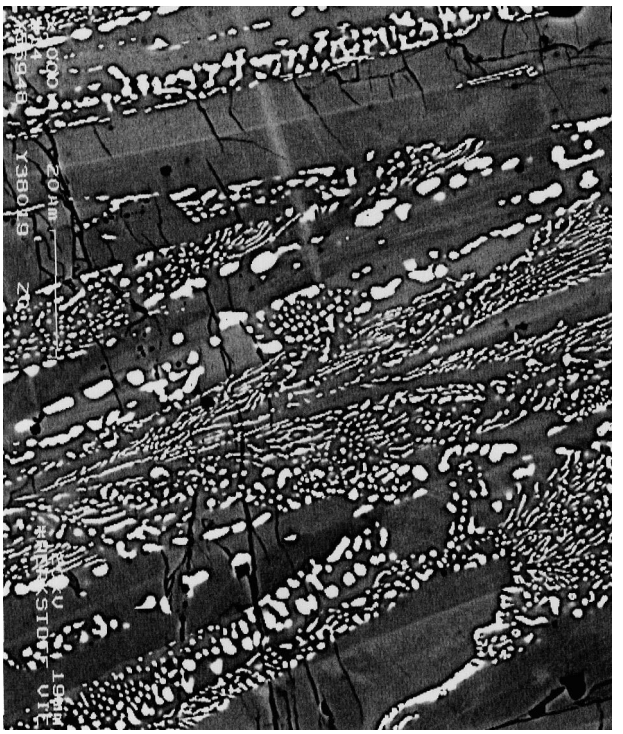

Fig. 1. SEM micrograph of as cast $Re_{27}Al_{73}$ showing primary Re_4Al_{11} + eutectic ($Re_4Al_{11}+(Re)$).

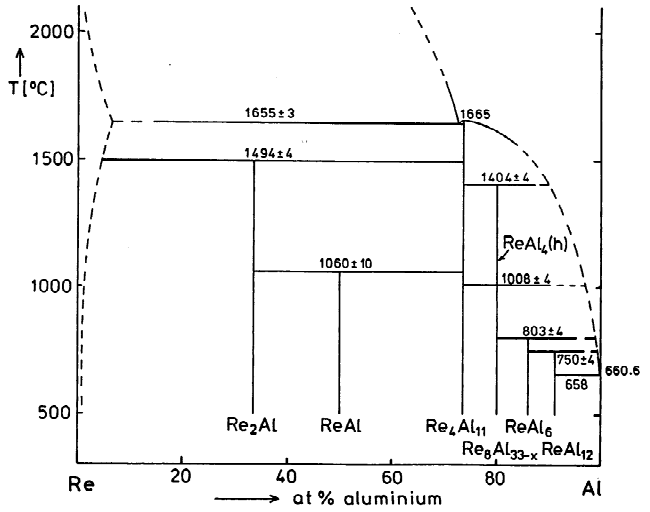

Fig. 2. The rhenium–aluminium phase diagram. The error limits given indicate the maximum experimental scatter of the measurements.

from the above findings is shown in Fig. 2. The occurrence of a congruently melting Al-rich intermetallic rather than a sequence of peritectic decomposition reactions puts the Re–Al system in line with Mo–Al [15,23] rather than W–Al [24].

4. Conclusions

The constitution of the binary system rhenium–aluminium was reinvestigated using DTA, XRD, and metallography and a modified phase diagram is proposed. Seven intermetallic phases are observed: Re_2Al (*tI6*, *I4/mmm*, $MoSi_2$-type), ReAl (*tP4*, *P4/nmm*, CuTi-type), Re_4Al_{11} (*aP15*, *P1*, Mn_4Al_{11}-type), $ReAl_4$(*h*) (WAl_4-type related), Re_8Al_{33-x}(*aP41*, *P1*), $ReAl_6$ (*oC28*, *Cmcm*, $MnAl_6$-type), and $ReAl_{12}$ (*cI26*, *Im3*, WAl_{12}-type). The melting temperatures respective solid state decomposition temperatures are determined for all phases. Two eutectics occur at 1655±3°C (~74 at%Al) and 658°C (>99 at%Al).

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