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The phase $D10_2$ type in the thorium-rhodium alloy system.

By RICCARDO FERRO and GABRIELLA RAMBALDI, *General Chemistry Institute and Physical Chemistry Institute of Genoa University, Genoa, Italy*

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In this paper are reported the results obtained in the preparation of some thorium–rhodium alloys with high thorium percentages.

The thorium used was prepared by reduction of ThO_2 with Ca and had a purity of about 99·8$_5$% (main impurity oxygen as ThO_2); the rhodium had a purity higher than 99·9%. The powders of the two metals, thoroughly mixed, were heated, in argon, up to 1800–1900 °C. (the synthesis appears to be strongly exothermic); the melted alloys were then slowly cooled and annealed for 1 day at 900 °C., for 1 week at 750 °C. and 2 weeks at 500 °C. The powders for the X-ray examination were further annealed for 50 hours at 500 °C.

The alloys, rather brittle and hard, were analyzed by the following method: the sample, finely ground, is treated with a mixture of HCl and H_2O_2 which dissolves nearly all the thorium and a good part of the rhodium; the residue is then rendered soluble by mixing it with NaCl and heating, in a current of Cl_2, up to 700 °C. After leaching with water, the rhodium is precipitated from the solution with H_2S (in the filtrate thorium is determined by titration with sodium ethylenediaminetetraacetate or by double precipitation with H_2O_2): the rhodium sulphide, after re-solution with aqua regia, is then treated with $NaBrO_3$ and $NaHCO_3$. The new precipitate, after ignition in H_2 atmosphere, is washed with dil. HCl, re-ignited in H_2 and, finally, weighed as Rh metal.

The micrographic examination was carried out, after dry polishing, by etching with $HF + HNO_3$ or H_2SO_4. The density was measured by use of a pyknometer which was filled with rectified benzene dried over sodium. The X-ray examination was carried out by the powder method (Straumanis arrangement) using chiefly Fe $K\alpha$ radiation ($K\alpha_1$, $\lambda = 1{\cdot}93597$ Å).

An alloy which by analysis contained 81·5$_9$% Th and, in two determinations, 18·4$_9$ and 18·1$_5$% Rh (i.e. very close to the theoretical composition for Th_2Rh) appeared, under micrographic examination, clearly biphase, in contrast to what one could expect by analogy with thorium–palladium alloys (Ferro & Capelli, 1961). On the other hand, the powder photograph of this alloy is identical with one of another alloy, nearly homogeneous under micrographic examination, containing 83·3$_3$% Th and 16·6$_7$–16·5$_5$% Rh and having a density of 11·5 g.cm.$^{-3}$.

The powder photographs of these alloys can be indexed with the following values for the constants (obtained by successive extrapolations with the function

$$\tfrac{1}{2}\,[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]):$$

$$a = 10{\cdot}028,\ c = 6{\cdot}293\ \text{Å},\ c/a = 0{\cdot}627_5$$

(hexagonal axes).

The structure corresponds to the $D10_2$ type (Pearson, 1958) or Th_7Fe_3 type (Florio *et al.*, 1956) with the following atomic positions referring to the ideal composition Th_7Rh_3 (theor.: 15·97% Rh):

Space group C_{6r}^4.

2 Th_I in (*b*) $\frac{1}{3}, \frac{2}{3}, u$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+u$;
6 Th_{II} in (*c*) s, $\bar{s}$, *v*; ↻;
6 Th_{III} in (*c*) t, $\bar{t}$, *w*; ↻;
6 Rh in (*c*) *x*, $\bar{x}$, *z*; ↻.

(The calculated density is 11·7 g.cm.$^{-3}$ in good agreement with the pycnometric value previously mentioned).

The structure is confirmed by the good agreement between observed and calculated intensities (for ca. 150 reflexions possible with the Fe $K\alpha$ radiation). The calculated intensities were obtained taking, as a first approximation, the following values for the parameters, in analogy with other similar substances:

$$u = 0{\cdot}06\ (Th_I);\ s = 0{\cdot}126,\ v = 0{\cdot}25\ (Th_{II});$$
$$t = 0{\cdot}544,\ w = 0{\cdot}03\ (Th_{III});\ x = 0{\cdot}815,\ z = 0{\cdot}31\ (Rh).$$

This phase is, therefore, isostructural with a number of other similar compounds of thorium with several elements of group VIII (Florio, Baenziger & Rundle, 1956), the structural characteristics of which are summarized in Table 1. In the table are reported the constants (Å) and the molar volumes (cm.^{3}) obtained both from crystallographica data (V_M) and by adding the atomic volumes (ΣV_A).

Table 1. *Structural data for* Th_7Me_3 *compounds*

Th_7Me_3	a	c	c/a	V_M	ΣV_A
Th_7Fe_3	9·85	6·15	0·624	156	160
Th_7Co_3	9·83	6·17	0·628	156	159
Th_7Ni_3	9·86	6·23	0·632	158	159
Th_7Rh_3	10·02$_8$	6·29$_3$	0·627$_5$	165	164

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