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Some constitutional studies on the molybdenum–rhodium system

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Abstract

Phase relationships in the system Mo–Rh in the temperature range 1100–1000 °C have been investigated using conventionally melted and ultra-rapidly solidified samples. The finely divided microstructures provided by the use of the latter technique were found on annealing to achieve equilibrium much more rapidly than conventionally prepared materials. Optical microscopy, X-ray diffraction methods and scanning and analytical electron microscopy were used for phase characterization. At the temperatures studied, very limited solid solubility of rhodium in molybdenum and comparatively large solid solubility of molybdenum in rhodium were established. Lattice parameter values are reported for the b.c.c., h.c.p. and f.c.c. phases. No evidence was found for the intermediate phases MoRh at 1100 °C or for $MoRh_3$ at temperatures down to 1000 °C. The normal h.c.p. intermediate phase remains stable down to this temperature.

1. Introduction

The constitution of the Mo–Rh system is of importance to the nuclear industry since the elements molybdenum and rhodium are found together with ruthenium, technetium and palladium as single- or two-phase metallic inclusions in irradiated UO_2 and (U, Pu) O_2 nuclear oxide fuels.

Previous work on this system has been concentrated on the upper part of the diagram, above 1100 °C. At very high temperatures there are large solid solubilities of rhodium in molybdenum and molybdenum in rhodium [1–3]. However, the rhodium solubility of the terminal molybdenum-rich phase is very temperature dependent whereas the variation in the rhodium-rich f.c.c. phase limit is slight. The maximum solid solubility of rhodium in molybdenum (20 at.% Rh) occurs at the eutectic temperature, 1940 ± 5 °C [2, 3]. The rhodium-rich f.c.c. phase is produced by the peritectic reaction liquid$+\epsilon$ (h.c.p.)$=$f.c.c. Rh (Mo) at 85 at.% Rh and 2000 ± 10 °C [3]. A high temperature h.c.p. phase of extensive composition range dominates the middle of the system. It is formed congruently at 67 at.% Rh and 2075 ± 10 °C [3]. The homogeneity range of the h.c.p. phase has been reported to extend approximately from 48 to 85 at.% Rh at temperatures between 1140 and 1300 °C [1–4]. It is stable down to 1100 °C and its solubility limits

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are only slightly temperature dependent. Anderson and Hume-Rothery [3] studied the lattice spacing–composition relations of the h.c.p. phase and found a minimum at 74 at.% Rh. This was attributed to the low temperature formation of a superlattice phase $MoRh_3$, rather than to an electronic (Brillouin zone) effect, since the minimum occurred so near to the 3:1 atomic ratio. No superlattice lines were detected since the atomic numbers and scattering factors of molybdenum and rhodium are close to each other. Another low temperature order–disorder transformation of the disordered h.c.p. phase to ordered MoRh has also been reported [5]. Giessen *et al.* [5] investigated an alloy of MoRh between 1200 and 900 °C. They suggested that an order–disorder transformation of the disordered h.c.p. phase to the ordered MoRh compound took place at 900–1200 °C. The ordered MoRh alloy was defined as an orthorhombic structure of the B_{19} MgCd type with $a = 0.2745$ nm, $b = 0.4785$ nm and $c = 0.4413$ nm. They also suggested that the $MoRh_3$ ordered phase, which was suggested by Anderson and Hume-Rothery [3], possessed the hexagonal structure $D0_{19}$ $MgCd_3$ with $a = 0.5456$ nm and $c = 0.4350$ nm. No experimental study was carried out on this phase but the data of Anderson and Hume-Rothery for $Mo_{26.1}Rh_{73.9}$ were used to calculate the a and c parameters. The $D0_{19}$ $MgCd_3$ type of structure was assumed by analogy with a WIr_3 sample. In recent assessments of the Mo–Rh system [6, 7] the order–disorder transformation temperatures are given as 1050 ± 75 °C for MoRh and 1200 ± 200 °C for $MoRh_3$. Both of these intermetallic phase fields are thought to extend about 1 at.% either side of their stoichiometric compositions.

As the above review demonstrates, further study at around 1100 °C and below is desirable. Since difficulties can be encountered in obtaining equilibrium at such relatively low temperatures a few studies of ultra-rapidly solidified samples were made, since previous experience with Co–Nb [8] and Mo–Pd [9] alloys has shown that their use can help to overcome slow diffusion problems. The present paper includes results obtained using these but is based mainly on investigations of conventionally melted alloys.

2. Experimental details

Starting alloy materials were kindly prepared by the Chemistry Division, Atomic Energy Research Establishment, Harwell, from molybdenum and rhodium of 99.9% and 99.5% purities respectively. Rapid solidification of samples was performed at the School of Metallurgy and Materials, Birmingham University. Initially the elemental constituents were melted under an argon atmosphere, first gettered by the melting of a zirconium button, using an arc-melting method. In general, only small weight losses were encountered during melting. The alloy buttons were checked for homogeneity prior to normal annealing or ultra-rapid solidification.

The melt-spinning apparatus used during the present investigation consists of an evacuated chamber, a silica tube surrounded by an r.f. coil, a vacuum feed-through rod and a Duralumin drum with a thick polished copper surface.

No crucible was used so as to avoid contamination of the samples. Samples were prepared in the same way as described previously [9] and therefore no details are given here.

Heat treatment was performed in a Kanthal-wound muffle furnace using the conventional sealed and evacuated silica capsule techniques. Temperatures were controlled by means of a Eurotherm controller and measured using a Pt–(Pt–13 wt.% Rh) thermocouple. The details of the heat treatments are shown in Table 1.

Electrolytic etching has been used for etching samples. The etching solution was HCl solution of specific gravity 1.19, used with a graphite cathode and a platinum probe connection.

X-ray diffraction methods, optical microscopy and scanning electron microscopy (SEM) observations were used for phase identification. Copper X-ray radiation with a nickel filter was employed and a computer-programmed Nelson–Riley least-squares method was used to derive accurate lattice parameters. Cell dimensions with accuracies of ±0.00002 nm were obtained.

TABLE 1

Scanning electron microscopy analyses of Mo–Rh alloys and individual phases

Nominal composition (at.%)	Element	Overall (at.%)	B.c.c. (at.%)	H.c.p. (at.%)	F.c.c. (at.%)	Annealing temperature (°C)
$Mo_{85}Rh_{15}$	Mo	85.43±1.97	87.67±1.32	48.65±0.42		1100
	Rh	14.57±1.97	12.33±1.35	51.35±0.42		
$Mo_{65}Rh_{35}$	Mo	61.03±0.40	–	–		1100
	Rh	38.97±0.40	–	–		
$Mo_{50}Rh_{50}$[a]	Mo	49.89±0.78	–	47.26±0.86		1100
	Rh	51.11±0.63	–	52.74±0.86		
$Mo_{50}Rh_{50}$[b]	Mo	49.23±0.17	–	47.90±0.09		1100
	Rh	50.77±0.17	–	52.10±0.09		
$Mo_{27}Rh_{73}$	Mo	26.76±0.67	–	26.76±0.67		1100
	Rh	73.24±0.67	–	73.24±0.67		
$Mo_{24}Rh_{76}$	Mo	24.08±0.28	–	24.08±0.28		1050
	Rh	75.92±0.23	–	75.92±0.23		
$Mo_{24}Rh_{76}$	Mo	24.00±0.18	–	24.00±0.18		1000
	Rh	76.00±0.18	–	76.00±0.18		
$Mo_{20}Rh_{80}$	Mo	18.94±0.31	–	18.94±0.31		1100
	Rh	81.06±0.31	–	81.06±0.31		
$Mo_{10}Rh_{90}$	Mo	9.26±0.15	–	–	9.26±0.15	1100
	Rh	90.74±0.15	–	–	90.74±0.15	
$Mo_{5}Rh_{95}$	Mo	4.89±0.30	–	–	4.89±0.30	1100
	Rh	95.11±0.30	–	–	95.11±0.30	

[a] Arc melted.
[b] Rapidly solidified.

The quantitative analysis of samples and individual phases has been carried out using ISI-100A and JEOL 840 energy-dispersive X-ray analysis units and their associated software. There were no absolute standards but instead virtual standards were used. Calculated alloy compositions were normalized by the software.

3. Results

Eight alloy compositions were chosen and one alloy composition, $Mo_{50}Rh_{50}$, was employed in rapid solidification experiments after difficulties in achieving equilibrium. As in the case of the Mo–Pd system [9], very finely divided structures providing very short diffusion distances were again obtained. Comparisons of as-cast and as-rapidly-quenched structures of $Mo_{50}Rh_{50}$ are shown in Figs. 1(a) and 1(b) respectively. An SEM micrograph of the alloy (Fig. 1(c)) reveals very fine molybdenum-rich phase precipitates in a matrix of the h.c.p. intermediate phase. Using an electron microprobe analyser it was found that these precipitates are of the molybdenum-rich b.c.c. phase. X-ray films obtained from the alloy samples showed only the h.c.p. phase pattern. No extra lines were observed.

Figure 2(a) is an SEM micrograph of the molybdenum-rich alloy $Mo_{85}Rh_{15}$ and shows that the h.c.p. phase precipitated as very coarse needles in the b.c.c. terminal solid solution on annealing. Very fine needles of the b.c.c. phase were also observed to have precipitated in the h.c.p. phase. The composition of each precipitate was confirmed by electron microprobe analyses and only b.c.c. and h.c.p. phase lines were observed on X-ray films. A well-developed eutectic morphology, typical of the experimental composition $Mo_{61}Rh_{39}$ (nominal $Mo_{65}Rh_{35}$ alloy), is shown in Fig. 2(b).

The microstructures of the alloys $Mo_{27}Rh_{73}$, $Mo_{24}Rh_{76}$ and $Mo_{20}Rh_{80}$ show only the presence of the single h.c.p. phase (see, for example, Fig. 3). $Mo_{24}Rh_{76}$ was annealed at 1150, 1073 and 1000 °C, $Mo_{27}Rh_{73}$ at 1100, 1050 and 1000 °C and $Mo_{20}Rh_{80}$ at 1100 and 1000 °C in attempts to confirm the presence of the reported intermediate phase $MoRh_3$. No change was observed in the microstructures or X-ray patterns, thus indicating that only the h.c.p. phase is present.

Two alloys, $Mo_{10}Rh_{90}$ and Mo_5Rh_{95}, from the rhodium-rich single-phase f.c.c. phase were examined and, after annealing, both alloys showed the f.c.c. phase only. An example of a micrograph of $Mo_{10}Rh_{90}$ is shown in Fig. 4. The presence of typical f.c.c. annealing twins is clearly seen.

SEM analyses were mainly used to assist in establishing the phase boundaries. Analyses were made on individual phases and of overall compositions. Table 1 assembles the SEM analyses obtained. The analyses obtained from the b.c.c. phase in $Mo_{85}Rh_{15}$ annealed at 1100 °C gave its composition to be 12.33 ± 1.32 at.% Rh. This result is rather high and could be the result of beam contamination from very fine second-phase precipitates within the b.c.c. phase.

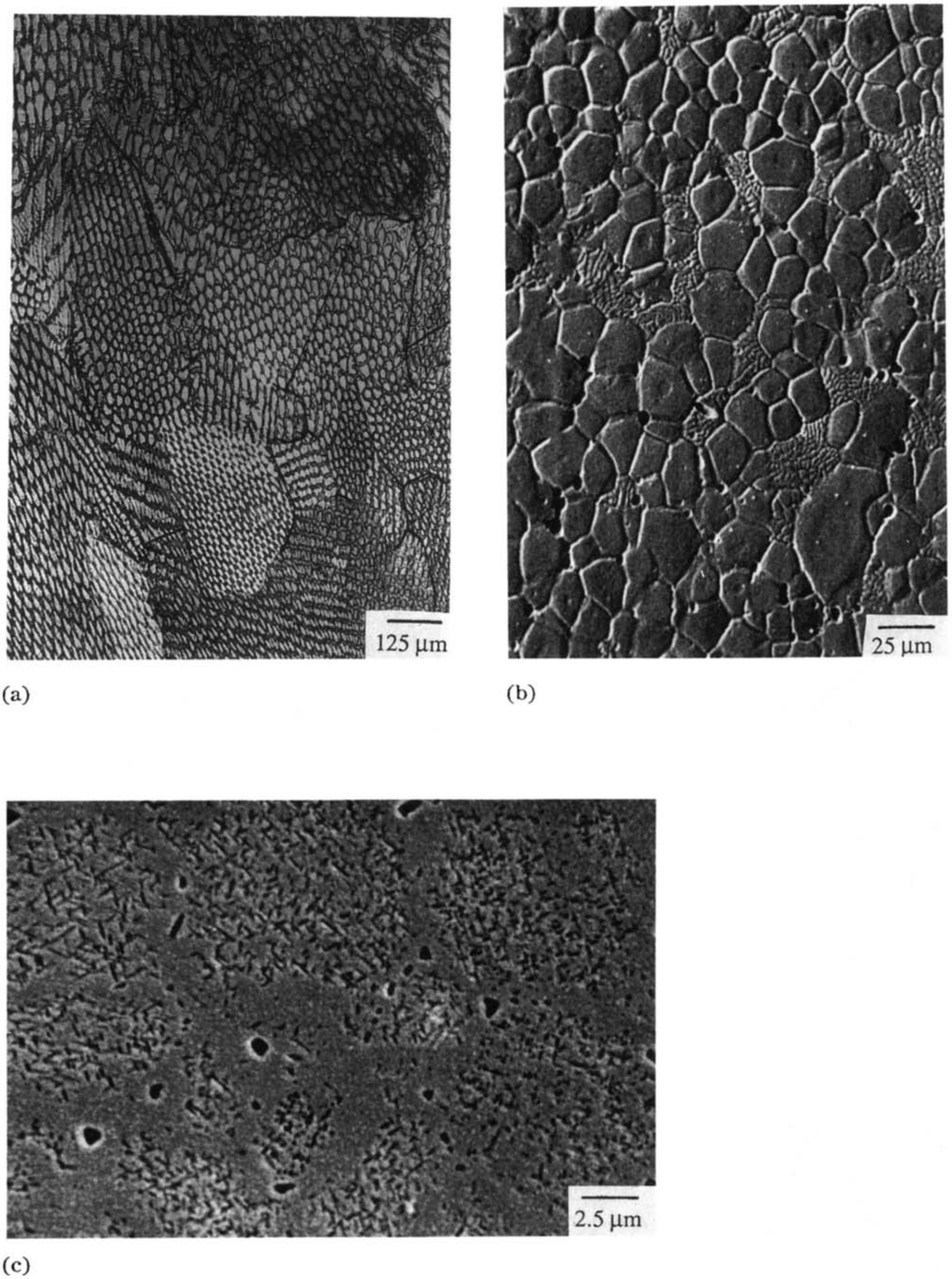
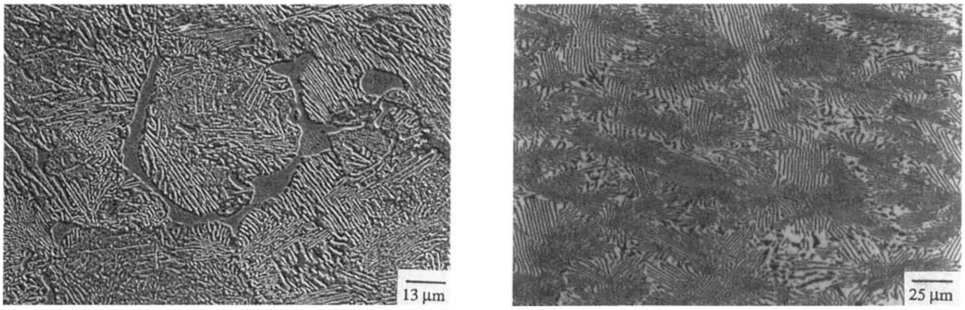
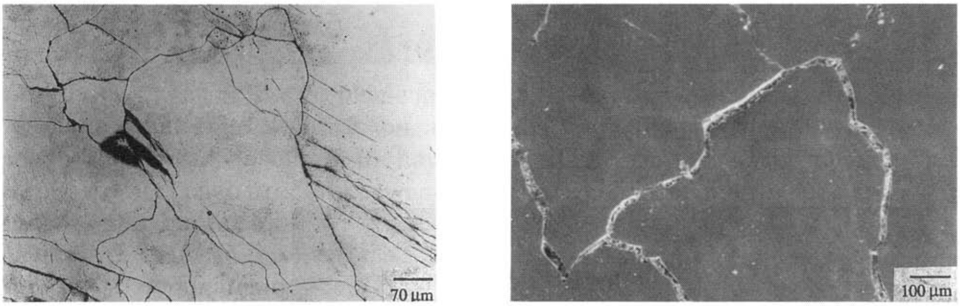


Fig. 1. (a) Nominal $Mo_{50}Rh_{50}$, as cast. Optical micrograph; cored h.c.p. solid solution; large columnar grains showing directional freezing. (b) Nominal $Mo_{50}Rh_{50}$, as rapidly solidified. SEM micrograph in secondary-electron mode; primary h.c.p. solid solution grains and structured regions of slightly higher molybdenum content. (c) Rapidly solidified $Mo_{50}Rh_{50}$ annealed at 1100 °C for 163 h. SEM micrograph in secondary-electron mode. Very fine b.c.c. phase precipitates within the solid solution h.c.p. phase matrix.



(a) (b)

Fig. 2. (a) Nominal $Mo_{85}Rh_{15}$, normally melted and annealed at 1100 °C for 84 h. SEM micrograph in secondary-electron mode. Showing saturated b.c.c. with the light h.c.p. single-phase needles. The grey areas are h.c.p. with very fine b.c.c. precipitates within. (b) Nominal $Mo_{65}Rh_{35}$, normally melted and annealed at 1100 °C for 163 h. Optical micrograph showing remains of the original eutectic morphology; the dark lamellae are the molybdenum-rich phase, and the light regions are h.c.p.



(a) (b)

Fig. 3. (a) Nominal $Mo_{27}Rh_{73}$ annealed at 1100 °C for 64 h. Optical micrograph showing uniform single-phase h.c.p. solid solution. (b) Nominal $Mo_{20}Rh_{80}$ annealed at 1000 °C for 96 h. SEM micrograph; single-phase h.c.p. solid solution.

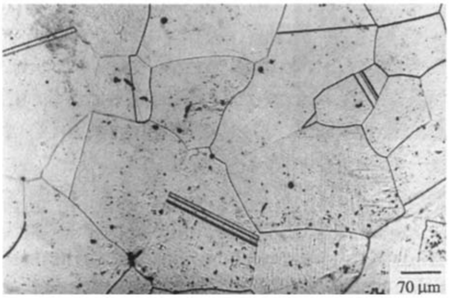


Fig. 4. Nominal $Mo_{10}Rh_{90}$ annealed at 1100 °C for 64 h. Optical micrograph showing uniform terminal rhodium-rich solid solution with annealing twins.

Measured values of X-ray lattice parameters of the phases, together with the heat treatments used, are shown in Table 2. The solid solubility limit of the molybdenum-rich phase at 1100 °C was established as 1.25 at.% Rh by comparing the current b.c.c. spacing values with those reported by Haworth and Hume-Rothery [2]. Three alloys, $Mo_{24}Rh_{76}$, $Mo_{27}Rh_{73}$ and $Mo_{20}Rh_{80}$, lying inside the h.c.p. phase field at high temperatures were annealed at 1150, 1100, 1073, 1050 and 1000 °C for different periods. No traces were seen of any second-phase lines, all lines being indexed simply as h.c.p. The h.c.p. phase and the rhodium-rich f.c.c. phase parameters measured in the current work and those given by Raub [1] and Anderson and Hume-Rothery [3] for both phases are compared in Figs. 5 and 6 respectively. The compositions used in the current work were those obtained from SEM analyses. As can be seen, there is good agreement between the values from different studies and the discrepancies are small and consistent with the probable uncertainties in the phase compositions and normal experimental errors.

4. Discussion

Microstructural examination of as-cast and as-rapidly-cooled samples of $Mo_{50}Rh_{50}$ demonstrate that samples prepared by arc melting retain a morphology of irregular coarse dendritic form, whereas samples produced by rapid solidification consisted of finely divided grains. Grain size differences of up to two orders of magnitude were observed. X-ray patterns obtained from these samples displayed all the principal lines sharply. These results indicate that, in this system also, it is possible to prepare good samples by the rapid cooling method to use in phase diagram studies.

TABLE 2

X-ray lattice parameters and the heat treatments of Mo–Rh alloys

Rh (at.%)	Heat treatment		B.c.c.	H.c.p.			F.c.c.
	Temperature (°C)	Time (h)	a_0 (nm)	a_0 (nm)	c_0 (nm)	c/a	a_0 (nm)
15	1100	84	0.31457				
35	1100	64	0.31449				
50	1100	163		0.27554	0.44238	1.6055	
50	1100	768		0.27541	0.44221	1.6056	
73	1150	70		0.27286	0.43530	1.5953	
73	1073	96		0.27277	0.43520	1.5955	
73	1000	168		0.27284	0.43526	1.5953	
76	1100	64		0.27300	0.43558	1.5955	
76	1050	137		0.27292	0.43522	1.5950	
80	1000	96		0.27230	0.43491	1.5972	
90	1100	64					0.38141
95	1100	120					0.38091

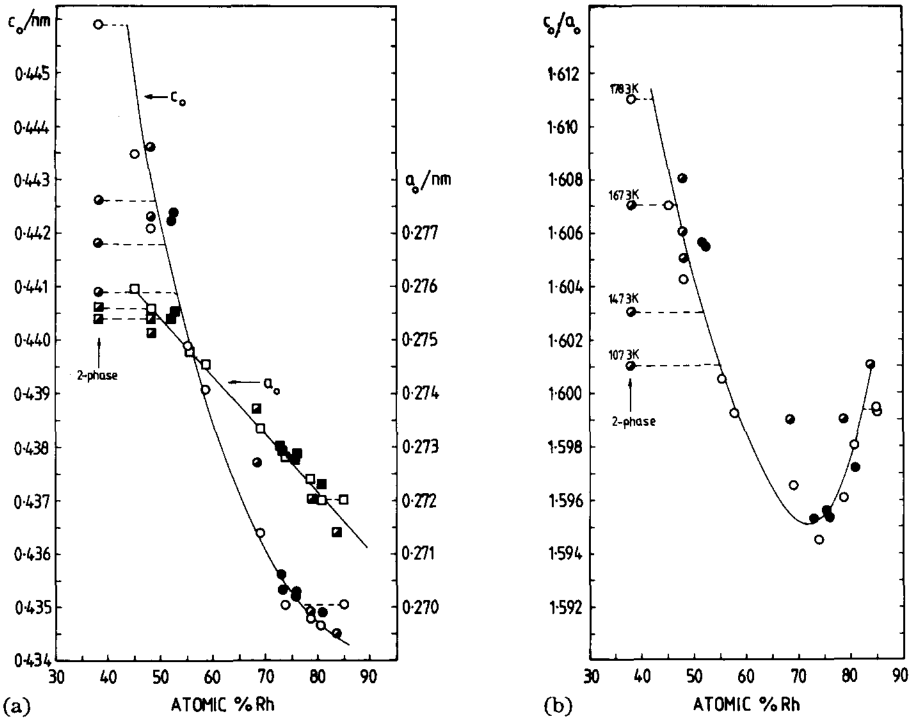


Fig. 5. Lattice parameters for an h.c.p. intermediate solid solution: ■, a_0, present work; □, a_0, data from Anderson and Hume-Rothery [3]; ▨, a_0, data from Raub [1]; ●, c_0 and c_0/a_0, present work; ○, c_0 and c_0/a_0, data from Anderson and Hume-Rothery [3]; ◐, c_0 and c_0/a_0, data from Raub [1].

The solid solubility limit of the molybdenum-rich b.c.c. phase, at 1100 ± 5 °C, was found to be 1.25 at.% Rh. This is in contrast with the solubility limit of 5.4 at.% Rh at 1300 °C suggested by Raub[1], but it is consistent with the value of less than 3 at.% Rh at 1140 °C reported by Haworth and Hume-Rothery [2]. No evidence was found for the intermediate phase MoRh and the molybdenum-rich boundary of the h.c.p. phase was established as 52.10 at.% Rh, at 1100 ± 5 °C. However, the possibility of the existence of MoRh at temperatures below this cannot be excluded.

The investigations between 1150 and 1000 °C of the three alloys $Mo_{20}Rh_{80}$, $Mo_{24}Rh_{76}$ and $Mo_{27}Rh_{73}$, lying near the reported second intermediate phase, gave no indication of its existence. The lattice parameters obtained are in good agreement with those reported by Raub [1] and by Anderson and Hume-Rothery [3] and show a similar minimum in the axial ratio at approximately 75 at.% Rh. The variation in the lattice parameters with composition and particularly the absence of any variation with annealing temperature are consistent with that of a single-phase solution range, rather than that for two-phase equilibria of the form implied by the existence of $MoRh_3$. The present X-ray results for the $Mo_{27}Rh_{73}$ alloy were consistent with a normal h.c.p. structure and lattice parameters $a_0 = 0.2728$ nm and $c_0 = 0.4349$ nm,

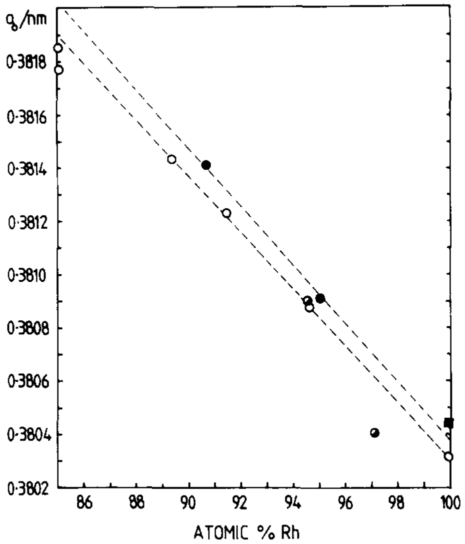


Fig. 6. Lattice parameters a_0 for an f.c.c. solid solution: ● present work; ○ Anderson and Hume-Rothery [3]; ◑ Raub [1]; ■ Pearson [10].

very similar to values obtained by Anderson and Hume-Rothery [3], rather than the $D0_{19}$ interpretation of Giessen *et al.* [5] with a doubled a_0 parameter. It is therefore concluded from the present study that the normal h.c.p. single-phase field persists at least down to 1000 °C, with its rhodium-rich limit at this temperature being 81 at.% Rh.

The limit of the f.c.c. solid solutions was not precisely defined by present results, but the single-phase structure observed for the $Mo_{10}Rh_{90}$ alloy at all the temperatures studied show that it extends to at least 10 at.% Mo at 1000 °C. This is inconsistent with the lower value of 7 at.% Mo reported by Raub [1] for the higher temperature of 1300 °C, but it supports the boundary value adopted in the published phase diagram [6, 7].

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