RHENIUM CARBIDES PREPARED BY THERMOBARIC TREATMENT OF NANOSIZED PRECURSORS

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The products of thermobaric treatment ($P = 6$ GPa; $T = 1800$ °C) of mechanical mixtures of nanosized rhenium powder and sibunit have been studied. The formation of high-temperature phases with composition Re_2C has been revealed.

Keywords: rhenium, carbide, high-pressure cell, X-ray phase analysis.

1. Introduction

Until the middle of the 20th century it was believed that rhenium did not form carbides [1–3], and there were no phases in the system, except for the interstitial solid solution based on the hexagonal close-packed (hcp) structure of rhenium. First, the partial Re–C diagram was drawn in reference [2], and solubility of carbon in rhenium at 2480 °C (eutectic temperature) was shown to be about 11.7 at.%. This solubility drops to 4.2 at.% at 1800 °C. The diagram and extent of the solubility of carbon in rhenium were confirmed in [4], and in addition, some considerations were expressed about the possibility of the existence of rhenium di- and monocarbides. In [5], the formation of rhenium-carbon compounds has been shown by thermal decomposition of rhenium carbonyl on the surface of molybdenum and graphite substrates heated up to 450–1180 °C. The authors, however, note that in such circumstances, one cannot exclude the formation of oxycarbide phases, as observed, for example, in the decomposition of tungsten carbonyl [6]. Indeed, the unit cell constants of the phase obtained in [5] (see Table 1) considerably exceed those of the hcp-lattice of rhenium [7] and the interstitial solid carbon-based solutions [2, 8]. In reference [9], a series of coatings were obtained by chemical vapor deposition of $Re_2(CO)_{10}$ and $Re(CO)_3(Cp)$ in conditions similar to [5]. It was shown that one can distinguish two groups. The first corresponds to the samples obtained at deposition temperatures ≥ 450 °C, the second — below this value. Unit cell constants of the first group coincide with the reference values of pure crystalline rhenium [7]. The second group is characterized by markedly increased unit cell constants, indicating the formation of interstitial solid solutions of carbon in rhenium (hereinafter $Re(C_x)$).

Significant progress in the synthesis of rhenium carbides is associated with the use of high temperature and pressure. For example, in [10] a phase, which the authors attributed to the γ'-C type of structure, was prepared at 6 GPa and 800 °C. Later, in [11], a phase with cubic NaCl type structure was obtained at 16–18 GPa and 1000 °C. Crystal data for the cubic and hexagonal

TABLE 1. Crystallographic data for rhenium carbides

Phases	a, Å c, Å	V/Z, Å^3 Sp. gr. (No.)	Cite
Re	2.7609 4.4576	14.71 $P6_3/mmc$ (194)	[7]
Re(C$_{0,2}$)	2.792 4.471	15.09 — ·· —	[2]
Re(C$_{0,11}$)	2.803 4.461	15.18 — ·· —	[8]
Re(C$_{0,28}$)	2.794 4.460	15.08 — ·· —	[8]
Re$_2$C	3.02 4.76	18.80 — ·· —	[5]
ReC	4.005	$Fm-3m$	[11]
Re$_2$C	2.840(1) 9.85(1)	17.21 $P6_3/mmc$ (190)	[10]
Re$_2$C	2.8425(1) 9.8599(2)	17.25 — ·· —	[13]
Re$_2$C	2.8407(1) 9.8580(6)	17.31 — ·· —	[14]
Re$_2$C	2.845(1) 9.877(3)	17.31 — ·· —	[15]

rhenium carbides are shown in the Table 1. A phase with cubic symmetry has been also found in the products of electro spark processing of rhenium [12], but the question of its composition is still open. Thus, its formation has not been confirmed [13,14]. In the study of rhenium-carbon diagram at pressures up to 70 GPa and temperatures up to 3730 °C, the authors argue that the formation of rhenium carbides below 10 GPa is impossible. However, in [15] hexagonal Re$_2$C was prepared at pressures of 2–6 GPa and temperatures of 600–1600 °C. In [16] we found such an impurity phase, which is formed in the experiment for obtaining Re$_7$B$_3$, through reaction of rhenium with the walls of the graphite heater. However, the thermobaric treatment of a mixture of nanocrystalline powder of rhenium and soot (high-pressure cell, 4 GPa, 2000 °C) did not result in the formation of Re$_2$C [17].

A model of the Re$_2$C crystal structure was first proposed in reference [10]. The authors showed that the phase belongs to the γ'-C structure type (space group $P6_3/mmc$, $Z = 4$). In the framework of this model, the most probable positions of carbon atoms were found by full-profile refinement of x-ray diffraction pattern [13]. The authors of [15] proposed to consider the Re$_2$C in the frame of ReB$_2$ type of structure, where the rhenium atoms occupy the $4f$ site (1/3; 2/3; 0.6085), and carbon atoms occupy the 2 site (1/3; 2/3; 0.25). In addition, they showed that the Vickers hardness of Re$_2$C reaches 17.5 GPa. Taking into account that hardness of ReB$_2$ is compatible with those of cubic BN and diamond [18], it seems to be interesting to study the possibility of formation of the rhenium carboborides. Several rhenium borides (ReB$_2$, Re$_7$B$_3$, Re$_3$B) have been prepared by us under high pressure and temperature (high-pressure cell, 10 GPa, 1800 °C) from mixtures of nanocrystalline rhenium and amorphous boron [16]. Preparation of phases in a high-pressure cell depends on a number of parameters. Besides the selection of the optimal program, describing the increase in pressure and temperature, holding time and decrease in pressure and temperature, the characteristics of the reaction mixture are

TABLE 2. Condition of the thermobaric treatment and results of X-ray phase analysis

No.	Ratio Re/C, weight	P, GPa T, °C t, min.	Phases	Content, weight %	a; c, Å	No. space group V, Å³
1	2 : 1	6; 1800; 10	Re(C)	38	2.799; 4.466	194; 30.30
			Re₂C	62	2.843; 9.858	190; 69.00
2	1 : 0.8	6; 1800; 10	Re(C)	4	2.804; 4.466	194; 30.41
			Re₂C	96	2.843; 9.850	190; 68.95
3	1 : 0.85	6; 1800; 20	Re₂C	100	2.842; 9.855	190; 68.93
4	1 : 1	10; 1800; 20	Re₂C	100	2.842; 9.856	190; 68.94
5	1 : 0.5C : 0.5B	10; 1800; 15	Re₇B₃*	69*	7.516; 4.877	186; 238.6
			ReB₂	31**	2.900; 7.480	194; 5448
6	1 : 0.5C : 1.5B	10; 1800; 15	Re₇B₃	60***	7.514; 4.879	186; 238.6
			ReB₂	33	2.901; 7.481	194; 54.48

* The sample contained 2 wt.% of CCO_3 (material of high-pressure cell).
** For Re_7B_3: $a = 7.509$, $c = 4.880$ Å [19]; for ReB_2: $a = 2.8985$, $c = 7.4798$ Å.
*** The sample contained 7 wt.% of graphite.

extremely important. These characteristics are associated with a history of preparation of reagents: homogenization, compacting, pressing, preliminary annealing, etc. These operations in turn depend on the fineness of the starting materials. Using nanocrystalline reagents can fundamentally change the course of synthesis. Preparation of rhenium-containing phases forces us to consider such a factor as the fast oxidation of polycrystalline rhenium. The form of carbon can play a decisive role for synthesis of rhenium carbides. As already mentioned, processing of the mixture of nanocrystalline rhenium powder and soot (high-pressure cell, 4 GPa, 2000 °C) did not result in formation of rhenium carbides. It seems interesting to replace the soot for the alternative reagent — sibunit, characterized by chemical stability, high electrical conductivity, high specific surface, etc. [19].

2. Experimental

Nanocrystalline powder of rhenium (coherent scattering region ~ 30 Å) was prepared analogously to [16] by decomposition of $NH_4(ReO_4)$ in hydrogen. Mixtures of rhenium and sibunit powders taken in desired ratios were thoroughly mixed. Thermobaric treatment of mechanical mixtures was performed in a 'toroid' type high-pressure cell in standard scheme [20]. The sample was compressed between the press anvils to the required pressure, and then temperature was slowly increased (~ 100 °/min). After holding under pressure at a given temperature the sample was quenched by a sharp decrease in temperature. Then the pressure was released and container with the sample was removed. Samples with boron (black amorphous boron was used) were prepared in similar way. Experimental conditions are given in Table 2.

Samples obtained in the experiments were mechanically strong pellets. For x-ray powder diffraction study, a part of the sample was cut and ground in heptane. Then, the suspension was applied on the polished side of a standard cell. After drying the samples consisted of layer of thickness ~ 100 microns. Polycrystalline silicon, prepared analogously, was used as an external standard. X-ray powder diffraction data were collected on the diffractometers STADI-P (STOE) (CuKα1 radiation, transmission geometry, linear PSD) and ARL X'TRA (CuKα radiation, Bragg-Brentano geometry, semiconductor detector) at room temperature. Unit
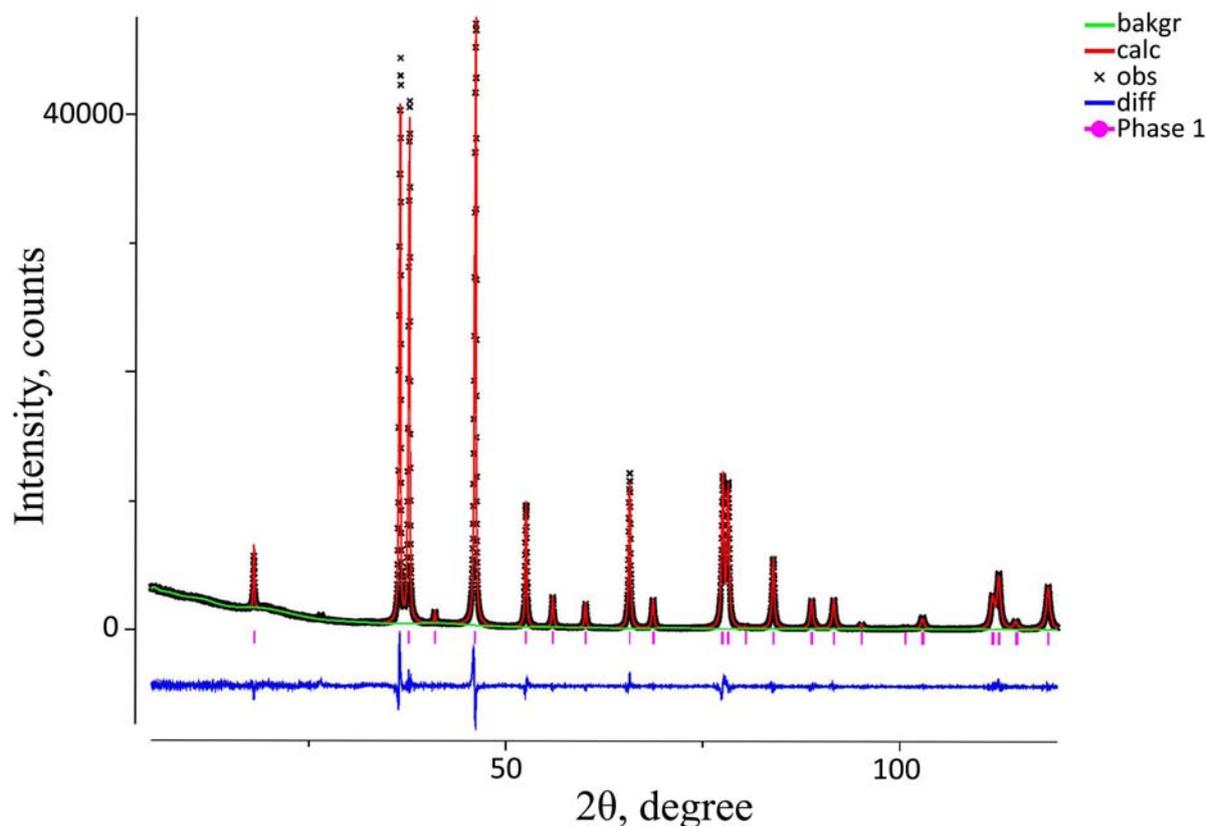
FIG. 1. Result of full-profile refinement of X-ray powder diffraction data for the sample obtained in experiment No. 4. $wRp = 6.42$, $Rp = 4.66$, CHI$^2 = 5.107$, $R(F^2) = 1.41$ %

cell constants were determined using Rietveld refinement with Powder Cell 2/4 program [21], the crystallographic data are given in Table 2.

3. Discussion and conclusion

An analysis of data in Table 1 and 2 leads to the following conclusions. In contrast to the experiments carried out in reference [17], where treatment (high-pressure cell, 4 GPa, 2000 °C, 3 min) of a mixture of rhenium and soot resulted in Re(C_x) only, use of sibunit [19] under approximately the same conditions allowed us to obtain samples containing Re$_2$C (experiments 1–4). Sibunit is a synthetic porous composite material which is obtained from soot. Using sibunit and nanocrystalline rhenium in our experiment allowed the reduction of synthesis time by a factor three compared to reference [17].

The single phase samples of Re$_2$C were shown to be formed only with an excess of carbon. The same conclusion was reached by the authors of [17], where single phase products were obtained by treatment of mixtures with Re/C ratios from 1:2 to 2 : 0.5 at 6 GPa and 1600 °C. In our experiments, single phase products were obtained by treatment of mixtures Re/C = 1 : 0.85 (exp. No. 3) and Re/C = 1 : 1 (exp. No. 4). The good agreement of the unit cell constants for Re$_2$C obtained in our experiments, as well as in [13–15], indicates good reproducibility of the composition for this phase. The results of full-profile refinement of x-ray powder diffraction data of sample No. 4 using GSAS [22] in the frame of ReB$_2$ type of structure (Re — 1/3; 2/3; 0.6085; C — 1/3; 2/3; 0.25) are shown in Fig. 1.

There were no rhenium carboborides found as a product of treatment of mixtures of nanocrystalline rhenium, sibunit and amorphous boron (exp. No. 5–6).

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