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# Ir–Re binary alloys under extreme conditions and their electrocatalytic activity in methanol oxidation

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Authors dedicate this paper to Dr. Iraida A. Baidina on the occasion of Her 70th Birthday.

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A B S T R A C T

The formation of the *hcp*-$Ir_{0.70}Re_{0.30}$ alloy from the single-source precursor $(NH_4)_2[Ir_{0.70}Re_{0.30}Cl_6]$ upon heating in hydrogen atmosphere can be associated with the formation of two intermediates: a crystalline iridium-based intermediate and a *fcc*-structured alloy. Ir–Re alloys show lower thermal expansion coefficients and smaller compressibility in comparison with individual metals. The high-temperature high-pressure treatment of *hcp*-$Ir_{0.70}Re_{0.30}$ alloy enable us to probe the Ir–Re pressure dependent phase diagram. The miscibility gap between *hcp* and *fcc* alloys slightly shifts towards the rhenium side below 4 GPa. Above 4 GPa, the miscibility gap does not drift with pressure and narrows with compression. The electrocatalytic activity of Ir–Re alloys has been tested for methanol oxidation in acidic water solution. Ir–Re alloys show higher electrocatalytic activity in comparison with pure Ir and Re, which makes them perspective candidates for fuel cells application. The highest electrocatalytic activity has been obtained for the two-phase $Ir_{0.85}Re_{0.15}$ composition.



## 1. Introduction

The detailed investigation of binary alloys and their phase diagrams provides the basement for further progress in the development of multicomponent alloy compositions. Pure metals and binary alloys can be considered important models for further progression towards more complex systems, such as high-entropy alloys, metallic glasses, metallic foams and heterogeneous metal matrix composites. Refractory alloys based on platinum group metals play an important role as materials with outstanding mechanical, thermal and chemical stability. Nevertheless, due to their high melting points and price their applications are still limited and information about their properties is fragmented.

Alloys based on platinum group metals with rhenium, especially Pt–Re alloys, were extensively investigated due to their extraordinary thermal stability and catalytic properties. At the same time, Ir–Re and Rh–Re alloys were investigated sporadically [1,2]. As an example, Ir–Re alloys were proposed as materials for thermocouples [3], crucibles [4], and as active heterogeneous catalysts [5–8]. CVD prepared Ir/Re films were applied to the construction of rocket combustion chambers [9].

Pure platinum group metals were broadly investigated under

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extreme conditions. Nevertheless, their alloys have seldom been studied. Only Ir—Os alloys were tested under high-pressure high-temperature conditions *in situ* up to 140 GPa and 3000 °C [10,11], and the Ir—Resystem has been investigated under high-temperature high-pressure up to 9 GPa and 2000 °C *ex situ* using a belt press [12–16]. High-temperature high-pressure studies may lead to a deeper understanding of the stability of ultra-hard ultra-incompressible alloys upon extreme conditions and eventually be exploited as tools for the construction of realistic pressure-dependent phase diagrams. These are especially needed to predict alloys properties under working conditions as well as to understand the formation of their metallic minerals from the melt in the Earth Core.

The Ir—Re binary metallic system has been investigated in detail during the last decade. Recently, existing experimental data have been critically reviewed with the aim of creating a realistic model for the Ir—Re ambient pressure binary phase diagram [2]. According to experimental data, the peritectic binary Ir—Re phase diagram has a miscibility gap between *fcc*- and *hcp*-structured alloys at 20 and 30 at.% Re. The Ir—Re phase diagram has been calculated using a sub-regular solution model based on experimental crystallographic and thermodynamic data (Fig. 1) [2].

Several Ir—Re alloys were prepared by arc-melting, high-temperature annealing and thermal decomposition of single-source precursors. Existing experimental data for single-phase Ir—Re alloys are summarized in the Supplementary Table S1. Atomic volumes for existing *hcp*- and *fcc*-structured alloys can be fitted using second order polynomial functions:

$$V/Z_{hcp} = 14.14(6) + 0.14(2)\cdot x_{Re} + 0.43(5)\cdot x_{Re}^2 \qquad (1)$$

$$V/Z_{fcc} = 14.15(1) + 0.17(1)\cdot x_{Re} + 0.82(7)\cdot x_{Re}^2 \qquad (2)$$

where atomic volumes, $V/Z$ ($V$ is a volume of the elemental cell and $Z$ corresponds to the number of atoms in the elemental cell, with $Z = 2$ for *hcp* and $Z = 4$ for *fcc* alloys) are plotted *versus* atomic rhenium composition, $x_{Re}$ (Fig. 1). *Hcp* and *fcc* alloys follow two functions, both displaying small negative deflection from linearity (<2%). The describing functions herein described can be used to estimate the composition of Ir—Re solid solutions with known lattice parameters.

In the present study, we report the investigation of *hcp*-structured Ir—Re alloys under high-temperature high-pressure conditions. Our primary goal is the construction of a pressure-dependent binary phase diagram for a system constituted by incompressible metals with ultra-high melting points. The compressibility curve for *hcp*-$Ir_{0.70}Re_{0.30}$ was collected using *in situ* X-ray powder diffraction in diamond anvil cells and a large-volume press. To investigate the formation of *hcp*-$Ir_{0.70}Re_{0.30}$ from the single-source bimetallic precursor $(NH_4)_2[Ir_{0.70}Re_{0.30}Cl_6]$ upon heating in hydrogen atmosphere, we employed *in situ* powder X-ray diffraction. Finally, we performed preliminary tests of the electrocatalytic activity of *hcp*-structured Ir—Re alloys for methanol oxidation in acidic solution, as model systems for fuel cells.

## 2. Experimental details

$Ir_xRe_{1-x}$ alloys were prepared using single-source bimetallic precursors $(NH_4)_2[Ir_xRe_{1-x}Cl_6]$ ($x$ = 0.23, 0.42, 0.70, 0.71, 0.86), similar to the $Ir_xOs_{1-x}$ alloys described elsewhere [10,11]. $(NH_4)_2[Ir_xRe_{1-x}Cl_6]$ were crystallized by adding an excess of saturated water solution of $NH_4Cl$ to a mixture of hot concentrated water solutions of $(NH_4)_2[ReCl_6]$ and $(NH_4)_2[IrCl_6]$. Salts were filtered and dried in air. Metallic powders were prepared by thermal decomposition of $(NH_4)_2[Ir_xRe_{1-x}Cl_6]$ in 5-vol.%-$H_2$/95-vol.%-$N_2$ stream (15–30 min) at 1000 K, followed by natural cooling (10–12 h).

*Hcp*-$Ir_{0.71(1)}Re_{0.29(1)}$ and *hcp*-$Ir_{0.23(1)}Re_{0.77(1)}$ were used for high-temperature experiments. *hcp*-$Ir_{0.71(1)}Re_{0.29(1)}$ and *hcp*-$Ir_{0.70(1)}Re_{0.30(1)}$ were characterised in the large-volume press and diamond anvil cell experiments respectively. The *hcp*-$Ir_{0.71(1)}Re_{0.29(1)}$ and *hcp*-$Ir_{0.70(1)}Re_{0.30(1)}$ alloys have nearly identical composition within experimental errors and are cited below as *hcp*-$Ir_{0.70}Re_{0.30}$. Elemental compositions were analysed in 10 points using a Hitachi S-4800 Field Emission scanning-electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analyser (Fig. S1, Table S2).

The thermal decomposition of $(NH_4)_2[Ir_xRe_{1-x}Cl_6]$ ($x$ = 0.23 and 0.70) was investigated *in situ* using the powder X-ray diffraction (PXRD) set-up located at the Swiss-Norwegian Beam Lines (BM01A), ESRF. Samples in powder form were placed in 0.5 mm fused quartz mark tubes (Hilgenberg GmbH, Germany). Tubes were connected to a 2 vol% $H_2$/He flow (0.1–0.5 ml/min) and heated with hot air stream from room temperature to 1000 K with a ramp rate of 10 K/min. Temperature was calibrated using the thermal

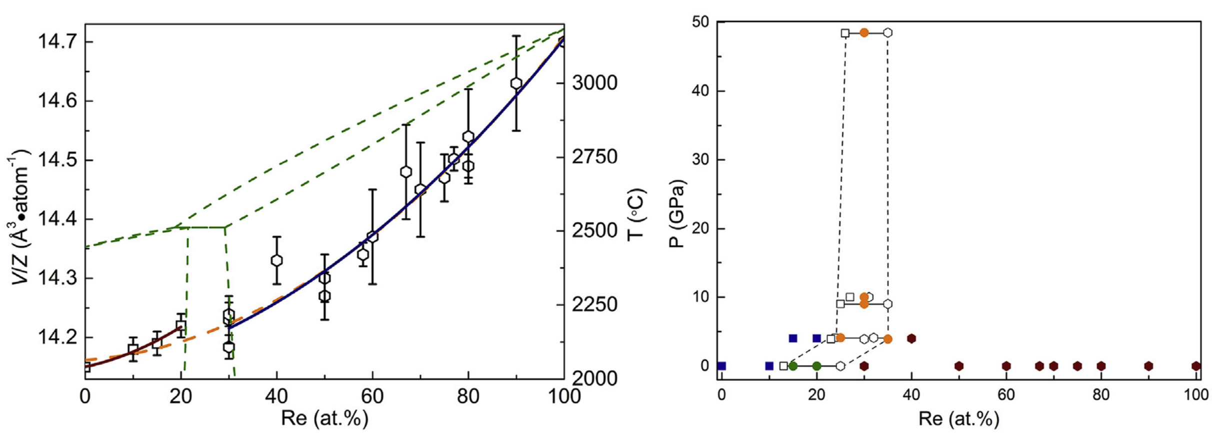


**Fig. 1.** *Left*: Dependence of atomic volumes ($V/Z$) on the composition for $Ir_xRe_{1-x}$ alloys (according to Table S1; dashed line represents a polynomial fitting for all *fcc* (*squares*) and *hcp* (*hexagons*) alloys; firm lines represent polynomial individual fittings for *fcc*- and *hcp*-structured alloys individually according to Equations (1) and (2)). Phase diagram was calculated in Ref. [2] using regular solutions model. *Right*: Phase separation for 0.80Ir+0.20Re and 0.75Ir+0.25Re mixtures [12–16] and in *hcp*-$Ir_{0.70}Re_{0.30}$ after annealing above 2000 K under compression (*circles* represent two-phase compositions).