

Coupled Reduction with Platinum Group Metals

THE PREPARATION OF HIGH PURITY RARE METALS

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Very pure metals of the actinide, lanthanide and alkaline earth series can be prepared from their oxides by coupled reduction by hydrogen in the presence of platinum group metals. During the process the platinum group metals form intermetallic phases with the metals from the oxides. These phases are decomposed to yield the pure metals in gaseous form and the platinum group metals in solid form. The pure gaseous metals condense to produce pure solid specimens.

In the course of our investigations dealing with phase equilibria in uranium oxide-rare earth oxide systems, we made the following unexpected observations (1):

- (1) In fluorite phases with a high content of rare earth oxides it is not possible to reduce higher valency states of uranium to tetravalent uranium, at least when using hydrogen and at temperatures below 1000–1100°C.
- (2) At higher temperatures and when using noble-metal crucibles, we observed weight changes which indicated a reduction of the uranium to valencies below four. The metallic appearance of the reaction product made a chemical reaction between the substance and the crucible very possible.

Detailed studies proved this assumption and we were able to demonstrate that the hydrogen reduction of metal oxides in the

presence of noble metals (platinum, palladium, rhodium, iridium) can be applied to prepare very pure noble metal alloys with actinide, lanthanide and alkaline earth elements, titanium, zirconium, hafnium, vanadium, niobium, tantalum, and even with lithium (2–6).

The direct synthesis of alloy phases of noble metals with base metals involves many serious problems caused by the relatively high vapour pressure of the base metals. In addition, the choice of the crucible material and of the gas atmosphere affects the results. Furthermore, ordered phases are obtained only by repeated homogenising and by prolonged and careful annealing. Also the usual methods of preparation of highly radioactive metals are somewhat difficult, and in some cases the elements, such as protoactinium (^{231}Pa) and curium (^{244}Cm), are only prepared in milligram quantities and have not yet been investigated sufficiently. Further methods for the preparation of intermetallic phases are the reactions of platinum metals with nitrides (7,8), sulphides (9), borides (10), or carbides (11,12) of the base metals; the reactions of the carbides with platinum metals have been investigated more thoroughly. However, the results of the reactions of base metal carbides with platinum metals do not give single-phase products but mixtures, e.g. UMe_3 and U_2MeC_2 (Me=Ru, Os, Rh, Ir, Pt), or UMe_3 and carbon corresponding to the initial metal concentration. The application of these methods to the preparation of intermetallic phases is further hindered, as the stoichio-

metric constitution of the carbides or nitrides must be examined by analyses before starting the reaction. The preparation of the pure oxygen-free carbides and nitrides of the transuranium elements is also complicated by practical problems. In the cases of curium and protoactinium no carbides and nitrides have yet been prepared.

From metallurgical practice it is known that oxides difficult to reduce are more easily reduced in the presence of nobler metals. This is the case for the preparation of ferrous alloys and results from the fact that with higher temperatures the oxygen partial pressure of the oxide is raised by the presence of the more noble metal. Reduction is then possible if both metals form mixed crystals and this is explained by the affinity forces occurring during the formation of the mixed crystals (13).

On this basis it was possible for Klemm and Bronger (14) to prepare some noble metal alloy phases by reduction of base metal oxides with platinum metals in the presence

of hydrogen or ammonia. Reaction mechanisms of coupled reactions in the case of the refractory oxides with practical reference to platinum thermocouples have been studied by Darling and his colleagues (15-19).

Details of this method of obtaining the very pure noble metal alloy-phases are as follows. When heating the oxides with finely powdered noble metals in an extremely pure stream of hydrogen, a reaction takes place which we have called "coupled reduction", i.e. the reduction of a metal oxide (carbonate)/fluoride in the presence of a noble metal, leading to the formation of a base metal-noble metal alloy.

The formula is general for the method used (in the case of an oxide):



Up to the present time we have been able to show that coupled reduction is possible when using platinum, palladium, iridium and rhodium as the noble metals. Attempts to prepare alloy phases with ruthenium, osmium,

Platinum Group Metal-Actinide Alloy Phases Prepared by Coupled Reduction during This Work								
	Th	Pa	U	Np	Pu	Am	Cm	Cf
Rh	Rh ₃ Th	Rh₃Pa	Rh ₃ U	Rh₃Np	Rh ₂ Pu Rh ₃ Pu	Rh₂Am Rh₃Am	(Rh ₂ Cm) Rh₃Cm	
Ir		Ir₃Pa	Ir ₃ U	Ir₂Np^a	Ir ₂ Pu ^a	Ir₂Am^a	Ir₂Cm^a	
Pd	Pd ₄ Th		Pd ₄ U Pd ₅ U	Pd₃Np	Pd ₃ Pu	Pd₃Am	Pd₃Cm	
Pt	Pt ₃ Th ^b Pt ₅ Th	Pt₃Pa Pt₅Pa	Pt ₃ U Pt ₅ U	Pt₃Np Pt₅Np	Pt ₂ Pu Pt ₃ Pu Pt ₅ Pu	Pt₂Am Pt₅Am	Pt₂Cm Pt₅Cm	(Pt ₅ Cf) ^c
a No Ir ₃ A compounds exist b Not obtained in pure form c Only indirect proof Compounds in bold type were prepared for the first time								

nickel, or cobalt by means of coupled reduction have been started. The temperature needed to achieve complete reduction increases when going from platinum to iridium and decreases with increasing atomic number of the actinide element. Furthermore, alloys with a high noble metal : actinide ratio are more easily prepared than compounds having a lower ratio. This means, for example, that Pt_5Cm may be prepared at about $1200^\circ C$, whereas the preparation of the iridium compound requires temperatures of $1550^\circ C$. The table shows the platinum-, palladium-, iridium-, and Rh-actinide intermetallic phases prepared by coupled reductions, among them the twenty compounds prepared for the first time.

Intermetallic Phase Structure

The structure of Pt_5A phases ($A=Th, Np-Cm$) was elucidated by comparison with compounds of the Pt_5RE type which were prepared by coupled reduction and were investigated by Bronger (20). The hitherto unknown structure of Pt_5Th and Pt_5Pu proved to be isostructural with Pt_5Sm ; Pt_5Pa and Pt_5U crystallise in the cubic Ni_5U -structure type.

The structure of the other new alloy phases could be established by comparison with known types of structures. The 2:1 compounds crystallise in the cubic Laves-phase type, whilst 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. Four different types of structures were found for the 3:1 compounds of the platinum system. Pt_3Th is the only compound whose type of structure is unknown. The Pt_3Pa and Pt_3U alloy phases crystallise 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 lan-

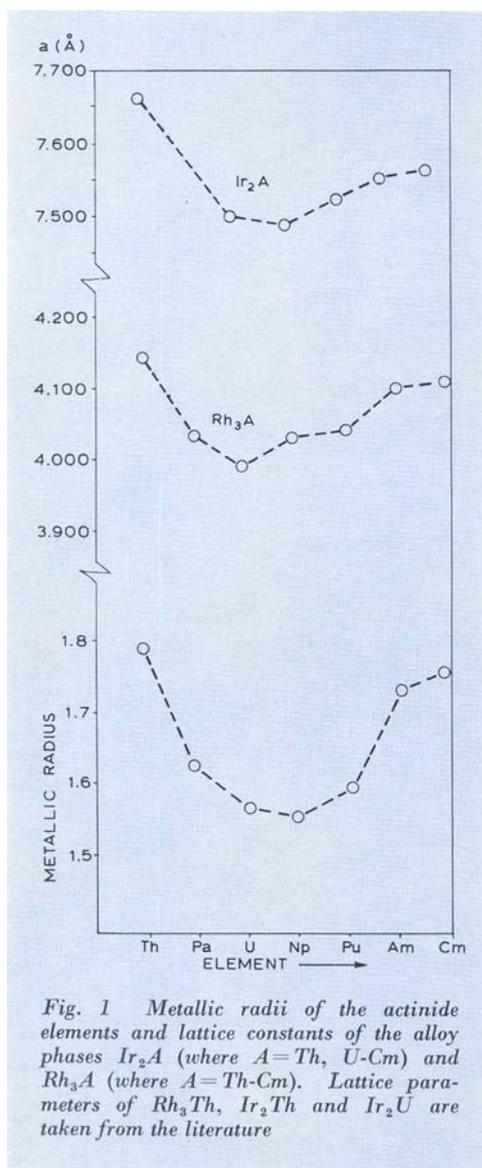


Fig. 1 Metallic radii of the actinide elements and lattice constants of the alloy phases Ir_2A (where $A=Th, U-Cm$) and Rh_3A (where $A=Th-Cm$). Lattice parameters of Rh_3Th, Ir_2Th and Ir_2U are taken from the literature

thanide 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 the isostructural series follow a trend which is generally known when comparing the radii of the actinide elements. In the case of the Ir_2A ($A=Th, U-Cm$) and Rh_3A ($A=Th-Cm$) compounds this may be seen in Fig. 1. A mini-

imum in the lattice constants is to be seen between uranium and neptunium, both of which metals have been shown to possess the highest valency in their metallic state. Such a dependence of molar volume with 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.

The preparation of the Pt_5RE phases ($RE=La-Tm, Y$) by coupled reduction was first performed by Bronger (20), who also prepared some Pt_3RE phases ($RE=Ho-Lu, Sc$).

Apart from the Pt_5RE ($RE=La-Tm, Y$) and Pt_3RE ($RE=Tb-Lu, Sc, Y$) compounds we have been able to prepare other types of alloy phases of the lanthanides, such as Pt_2RE ($RE=La-Gd$) and Pd_3RE ($RE=La-Lu, Sc, Y$) and also Rh_3Sc . All these compounds have been prepared earlier by conventional metallurgical techniques except Pd_3Tm , which could not have been prepared (21) in pure form owing to the relatively low ΔH_V of thulium metal. Further information on Pd_3Tm is available elsewhere (3,4).

The hydrogen used was the purest cylinder hydrogen available with oxygen and water vapour contents of about 10 p.p.m. each. In order to prepare high purity hydrogen from it several stages of purification by physical and chemical methods were necessary (3, 22). After passing through heated titanium cuttings, heated platinum/asbestos and molecular sieves, the hydrogen was further purified by bubbling through a series of three bottles containing liquid potassium-sodium alloy (approximate composition $K:Na=2.5:1$ (23)) and finally by 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 (22, 24). 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 with an "Hygrometer PA 1000" made by Panametrics, Waltham, U.S.A. The same method was also used to purify helium and argon, which sometimes were used as inert gas when cooling reaction products.

Coupled reductions for the preparation of most of the platinum alloy phases and all of the palladium, iridium and rhodium alloy phases were unsuccessful when performed with two commercial hydrogen diffusion apparatuses (3).

Some comment should be made concerning the analytical purity of the alloys. Because the noble metal: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 initial mixtures; this has been demonstrated by chemical analyses on several characteristic compounds. Exceptions to this rule will be discussed later. Determinations of the oxygen contents were made on most of the alloy phases; some phases were also analysed for nitrogen and hydrogen. All determinations were performed by vacuum hot extraction. The oxygen contents of most of these alloy phases do not exceed 500 p.p.m.; the hydrogen and nitrogen contents are always less than 100 p.p.m. This means that these phases are not stabilised by the incorporation of oxygen or nitrogen (3).

An increase in stability, however, is to be observed when carbon is incorporated in the lattice of the compounds of Cu_3Au -type structure. The reaction, for example, of $ThRh_3$ with carbon yields $ThRh_3C_x$ with a maximum value of $x=0.5$ (25, 26). The increase in stability may be obtained from thermodynamic data. Using a high temperature galvanic cell of the type



a preliminary ΔG_{1000K} value of -49.1 kcal/mole for UPt_5 was obtained (27). Using similar galvanic cells the following data were obtained:

URu_3	$\Delta G_{1000K} = -45.5$ kcal/mole
URh_3	$\Delta G_{1000K} = -62.4$ kcal/mole

The increase in stability of the carbon-doped compounds may be seen by comparing the ΔG values of URu_3 and $URu_3C_{0.7}$, the compound with the highest carbon content (12). By using a galvanic cell of the type



a ΔG_{1000K} value for $URu_3C_{0.7}$ of -60.1 kcal/mole was obtained. The increase in stability increases with the carbon content of the intermetallic phases. The influence of carbon in the octahedral positions on the stability of the metal lattice can be interpreted by an increase of the effective valency of the platinum metals.

Preparation of Metals

When preparing americium-platinum alloys at temperatures in excess of $1300^\circ C$ we observed mainly a loss of americium in the reaction product. Detailed studies showed that the americium-platinum alloys decomposed at temperatures of about $1300^\circ C$ or higher, in vacuum or inert gas atmospheres, to yield solid noble metal and americium. These could be condensed at cooled parts of the reaction apparatus.

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 (3, 5, 6).

Not yet investigated by us is the preparation of the rare earth metals by this method. However, remembering the above-mentioned fact, that the conventional metallurgical technique for the preparation of Pd_3Tm was not successful (21), it should obviously be possible to prepare rare earth metals, at least those with a relatively low ΔH_V (e.g. thulium).

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. Detailed studies of these processes and their thermodynamic relationships are now under our investigation.

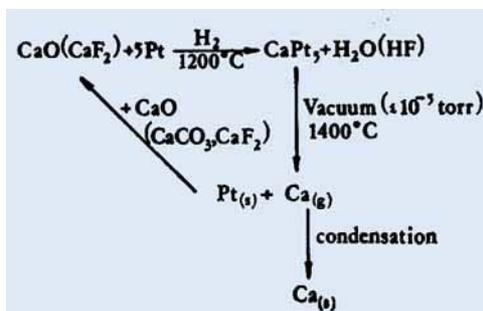


Fig. 2 Scheme showing how the coupled reduction process can lead to the preparation of the pure metals Li, Ca, Sr, Ba, ^{241}Am , and ^{252}Cf (^{244}Cm). Here pure calcium is prepared. The hydrogen used at $1200^\circ C$ must be extremely pure, i.e. O_2 and $H_2O(g)$ contents must be very low

This means that metals like Am, Cf, Cm, 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 scheme in Fig. 2.

The significance of this type of reduction is that using alloy phases as intermediates it is possible to prepare volatile metals by hydrogen reduction of the oxide. Preliminary data even indicate that it is possible to separate two elements, for example, californium from americium or from curium, by utilising the difference in volatility of the actinide metals. With tracer amounts of ^{252}Cf we have been able to show that californium is volatilised by more than 90 per cent at $1250^\circ C$ in extremely pure hydrogen or in vacuum from californium oxide-platinum mixtures, at which temperature curium does not volatilise. Detailed studies of these processes and their thermodynamic relationships are now under investigation.

References

- 1 H. G. Diehl and C. Keller, *J. Solid State Chem.*, 1971, 3, 621
- 2 B. Erdmann and C. Keller, *Inorg. Nucl. Chem. Lett.*, 1971, 7, 675
- 3 B. Erdmann, *Kernforschungszentrum Karlsruhe Rept. KFK-1444*, 1971
- 4 B. Erdmann and C. Keller, *J. Solid State Chem.*, 1973, 7, 40

- 5 U. Berndt, B. Erdmann and C. Keller, *Angew. Chem.*, 1972, **84**, 537; *Angew. Chem. Internat. Ed. En.*, 1972, **11**, 515
- 6 U. Berndt, B. Erdmann and C. Keller, *U.S. Patent*
- 7 H. Holleck, *Kernforschungszentrum Karlsruhe Rept. KF K-1011*, 1969
- 8 H. Holleck, Proc. 3rd Internat. Conf. on Solid Compounds of Transition Elements, Oslo, 1969
- 9 E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *J. Am. Ceram. Soc.*, 1951, **34**, 128
- 10 R. A. Mercuri and J. M. Criscione, *Abstr. Papers, 158th Mtg., Am. Chem. Soc.*, 1969, INOR 33
- 11 H. Holleck, *J. Nucl. Mater.*, 1968, **28**, 339
- 12 H. Holleck and H. Kleykamp, *J. Nucl. Mater.*, 1970, **35**, 158
- 13 G. Grube and M. Flad, *Z. Elektrochem.*, 1942, **48**, 377
- 14 W. Bronger and W. Klemm, *Z. Anorg. Allgem. Chem.*, 1962, **319**, 58
- 15 A. S. Darling, G. L. Selman and R. Rushforth, *Platinum Metals Rev.*, 1970, **14**, 54
- 16 *Ibid.*, 1970, **14**, 95
- 17 *Ibid.*, 1970, **14**, 124
- 18 *Ibid.*, 1971, **15**, 13
- 19 A. S. Darling, *Platinum Metals Rev.*, 1967, **11**, 138
- 20 W. Bronger, *J. Less-common Metals*, 1967, **12**, 63
- 21 R. D. Hutchens, V. U. S. Rao, J. E. Greedan, W. E. Wallace and R. S. Craig, *J. Appl. Phys.*, 1971, **42**, 1293
- 22 B. Erdmann, *GIT*, 1972, **16**, 1283
- 23 M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 1958, p. 876
- 24 B. Erdmann, *Messen u. Steuern*, 1972, **H29**, 27
- 25 H. Holleck, *J. Nucl. Mater.*, 1972, **42**, 278
- 26 H. Holleck, *Monatsh. Chem.*, 1971, **102**, 1699
- 27 N. Schmidt and C. Keller, unpublished data

Science Awards to Platinum Metals Research Workers

PROFESSOR GEOFFREY WILKINSON AND DR VLADIMIR HAENSEL

The achievements of two research workers prominent in the platinum metals field were recognised in October 1973, when awards to Professor Geoffrey Wilkinson and Dr Vladimir Haensel were announced. Both recipients have contributed to past issues of *Platinum Metals Review*. In the January 1959 issue Dr Haensel described "The Penex Process for Pentane Isomerisation". In January 1964 he contributed "Duofunctional Catalysts in the Petroleum Industry", while Professor Wilkinson reviewed "Organometallic Compounds of the Platinum Metals". Wilkinson then reviewed "Tertiary Phosphine Complexes of the Platinum Metals" in the April 1968 issue.

Professor Wilkinson, now of Imperial College, London, has been awarded the Nobel Prize for chemistry jointly with Ernst Fischer. The award was made for determining the structure of "sandwich" compounds, initially of ferrocene, and subsequently synthesising many other such compounds. Ruthenocene is one such platinum metal compound. The original work was carried out in 1952 when Wilkinson was teaching at Harvard. Since returning to London in 1956 his interests have gradually shifted to other areas, among which the development of some of the most active homogeneous catalysts is of particular importance to the chemistry of

the platinum metals. His name is closely associated with the family of catalysts based on tris(triphenylphosphine)chlororhodium, $(\text{Ph}_3\text{P})_3\text{RhCl}$, from which the carbonyl complexes $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ and $\text{RhH}(\text{CO})(\text{Ph}_3\text{P})_3$ used in hydroformylation reactions have been developed.

The National Medal of Science, the U.S. Federal Government's highest award for distinguished achievement in science, mathematics and engineering, was presented by President Nixon at the White House on October 10th to ten scientists, among whom was Dr Haensel, Vice-President for Science and Technology of the Universal Oil Products Company, Des Plaines, Illinois, for "his outstanding research in the catalytic reforming of hydrocarbons which has greatly enhanced the economic value of our petroleum natural resources". Dr Haensel's work has, of course, included responsibility for the development and improvement of the series of U.O.P. Platforming catalysts since their inception. Platinum-based catalysts for the reforming of hydrocarbons were first developed at U.O.P. and Haensel's team has constantly upgraded their performance, more recently by the introduction of bimetallic catalysts in which a second metal synergistically improves the reforming performance of platinum.

F. J. S.