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Actinide(Lanthanide)–Noble Metal Alloy Phases, Preparation and Properties

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Actinide (A=Th—Cm)–noble metal phases with platinum, palladium, rhodium, and iridium (=B)– and lanthanide–noble metal phases with platinum and palladium have been prepared by reduction of corresponding oxides or fluorides in the presence of noble metals by extremely purified hydrogen. Alloy phases of composition AB_2, AB_3, and/or AB_5 have been identified, most of which crystallize in the Cu_2Mg, Cu_3Au, Ni_3Ti, Cd_3Mg, Ni_5U, and Pt_5Sm types of structure. The lattice constants of isostructural series show a trend which also is known for the radii of the actinide elements. Analytical data, self-irradiation effects, magnetic data, nuclear γ resonance spectra, and thermal behaviour of selected alloy phases as well as the preparation of alloy phases of some other transition and main group elements, e.g., Zr, Hf, Nb, Ta, Mg–Ba, are reported.

Introduction

In the course of our investigations on the phase equilibria in the systems UO_2–UO_3–$REO_{1.5}$ (RE = La–Lu), the following unexpected observations have been made:

a. In the fluorite phases $(U,RE)O_{2+x}$, it is not possible to reduce uranium in higher valence state with hydrogen quantitatively to U(IV) at a temperature below 1000°C; this phenomenon is due to the especially high stability of the fluorite lattice (*1*).
b. At higher temperatures and when using noble metal crucibles, we observed weight changes which indicated a reduction of the uranium to valences below four. The metallic appearance of the reaction product indicated the possibility of a chemical reaction between the substance and the crucible material.

Detailed studies confirmed this assumption and we were able to demonstrate that the hydrogen reduction of metal oxides in the presence of noble metals—the so-called coupled reduction (*2*, *3*, *8*, *13*)—can be applied to prepare very pure noble metal alloy phases not only with actinide elements but also with lanthanide (+ Sc, Y) and alkaline earth elements, Ti, Zr, Hf, V, Nb, Ta, and even with lithium. Earlier results of these studies have already been published elsewhere (*2*).

Experimental

Mixtures of oxides, carbonates and/or fluorides [e.g., actinide dioxides (Th–Cm), Pa_2O_5, RE-oxides (RE = La–Lu), $ScO_{1.5}$, $YO_{1.5}$, Li_2CO_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, Al_2O_3, TiO_2, ZrO_2, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, UF_4, UF_3, ThF_4, NdF_3, GdF_3, ErF_3, CaF_2] with very fine powders of noble metals (Pt, Pd, Ir, Rh) in alumina, iridium, or nickel crucibles placed in an alumina tube were heated in a high temperature furnace. The reduction temperatures ranged between 950 and 1550°C; the reaction times varied from 40 to 60 hr. The temperature needed to achieve complete reduction increased when going from Pt to Ir(Rh); furthermore, alloy phases with a high noble-metal-to-base-metal ratio are more easily prepared than compounds having a lower ratio. This means, e.g., that Pt_5Cm may be prepared at about 1200°C, whereas the preparation of Ir(Rh)-compounds (e.g., Ir_2Cm, Rh_3Cm) requires temperatures of 1550°C. Temperature measurements were performed using Pt–Pt/Rh thermocouples. In nearly all cases the reaction product was a fine powder which was directly suitable for X-ray analysis; in some cases, small crystals (~0.2 × 0.2 × 0.2 mm) were obtained.

The lattice parameters of the cubic compounds were determined by the Debye-Scherrer method, while the hexagonal and orthorhombic com-

pounds were analyzed by the diffractometer method. The lattice constants were computed on the IBM 360/65 by use of Program B106 (*6*). Reductions took place only with hydrogen at an extremely low partial pressure of oxygen and water vapour. The hydrogen used was purest bomb hydrogen available with an oxygen and water vapour content of about 10 ppm each. In order to prepare high purity hydrogen, several steps of purification were necessary. After passing through heated (~500°C) Ti-cuttings, heated Pt-asbestos, and molecular sieves, the hydrogen was further purified by bubbling through a series of three bottles containing liquid K–Na alloy [approximate composition K:Na = 2.5:1 (*7*)] and finally cooling to liquid nitrogen temperature to remove organic contaminants. The hydrogen thus purified had an oxygen content of less than 10^{-26} Torr and a partial water vapour pressure of less than 10^{-7} Torr. The oxygen content of the purified gas was determined by using a ThO_2 solid galvanic cell with Fe/FeO as the reference electrode; the water vapour content was measured by a hygrometer (type PA 1000, Panametrics Inc., Waltham, MA). The above-described purification apparatus was also used for the preparation of highly purified helium (oxygen content $\leq 10^{-19}$ Torr). Coupled reductions for the preparation of most of the Pt-, and all Pd-, Ir- and Rh-alloy phases were unsuccessful when performed with two commercial hydrogen diffusion apparatus supplied by different firms.

All investigations with radioactive materials were carried out in glove boxes. The following nuclides were used in this work (degree of purity in brackets): $^{231}Pa_2O_5$ (98%), $^{237}NpO_2$ (99.9%), PuO_2 (99.9%, ~92% ^{239}Pu + 7% ^{241}Pu), $^{241}AmO_2$ (99.9%), and CmO_2 (98%; 94% ^{244}Cm + 2% ^{245}Cm + 4% ^{246}Cm). Natural thorium and uranium were of nuclear grade quality. The platinum metals used had a purity of ≥99.9%; the base metal oxides used were of the best high quality available (W. C. Heraeus, Hanau/Germany). The quantities of oxides applied in the experiments amounted to about 5–2000 mg, depending on the base metal available. A very detailed description of the experimental part is given in (*3*).

Attempts to prepare alloy phases of the actinide elements with ruthenium, osmium, nickel, or cobalt have been started.

Results

A. Noble Metal (Pt, Pd, Ir, Rh)–Actinide Alloy Phases

The noble metal (B = Pt, Pd, Ir, Rh)–actinide (A = Th–Cm) alloy phases which we have prepared up to the present date by this "coupled reduction" are summarized in Table I. In the course of this investigation, 20 compounds have been prepared for the first time, which are listed in Table II together with preparation conditions, their structure types, and lattice constants.

The intermetallic phases prepared by coupled

TABLE I

NOBLE METAL (Rh, Ir, Pd, Pt)–ACTINIDE ALLOY PHASES PREPARED BY COUPLED REDUCTION DURING THIS WORK

	Th	Pa	U	Np	Pu	Am	Cm	Cf
Rh					Rh_2Pu	Rh_2Am	(Rh_2Cm)	
	Rh_3Th	Rh_3Pa[d]	Rh_3U	Rh_3Np	Rh_3Pu	Rh_3Am	Rh_3Cm	
Ir				Ir_2Np[a]	Ir_2Pu[a]	Ir_2Am[a]	Ir_2Cm[a]	
		Ir_3Pa	Ir_3U					
Pd				Pd_3Np	Pd_3Pu	Pd_3Am	Pd_3Cm	
	Pd_4Th		Pd_4U					
			Pd_5U					
Pt					Pt_2Pu	Pt_2Am	Pt_2Cm	
	Pt_3Th[b]	Pt_3Pa	Pt_3U	Pt_3Np	Pt_3Pu			
	Pt_5Th	Pt_5Pa	Pt_5U	Pt_5Np	Pt_5Pu	Pt_5Am	Pt_5Cm	(Pt_5Cf)[c]

[a] No Ir_3A compounds exist.
[b] Not obtained in pure form.
[c] Only indirect proof.
[d] Compounds which are underlined were prepared for the first time.

TABLE II

PREPARATION AND STRUCTURE OF NOBLE METAL (Rh, Ir, Pd, Pt)–ACTINIDE ALLOY PHASES PREPARED FOR THE FIRST TIME

Compound	Reduction temperature (±50°C)	Structure type	Lattice constants (Å)[a]		
			a	*b*	*c*
Rh_3Pa	1550	Cu_3Au	4.037		
Rh_3Np	1550	Cu_3Au	4.034		
Rh_2Am	1550	Cu_2Mg	7.548		
Rh_3Am	1550	Cu_3Au	4.098		
Rh_3Cm	1550	Cu_3Au	4.106		
Ir_3Pa	1550	Cu_3Au	4.047		
Ir_2Np	1550	Cu_2Mg	7.483		
Ir_2Am	1550	Cu_2Mg	7.550		
Ir_2Cm	1550	Cu_2Mg	7.561		
Pd_3Np	1350	Cu_3Au	4.069		
Pd_3Am	1300	Cu_3Au	4.158		
Pd_3Cm	1300	Cu_3Au	4.147		
Pt_3Pa	1250	Cd_3Mg(hex)[b]	5.704		4.957
Pt_5Pa	1200	Ni_5U	7.413		
Pt_3Np	1300	Ni_3Ti(hex)	5.822		9.575
Pt_5Np	1250	Pt_5Tm	5.225	9.134	27.43
Pt_2Am	1400	Cu_2Mg	7.615		
Pt_5Am	1200	Pt_5Sm	5.319	9.090	26.42
Pt_2Cm	1400	Cu_2Mg	7.625		
Pt_5Cm	1250	Pt_5Sm	5.329	9.108	26.38

[a] ±0.003 Å for cubic compounds; ±0.010 Å for hexagonal or orthorhombic compounds.
[b] Hex, hexagonal.

reduction, compiled in Table III, have previously been obtained by direct syntheses from the metallic components (for detailed references, *3*, *5*, *7*, *10*, *25–28*). Preparation of Pt_3Th and Pt_4Th by coupled reduction was not yet possible up to temperatures of 1600°C.

The structure of the Pt_5A phases (A = Th, Np–Cm) was determined by comparison with compounds of the Pt_5RE type which were prepared by coupled reduction and investigated by Bronger (*8*). The hitherto unknown structure of Pt_5Th (*9*) and Pt_5Pu (*10*, *11*) proved to be the same as that of Pt_5Sm; Pt_5Pa and Pt_5U crystallize in the cubic Ni_5U-structure type.

In the Ir–Pa and Ir–U systems, the alloy phases with 3:1 composition having ordered copper–gold structure are the compounds with the highest Ir content, whereas, for the transuranium elements, no such compounds but only alloy phases with 2:1 composition exist. These intermetallic phases are of Laves-phase type with cubic Cu_2Mg structure.

The platinum–actinide systems show some interesting features. In the case of the light actinide systems, compounds with 2:1, 3:1, and 5:1 alloy phases can be detected; it was not yet possible, however, to prepare the compounds Pt_2Th, Pt_2U (both are already prepared by common metallurgical techniques) and "Pt_2Np" yet unknown by coupled reduction. For the transplutonium elements, however, there exist only the 2:1 and 5:1 phases. Starting mixtures with ratios $Pt:AmO_2 = 3:1$ and $Pt:CmO_2 = 3:1$ yielded two-phase products consisting of Pt_2Am and Pt_5Am and Pt_2Cm and Pt_5Cm, respectively. As has been shown for the platinum–uranium system, the Pt_3U and Pt_5U alloy phases take up neither uranium nor platinum into solid solution, since no change in lattice parameters can be detected when varying the Pt:U ratio.

The structure of nearly all alloy phases could be determined by comparison with known types of structures. The 2:1 compounds crystallize in the cubic Laves phase type, while most 3:1 phases have the ordered Cu_3Au structure type. Deviation from this structure type could be observed only for the platinum alloy phases of the light actinide elements. As can be seen from the data of Tables II and III, four different types of structures were found for the 3:1 compounds of the platinum systems. Pt_3Th is the only compound whose type of structure is unknown. The Pt_3Pa and Pt_3U alloy phases crystallize in the hexagonal Cd_3Mg structure type, Pt_3Np has the hexagonal Ni_3Ti lattice, while the Pt_3Pu phase has the expected Cu_3Au structure type. This fact is remarkable because no case has been reported as yet in which a simple compound of three neighbouring elements in either the lanthanide or the actinide series has the same stoichiometric formula but different lattice structures. The structures of these different lattice types, however, are very similar, only the stacking order being different.

The lattice constants of an isostructural series follow a trend which is generally known when comparing the radii of the actinide elements. In the case of the Ir_2M (M = Th, U–Cm) and Rh_3M (M = Th–Cm) compounds, this may be seen in Fig. 1. A minimum in the lattice constants is to be seen between uranium and neptunium, both metals of which have been shown to possess the highest valence in their metallic state. Such a dependence of molar volume on the atomic number could not be observed in the series of platinum compounds because of the different types of structures, having more or less dense packing of the atoms.

Because of the inherent high radioactivity an increase in the lattice constants can be observed for the compounds Pd_3Am and Pd_3Cm, which seems to follow an exponential trend as has been found earlier for oxides and carbides of some transuranium elements. The increase in the lattice

TABLE III

KNOWN INTERMETALLIC PHASES OF THE ACTINIDES WITH NOBLE METALS (Rh, Ir, Pd, Pt) PREPARED BY COUPLED REDUCTION WITH PREPARATION CONDITIONS AND STRUCTURE

Compound	Reduction temperature (±50°C)	Structure type	Lattice constants (Å)[a]		
			a	*b*	*c*
Rh_3Th	1550	Cu_3Au	(4.139)		
Rh_3U	1550	Cu_3Au	3.990		
Rh_2Pu	1550	Cu_2Mg	7.488		
Rh_3Pu	1550	Cu_3Au	4.042		
Ir_3U	1550	Cu_3Au	4.037		
Ir_2Pu	1550	Cu_2Mg	7.518		
Pd_4Th	1400	Cu_3Au	4.113		
Pd_4U	1250	Cu_3Au	4.069		
Pd_5U	1200	unknown			
Pd_3Pu	1300	Cu_3Au	4.095		
Pt_5Th	1200	Pt_5Sm	5.364	9.157	26.60
Pt_3U	1200	Cd_3Mg(hex)[b]	5.753		4.898
Pt_5U	1200	Ni_5U	7.417		
Pt_2Pu	1400	Cu_2Mg	7.633		
Pt_2Pu	1200	Cu_3Au	4.105		
Pt_5Pu	1200	Pt_5Sm	5.314	9.100	26.51

[a] The lattice constants are values determined by the authors: ±0.003 Å for cubic compounds, ±0.010 Å for hexagonal or orthorhombic compounds.

[b] Hex, hexagonal.

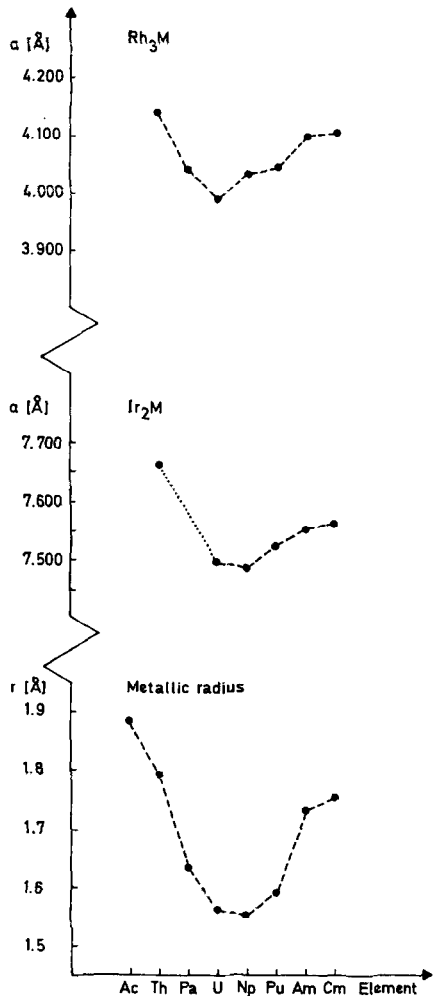


FIG. 1. Metallic radii of the actinide elements and lattice constants of the alloy phases Ir_2M (M = Th, U–Cm) and Rh_3M (M = Th–Cm). The lattice parameter of Rh_3Th, Ir_2Th, and Ir_2U are taken from Refs. (*12*), (*23*), and (*24*), respectively.

parameter is higher for $Pd_3{}^{244}Cm$ (Fig. 2) than for the corresponding ^{241}Am compound by a factor of about three. For $Pd_3{}^{244}Cm$, the change in the lattice constant varies from $a = 4.147$ Å at the time of preparation to $a = 4.167$ Å after about a week, the corresponding values for $Pd_3{}^{241}Am$ are $a = 4.158$ Å (at preparation) to 4.165 Å after 43 days. Mathematically the changes of lattice constants for these two compounds may be given as follows:

$$\frac{\Delta a}{a} = 5.7 \times 10^{-3}\,(1 - e^{-1.3\times10^{-2}\times t[h]}) \text{ for } Pd_3{}^{244}Cm,$$

$$\frac{\Delta a}{a} = 1.7 \times 10^{-3}\,(1 - e^{-8.5\times10^{-2}\times t[d]}) \text{ for } Pd_3{}^{241}Am.$$

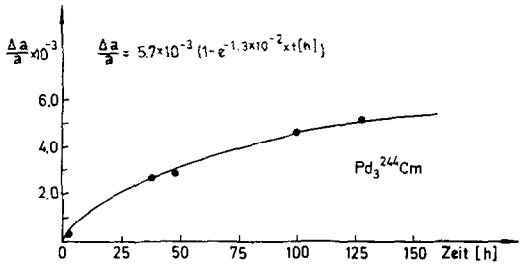


FIG. 2. Increase in the lattice constant of $Pd_3{}^{244}Cm$ resulting from self-irradiation.

Mössbauer studies of Pt_3Np at 4.2°K have shown that the nuclear γ-resonance spectrum of this compound consists of a somewhat broadened single line ($\Gamma = 6.4 \pm 0.3$ mm/sec) with an isomer shift of $\delta = -0.2$ mm/sec relative to NpO_2 (Am(Th) as the source), indicating a formal zero-valency of neptunium, for Np-metal: $\delta = -0.13$ cm/sec and +0.13 cm/sec, respectively, reflecting the two inequivalent lattice sites of α-Np (*5*).

Magnetic measurements with a magnetic balance working on the Faraday principle were performed on the compounds Pt_3Np and Pd_3Pu in the temperature region 4.2–280°K and 1.8–296.3°K, respectively. The magnetic measurements show that Pt_3Np and Pd_3Pu follow the Curie-Weiss relationship up to low temperatures.

Pt_3Np: 47–280°K, $\theta = -47$°K,
$\mu_{eff}(280°K) = 2.95\ \mu_B$;

Pd_3Pu: 134–296°K, $\theta = -108$°K,
$\mu_{eff}(296.3°K) = 0.907\ \mu_B$.

At very low temperatures, both compounds show magnetic transitions and become antiferromagnetic. Figure 3 shows this effect for the compound Pd_3Pu. The Néel-temperature has been determined to be 20.5°K for Pd_3Pu and 22°K for Pt_3Np. Pd_3Am shows a quite different behaviour, which as yet could not be explained. The most striking feature is the strong dependence of susceptibility on the magnetic field strength. On extrapolation to infinite magnetic field strength, the magnetism of Pd_3Am follows the Curie-Weiss relationship up to at least 10°K (*21*).

B. Noble Metal(Pt, Pd, Rh)–Lanthanide(+Sc, Y) Alloy Phases

The preparation of the Pt_5RE phases (RE = La–Tm, Y) by coupled reduction was first performed by Bronger (*8*) who also prepared some Pt_3RE phases (RE = Ho–Lu, Sc).

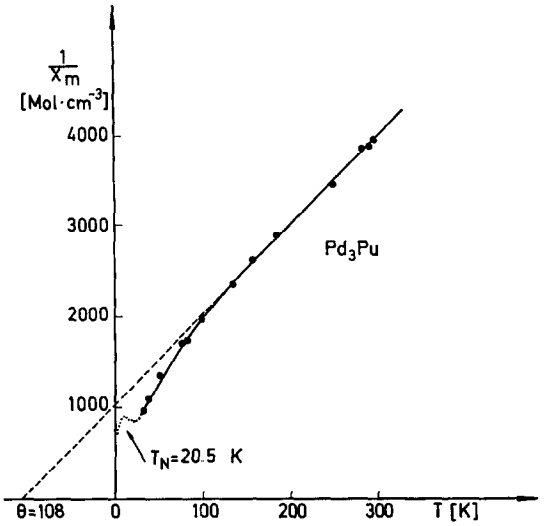


FIG. 3. Magnetic behaviour of Pd_3Pu as a function of temperature. The small points at low temperatures are measuring points.

While preparing the compounds Pt_5RE (RE = La–Tm, Y) during this work, we could reproduce the results of Bronger (*8*). The preparation of the phases "Pt_5Yb" and "Pt_5Lu", however, was unsuccessful; the experiments at 1200–1400°C from initial mixtures $Pt:YbO_{1.5}(LuO_{1.5})$ of 5:1 resulted in two-phase products of $Pt_3Yb + Pt$ and $Pt_3Lu + Pt$, respectively. As there was no change in lattice parameters compared with the pure phases, it is possible that the compounds "Pt_5Yb" and "Pt_5Lu" do not exist. Preparation of most Pt_5RE phases was accomplished at 1200°C; in the case of Pt_5Sm and Pt_5Eu, 1300°C was necessary to complete the reaction.

The Pt_5RE compounds show three different types of structure, described by (*8*) as *a*-, *b*-, and *c*-type. The phases of the *a*-type Pt_5La, Pt_5Ce, Pt_5Pr, and Pt_5Nd are of the hexagonal Cu_5Ca-type (*22*); Pt_5Sm, Pt_5Eu, and Pt_5Gd belong to the *b*-type which show orthorhombic symmetry. The phases of the *c*-type Pt_5Tb, Pt_5Dy, Pt_5Ho, and Pt_5Er, also of orthorhombic symmetry, are very similar to the phases of the *b*-type. A further change in structure may occur at Pt_5Tm. This is not certain since "Pt_5Yb" and "Pt_5Lu" are probably nonexistent. According to experimental results for the Pt–U-system, the phase Pt_5La takes up neither lanthanum nor platinum into solid solution at 1200°C, since no change in lattice parameters can be detected when varying the Pt:La ratio.

Apart from the Pt_5RE compounds, we were able to prepare other types of alloy phases of the lanthanides such as Pt_3RE (RE = Tb–Lu, Sc, Y), Pt_2RE (RE = La–Gd) and Pd_3RE (RE = La–Lu, Sc, Y) in addition to Rh_3Sc. All these compounds have been prepared earlier by conventional techniques, while Bronger *et al.* (*8*, *13*, *14*) were only successful in preparing the compounds Pt_3RE (RE = Ho–Lu, Sc). Table IV shows the phases Pt_3RE (RE = Tb–Lu, our Sc) prepared during this work; the lattice constants are values determined by the authors.

In case of the lanthanides, RE = La–Gd, no 3:1 phases are existent. Coupled reduction at 1400°C of initial mixtures $Pt:REO_{1.5}$ (RE = La–Gd) = 3:1 resulted in two-phase products of Pt_2RE and Pt_5RE. This observation is in accordance with results of Harris (*15*), while Moriarty *et al.* (*16*, *17*) have reported compounds of the Pt_3RE-type for RE = La–Gd. Moreover, the lattice constants for these compounds given by Moriarty *et al.* (*16*, *17*) are smaller than those for the phases Pt_3RE (RE = Tb–Lu), and this fact is contrary to the trend of the metallic radii of the lanthanide elements.

Starting from this observation we were able to prepare the Pt_2RE (RE = La–Gd) compounds which are listed in Table V.

All compounds of the type Pd_3RE (RE = La–Lu, Sc, Y) have been prepared earlier by

TABLE IV

ALLOY PHASES Pt_3RE (RE = Tb–Lu, Sc, Y) AND Rh_3Sc WITH Cu_3Au TYPE OF STRUCTURE PREPARED BY COUPLED REDUCTION

Compound	Reduction temperature (±50°C)	Lattice constant *a* (Å)[b]
Rh_3Sc	1550	3.909
Pt_3Sc[a]	1250	3.953
Pt_3Y	1300	4.069
Pt_3Tb	1300	4.085
Pt_3Dy	1250	4.073
Pt_3Ho[a]	1200	4.064
Pt_3Er[a]	1200	4.052
Pt_3Tm[a]	1200	4.040
Pt_3Yb[a]	1200	4.035
Pt_3Lu[a]	1200	4.027

[a] These compounds were also prepared by Bronger (*8*) by means of coupled reduction.

[b] The lattice constants are values determined by the authors, ±0.003 Å.

TABLE V

ALLOY PHASES Pt_2RE (RE = La–Gd) WITH Cu_2Mg TYPE OF STRUCTURE PREPARED BY COUPLED REDUCTION[a]

Compound	Lattice constant a (Å)[b]
Pt_2La	7.781
Pt_2Ce	7.729
Pt_2Pr	7.713
Pt_2Nd	7.689
Pt_2Sm	7.660
Pt_2Eu	7.641
Pt_2Gd	7.637

[a] Reduction temperature = 1400 ± 50°C.

[b] The lattice constants are values determined by the authors, ±0.003 Å.

TABLE VI

ALLOY PHASES Pd_3RE (RE = La–Lu, Sc, Y) WITH Cu_3Au TYPE OF STRUCTURE PREPARED BY COUPLED REDUCTION[a]

Compound	Lattice constant a (Å)[b]
Pd_3La	4.224
Pd_3Ce	4.141
Pd_3Pr	4.135
Pd_3Nd	4.120
Pd_3Sm	4.101
Pd_3Eu	4.093
Pd_3Gd	4.089
Pd_3Tb	4.074
Pd_3Dy	4.067
Pd_3Ho	4.058
Pd_3Er	4.051
Pd_3Tm	4.044
Pd_3Yb	4.040
Pd_3Lu	4.029
Pd_3Sc	3.969
Pd_3Y	4.061

[a] Reduction temperature = 1350 ± 50°C.

[b] The lattice constants are values determined by the authors, ±0.003 Å.

conventional metallurgical techniques, while Schulz *et al.* (*14*) did not succeed in preparing the phases by coupled reduction. Our detailed studies showed that for preparation of these compounds the experimental conditions, particularly the purity of the hydrogen, must be rigidly controlled, otherwise the experiments result in mixtures of oxides and palladium–lanthanide(+ Sc, Y)-mixed crystals. While Hutchens *et al.* (*18*) were able to prepare all Pd_3RE phases except Pd_3Tm, this work gives the lattice constant of the pure phase Pd_3Tm for the first time. The phases prepared by coupled reduction are compiled in Table VI.

C. Noble Metal (Pt, Pd, Ir, Rh) Alloy Phases of Transition and Main Group Elements

In addition to the actinide and lanthanide (+ Sc, Y), a lot of intermetallic phases of transition and main group elements were prepared by this method of coupled reduction. All of these compounds have been prepared earlier by conventional metallurgical techniques. Some of them (noted with asterisks in the enumeration below) have been formerly obtained by Bronger and co-workers (*8*, *13*, *14*) by means of coupled reduction. The lattice constants of these compounds have been determined in this work [for experimental details, see (*3*)]: Pt_7Li*, Pd_3Mg, Pt_2A (A = Ca*, Sr*, Ba*), Pt_3A (A = Mg*, Sr*, Al*), Pt_5A (A = Ca*, Sr*, Ba*), Pd_5A (A = Sr, Ba), Pt_2Si, Pd_2Si*, Pt_3A (A = Ti*, Zr, Hf), Pd_3A (A = Ti*, Zr, Hf), Ir_3A (A = Ti*, Zr, Hf), Rh_3A (A = Ti*, Zr, Hf), Pt_3A (A = Cr, V, Nb, Ta), Pd_3A (A = Cr, V, Nb, Ta), Ir_3A (A = V, Nb, Ta), Rh_3A (A = V, Nb, Ta), Ir_3Cr, Rh_3Cr, Pt_3Mn, Pd_3Mn.

Analyses

Some comments should be made concerning the analytical purity of the alloys. Because the noble-metal-to-base-metal ratio does not change during the coupled reduction, the ratio of the elements in the final products is the same as in the starting mixtures; this has been demonstrated by chemical analyses on several characteristic compounds. Exceptions to this rule will be discussed later on. Determinations of the oxygen content were made on most of our alloy phases; some phases were also analyzed for nitrogen and hydrogen. All determinations were performed by vacuum hot extraction. In Table VII, characteristic and not necessarily the best analytical data are summarized for some noble metal alloy phases.

The contents of nitrogen and hydrogen are very low, especially when cooled in a helium gas

TABLE VII

ANALYTICAL DATA FOR NOBLE METAL ALLOY PHASES

Compound	O_2 (ppm)	N_2 (ppm)	H_2 (ppm)
Ir_3U	1600	<100	<20[a]
Ir_3Zr	900	<100	<20[a]
Pd_3Lu			<10[a]
Pd_4U			15[a]
Pt_3Np	580	<100	80
Pt_5Np	540	200	20
Pt_3Pu	150	<100	300
Pt_5Pu	230	<100	140
Pt_5U	330		10[a]
Pt_5Th	65		

[a] Cooled in a highly purified helium gas stream; all other cooled in H_2.

stream. The oxygen content is somewhat higher but exceeds 1000 ppm only in one case, most values being between 300 and 500 ppm. This excludes the stabilization of these phases by the incorporation of oxygen in the different lattices as has been observed for some inverse perovskite compounds of, e.g., niobium.

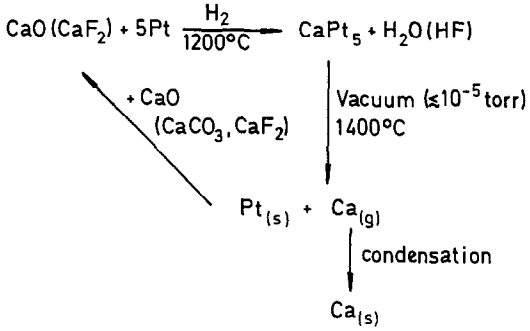
In the course of our investigations, we also determined the oxidation ranges of some representative intermetallic compounds. All determinations were performed under 1 atm of oxygen by means of thermogravimetric analysis using a Mettler thermomicrobalance. Oxidation ranges (the maxima of the oxidation ranges are in parentheses) of 400–600°C (520) for Pt_5Th, 360–420°C (370) for Pt_3U, 320–560°C (430) for Pt_5U, 250–650°C (470) for Pt_3Np, 310–620°C (530) for Pt_5Np, 320°–580°C (490) for Pt_2Pu, 350–530°C (470) for Pt_3Pu, 450–600°C (560) for Pt_5Pu, 500–800°C (630) for Pd_3Pu, and 390–630°C (450) for Pt_5La, 390–600°C (550) for Pt_5Eu, 450–600°C (560) for Pt_5Tb, and 470–680°C (570) for Pt_5Tm were observed.

Preparation of Metals (Am, Cf, Ca–Ba, Li) from Noble Metal Alloy Phases

When preparing platinum–americium alloy phases at temperatures above 1300°C, we observed mainly a loss of americium in the reaction product. Detailed studies showed that these intermetallic phases are decomposed at temperatures of 1300°C or higher in vacuum or inert gas atmospheres to yield solid noble metal and americium vapour which could be condensed at cooled parts of the reaction apparatus. Müller (*19*) was able to prove that this method could be used to prepare very pure americium metal.

We also have been able to demonstrate that not only americium but also other volatile metals (e.g., Cf, Ca–Ba, Li) could be prepared by this method (*20*). It is interesting to note that we were able to prepare calcium also from the mineral fluorite practically in one step by coupled reduction to the compounds Pt_2Ca or Pt_5Ca followed by decomposition in vacuum at higher temperatures.

This means that metals like Am, Cf, Ba–Ca, and Li can be prepared by direct hydrogen reaction of the corresponding oxides, the noble metals only serving as a catalyst. This is shown by the following scheme for, e.g., Ca:



It shows that the platinum, which results from the thermal decomposition of the intermetallic phase, can be mixed with new starting materials (CaO, $CaCO_3$, CaF_2) for the preparation of new intermetallic compounds.

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