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Study of nanoalloys formation mechanism from single-source precursors $[M(NH_3)_5Cl](ReO_4)_2$, M = Rh, Ir

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Abstract. In this work we have studied the thermolysis of complex compounds $[M(NH_3)_5Cl](ReO_4)_2$ (M = Rh, Ir) in helium and hydrogen. General features concerning the decomposition of these compounds and the formation of the $M_{0.33}Re_{0.67}$ solid solution has been revealed. The two-phase range in the Rh-Re phase diagram at 1100ºC has been re-determined.

Introduction

Fundamental and applied studies of nanocrystalline alloys are highly topical in materials technology. Large interest to these systems comes from their unique physical and chemical properties, e.g. catalytic and chemical activity, optical and electronic properties [1-3], which are strongly related to particle sizes. Along with crystallization of amorphous alloys and mechanical alloying, the decomposition of metal-containing single-source precursors is used to prepare heteroatomic metal phases and composites with crystallite sizes below 100 nm. Here we report a synthetic approach which makes possible the preparation of 1:2 M-Re (M = Rh, Ir) solid solutions by using a well-characterized single-source bimetallic precursor $[M(NH_3)_5Cl](ReO_4)_2$, M = Rh, Ir. Uniform mixing of the M and Re species at the molecular level in this compound is the main reason making it a very convenient source for synthesizing hexagonal closely packed (hcp) M-Re nanoparticles under comparatively mild conditions. Understanding of the formation mechanism of solid solution particles upon decomposition of precursors allows us to control particle sizes and phase composition of the resulting powder.

Experimental

Preparation of the precursors

Coordination compounds $[M(NH_3)_5Cl](ReO_4)_2$ (M = Rh, Ir) were prepared by precipitation from water solutions and characterized by IR spectroscopy and XRD phase analysis. Synthesis, crystal structure and thermal properties of $[M(NH_3)_5Cl](ReO_4)_2$ complexes, M = Co, Cr, Ru, Rh, Ir, were reported in detail earlier [4].

Instrumentation

Thermogravimetric properties of the compounds were studied with a STA 409 PC Luxx® derivatograph (NETZSCH, heating rate 5 K/min in helium, γ-Al_2O_3-crucible) equipped with a mass-spectrometer gas analyzer QMS 100 Series (TGA-MSA). Powder X-ray diffraction studies of thermolysis products of the prepared compounds were made on a DRON-RM4 diffractometer (CuK_α-radiation, graphite monochromator, ambient temperature). The refinement of lattice parameters was performed by the full profile technique applied to full-range diffraction data using PowderCell 2.4 program [5]. Crystallite sizes of the metal phases were determined by Fourier decomposition of profiles of single diffraction peaks, and with the Scherrer equation (WINFIT 1.2.1 [6]). The images of annealed samples were obtained with a scanning electron microscope JSM 6700F (accelerating voltage 50 keV) equipped with energy dispersive spectrometer EX-23000BU.

Results

Thermolysis of precursors in hydrogen atmosphere

A weighed samples of the complexes were heated in hydrogen stream in a silica boat placed in a flow reactor to the specified temperature and kept at this temperature for an 1 hour. After cooling, the samples were weighed and the X-ray diffraction patterns were recorded at room temperature in air. Figure 1 illustrates the evolution of phase composition on reduction of $[Rh(NH_3)_5Cl](ReO_4)_2$. It was found that the complex is decomposed in four continuous stages. At the first stage (190^{o}C) the cationic and anionic moieties are partially reduced resulting in decreased intensities of reflections belonging to the complex and appearance of a very broad diffuse maximum at the angles corresponding to the range of the most intense peaks of the Re (100, 002, 101) and Rh (111, 200). On further heating (the second stage - 200ºC) the reflections of the complex completely vanish and the peaks of NH_4ReO_4, NH_4Cl and $[Rh(NH_3)_5Cl]Cl_2$ emerge in the diffraction pattern. At 220^{o}C (the third stage) the diffraction pattern reveals only weak reflections of NH_4ReO_4 and broadened peaks of the $Rh_{0.70}Re_{0.30}$ solid solution with hcp lattice parameters a = 2.72(1) Å, c = 4.36(2) Å. The composition of the solid solutions was determined from the previously studied dependence of atomic volume (V/z) on the composition. Thus, it is evident that the solid solution phase formed at the first stage is rhenium-deficient. At the fourth stage (220-280ºC) NH_4ReO_4 entirely decomposes and rhenium atoms penetrate into the lattice of the solid solution. As a result, lattice parameters gradually increase reaching a = 2.75(1) Å, c = 4.39(2) Å corresponding to the composition $Rh_{0.30}Re_{0.70}$. This composition is very close to $Rh_{0.33}Re_{0.67}$ predetermined by the stoichiometry of the starting complex. Vacuum annealing of the reduction product at 950 ^{o}C for 400 h leads to the increase in crystallite sizes of the resulted

powder from 100-150 Å to 300-400 Å with lattice parameters remaining virtually the same (a = 2.746(1) Å, c = 4.387(2) Å). On reduction of the iridium compound $[Ir(NH_3)_5Cl](ReO_4)_2$ phase composition develops in a similar way, the broad diffuse maximum at the hexagonal phase angle range also being observed. The reflections of ammonium perrhenate are detected too. Finally, after vacuum annealing at 950ºC for 400 h a single-phase sample was obtained, the sample having hcp lattice parameters a = 2.757(1) Å, c = 4.385(2) Å and crystallite size 350-550 Å. Relying on the stoichiometry of the starting complex, the powder obtained is accepted for a fact to be the solid solution $Ir_{0.33}Re_{0.67}$.

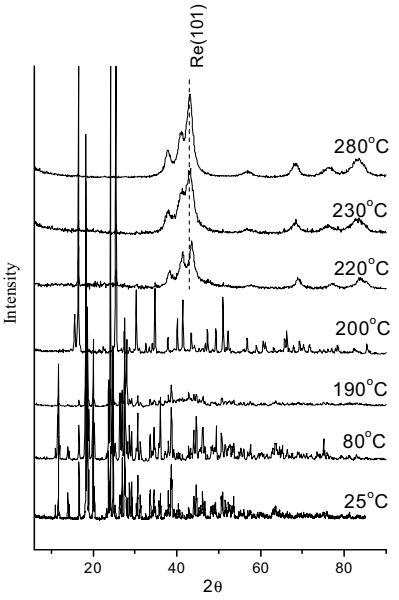

Figure 1. Evolution of the phase composition during the reduction of $[Rh(NH_3)_5Cl](ReO_4)_2$ in hydrogen.

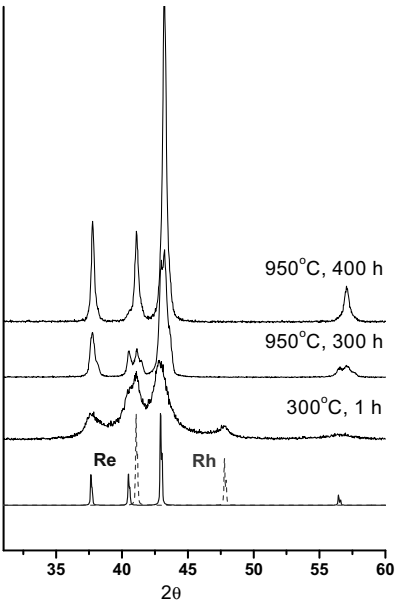

Figure 2. Formation of $Rh_{0.33}Re_{0.67}$ solid solution upon reduction of the mixture of $[Rh(NH_3)_5Cl]Cl$ and NH_4ReO_4..

Atomic volume versus concentration of the solid solutions

Metallic Rh and Ir adopt the Cu-type structure, i.e. they have face-centered cubic lattices (fcc). Re adopt the Mg-type of structure, i.e. it has a hcp lattice. So solid solutions composition can be determined using additivity of atomic volume of solid solution (Retgers rule): $V/z = x_1 \cdot V_1/z_1 + x_2 \cdot V_2/z_2$, where V - volume of lattice, z - number of atoms in lattice, x - fraction of components [7]. Figure 3 and Table 1 illustrate experimental dependences of this parameter versus the solid solution compositions. Light points are previous data; black points are data of this work. Rhodium-rhenium and iridium-rhenium systems are characterized by systematic negative deviations of experimental atomic volume from linear dependence.

Rh-Re phase diagram

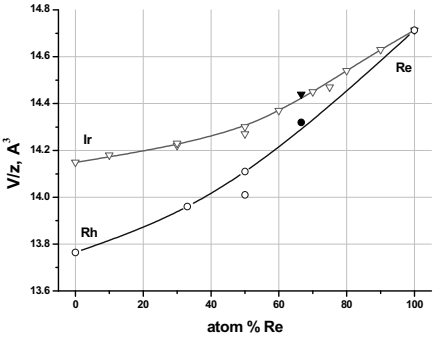

Figure 3. Atomic volume versus concentration of the solid solutions.

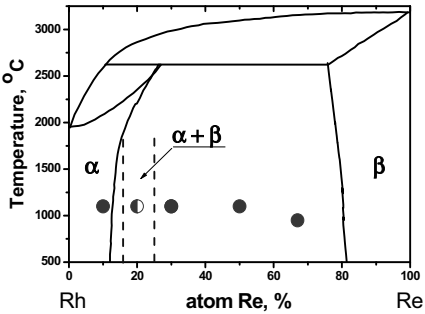

Figure 4. Rh-Re phase diagram according to the date [13] and the data of this work. Black circles – single-phase samples, black-white circle – two-phase sample.

Table 1. X-ray data of the bimetallic phase.

Phase	Conditions of preparation	Lattice parameters, Å		Atomic volume, Å^3	Space group
		a	*c*		
$Rh_{0,33}Re_{0,67}$ [this work]	H_2, 600°C	2,740(5)	4,370(6)	14,32(8)	$P6_3/mmc$
$Rh_{0,50}Re_{0,50}$[8]	H_2, 600°C	2,733(5)	4,364(6)	14.11(8)	$P6_3/mmc$
$Rh_{0,50}Re_{0,50}$[9]	Ar, 550°C	2,727(5)	4,352(6)	14.01(8)	$P6_3/mmc$
$Rh_{0,67}Re_{0,33}$ [9]	H_2, 700°C	2.722(5)	4.350(6)	13.96(8)	$P6_3/mmc$
$Ir_{0,10}Re_{0,90}$ [10]	vacuum, 1 h, 2400°C	2.7610(7)	4.4314(12)	14.63(3)	$P6_3/mmc$
$Ir_{0,20}Re_{0,80}$ [10]	vacuum, 1 h, 2400°C	2.7608(7)	4.4052(12)	14.54(3)	$P6_3/mmc$
$Ir_{0,25}Re_{0,75}$ [11]	H_2, 800°C	2.758(2)	4.394(3)	14.47(4)	$P6_3/mmc$
$Ir_{0,25}Re_{0,75}$ [11]	vacuum, 48 h, 800°C	2.758(2)	4.392(3)	14.47(4)	$P6_3/mmc$
$Ir_{0,30}Re_{0,70}$ [10]	vacuum, 1 h, 2400°C	2.7578(7)	4.3865(12)	14.45(3)	$P6_3/mmc$
$Ir_{0,33}Re_{0,67}$ [this work]	H_2, 600°C	2,756(5)	4,383(6)	14.48(8)	$P6_3/mmc$
$Ir_{0,40}Re_{0,60}$ [10]	vacuum, 1 h, 2400°C	2.7545(7)	4.3739(12)	14.37(3)	$P6_3/mmc$
$Ir_{0,50}Re_{0,50}$ [12]	H_2, 800°C	2.743(2)	4.380(3)	14.27(4)	$P6_3/mmc$
$Ir_{0,50}Re_{0,50}$ [12]	H_2, 800°C	2.749(2)	4.371(3)	14.30(4)	$P6_3/mmc$
$Ir_{0,70}Re_{0,30}$ [12]	H_2, 800°C	2.736(2)	4.390(3)	14.23(4)	$P6_3/mmc$
$Ir_{0,70}Re_{0,30}$ [11]	H_2, 800°C; 1GPa, 1900°C	3.846(2)	-	14.22(3)	Fm-3m
$Ir_{0,90}Re_{0,10}$ [12]	H_2, 800°C	3.842(2)	-	14.18(3)	Fm-3m

The phase diagram of the rhenium-rhodium system belongs to the peritectic type. The obtained single-phase solid solution $Rh_{0.33}Re_{0.67}$ falls in the two-phase area of the relevant phase diagram [13]. This means that in equilibrium a sample of this composition should decay in two solid solutions – one based on the crystal lattice of rhodium, and the other – on the crystal lattice of rhenium. However, annealing for 400 h at 950 ºC under conditions similar to that reported in ref. [14] (300 h at 1000ºC) has not resulted in the decomposition of the solid solution. So, either the sample obtained is non-equilibrium, or the solid solution boundary in the known diagram has been determined incorrectly.

Admitting a possible influence of the low diffusion rate and high surface energy of small particles on the equilibrium state, we performed experiments aimed at the preparation of the solid solutions by annealing the mixtures of the starting pure rhodium and rhenium metals – a bottom-up approach – to the equilibrium. To relieve kinetic effects, the mixed metal samples were prepared as follows: appropriate mixtures of $[Rh(NH_3)_5Cl]Cl_2$ and NH_4ReO_4 were grinded. Then the mixtures thus obtained were reduced in hydrogen atmosphere at the temperature of 300 ºC. The reduction yielded a black finely dispersed powder of the two-phase mixture of the pure metals, the mixture having pre-determined composition. Unit cell parameters of the phases coincide with reference values for pure metals ([15], Rh 5-685, Re 5-702). Crystallite sizes were 60-75 Å and 35-40 Å for rhodium and rhenium, respectively (figure 2). Then, the powders were pressed and annealed in evacuated silica ampoules at 950ºC for 300 h. As a result, a non-equilibrium three-phase sample was obtained for the Rh-Re mixture with 1:2 molar ratio (figure 2), the phases being solid solutions with rhenium content 93, 67 and 37 at. %. Second annealing at 950ºC for 400 h resulting a single-phase solid solution $Rh_{0.33}Re_{0.67}$ based on the hcp lattice of rhenium (table 2, figure 2). STM-EDS data confirm the composition of the solid solutions under consideration. The average particle size, as observed with a scanning electron microscope, practically coincides with the crystallite size obtained from the diffraction data.

Table 2. Data on sample annealing.

Content of Re in the mixture, % (at.)	Annealing parameters	Products of annealing	Lattice parameters, Å		V/Z, Å^3	crystallite size, Å
			a	*c*		
10	1100ºC, 200 h.	fcc	3,810(1)	-	13,8(2)	180-590
20	1100ºC, 200 h.	fcc + hcp	3,812(1) 2,715(1)	- 4,3490(2)	13,9(2) 13,9(2)	310-100 390-955
30	1100ºC, 200 h.	hcp	2,719(1)	4,348(2)	14,0(2)	340-870
50	1100ºC, 200 h.	hcp	2,730(1)	4,354(2)	14,1(2)	200-250
67	950ºC, 400 h.	hcp	2,746(1)	4,387(2)	14,3(2)	300-400

Metal mixtures containing 10, 20, 30 and 50 at. % of rhenium were prepared in the similar manner and annealed for 200 h at 1100ºC. The results of annealing are summarized in Table 2. At compositions of 100 to 30 at. % rhenium there is a single-phase solid solution region based on the rhenium hcp lattice, while between 0 and 10 at. % of rhenium there is another

single-phase solid solution region based on the iridium fcc lattice (figure 4). The two-phase region is situated between 10 and 30 at. % of rhenium.
The formation of rhenium-rich solid solutions on high-temperature annealing of the pure components indicates that the field of rhenium-rhodium solid solutions is much wider than it has been found previously. Thus, the subsolidus part of phase diagrams of the relevant systems needs further exploration.

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