17th International Research/Expert Conference
”Trends in the Development of Machinery and Associated Technology”
TMT 2013, Istanbul, Turkey, 10-11 September 2013

INVESTIGATION OF THE Os-Hf SYSTEM CONSTITUTION

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ABSTRACT
The considerations of the Os-Hf system constitution are presented in this paper. The results - based on metallographic investigation of selected binary alloys from investigated system, prepared by arc-melting under purified argon atmosphere, were compared with available literature data.
Keywords: Os-Hf, alloys, binary system, metalography, phase diagram

1. INTRODUCTION
Osmium and hafnium present metals with specific characteristics and applications.
Osmium belongs to the platinum group of metals. Due to the fact that this transition metal is very hard and brittle, presenting the densest naturally occurring metal, osmium and its compounds are usually applied where extreme durability and hardness are needed [1,2]. So, osmium diboride was recently described and determined as one of new superhard materials [3], with many industrial applications considering resistance to abrasion and wear. Also, osmium has high reflectivity in the ultraviolet range of the electromagnetic spectrum, desirable in space-based UV spectrometers which have reduced mirror sizes due to space limitations [1], and therefore osmium-coated mirrors were flown in several space missions aboard the Space Shuttle [4].
Hafnium is transition metal, primarily used as a good material for neutron absorption in control rods in nuclear power plants for the control and safety mechanisms of the reactors [5,6]. Being highly corrosion resistive and able to withstand high temperatures and pressures, it is also used as an alloying element in different superalloys [7] and also in medical implants and devices [8], aerospace applications, etc.
According to the properties of these two metals, it is clear that their alloys could also be applicable in different fields of techniques and technology, due to the enhanced characteristics. Therefore, Hf-Os system was a subject of different investigations and researches.

2. LITERATURE REVIEW
The constitution of the Os-Hf system has been investigated by several investigators [9-16] and also thermodynamically assessed by Guo and Du [17]. Firstly, $HfOs_2$ (hexagonal isotopic with $MgZn_2$ structure) was established by Compton and Matthias [9] and confirmed by Dwight, who proposed HfOs compound (a cubic CsCl-type structure of equiatomic composition) [10]. Further, Waterstrat [11] worked on this system phase diagram and reported five intermetallic compounds - HfOs, $HfOs_2$, Hf_2Os, $Hf_{71}Os_{29}$, and $Hf_{77}Os_{23}$, while Stuparević et al. [12] studied Os-Hf system using XRD and microprobe analysis. Later, Eremenko et al. [13] confirmed that the stoichiometry of the phase $Hf_{77}Os_{23}$ reported by Waterstrat [11] is in fact $Hf_{54}Os_{17}$, which was also reported by Censual et al. [14]. Eremenko et al. [13] also confirmed the existence of HfOs, $HfOs_2$, and $Hf_{54}Os_{17}$ compounds, but not found Hf_2Os and $Hf_{71}Os_{29}$, as similarly noticed by Stuparević et al. [15]. The Hf–Os phase diagram, based on the work of

Eremenko et al., was suggested in literature by Okamoto [16]. The most recent work on hafnium binary alloys from experiments and first principles was given by Levy et al.[18]
As a contribution to the better knowledge of this system constitution, some experimental results of selected Os-Hf alloys investigation are presented in this paper.

3. EXPERIMENTAL PROCEDURE

The results of selected Os-Hf alloys metallographic investigation (compositions given in Table 1), prepared by arc-melting under purified argon atmosphere, are presented in this paper.

Table 1. Composition of investigated Os-Hf samples

Sample	mass % Os	mass % Hf	at %Os	at %Hf
S1	10	90	9.44	90.56
S2	20	80	19	81
S3	30	70	28.68	71.32
S4	48	52	46.42	53.58
S5	50	50	48.41	51.59
S6	64	36	62.52	37.48
S7	67	33	65.58	34.42

Powder mixtures of high purity (>99.5%) osmium and hafnium were pressed into pellets (mass of 2 g) and then arc-melted under purified argon atmosphere (99.9999%) in a water-cooled crucible. To be sure a sufficient homogeneity, samples were cut and remelted for several times. The samples were drop shaped.
Heat treatment and melting-point measurements were carried out in a tungsten mesh resistance furnace by using hot pressed boron nitride crucibles at several temperatures between 1300 and 2000 K. The liquidus and liquidus-solidus lines were measured by pyrometrical melting point measurements using two-color pyrometer, enabling the observation of all changes on the sample surface during the melting and solidification processes.
Metallography was used for the determination of phases and their regions and structural analysis was done by optical microscopy. The samples were ground on silicon water resistance paper (220, 500, 800, 1200, 4000) and polished on silk with 1 mm diamond paste. As for the appropriate etchant, fine results could be achieved by revealing of osmium borides with H_2O+H_2O_2+HF (4:1:1).

4. RESULTS AND DISCUSSION

The Os-Hf phase diagram with signed samples investigated in this work is shown in Fig.1. The results of metallographic investigation of selected Os-Hf alloys are presented in Fig.2.

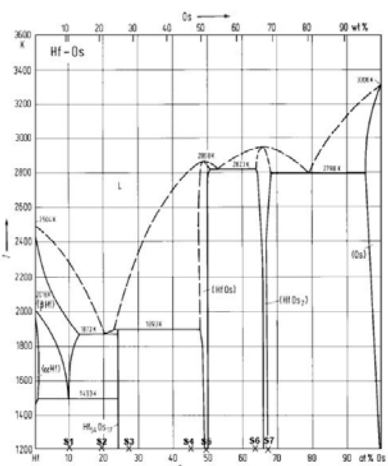
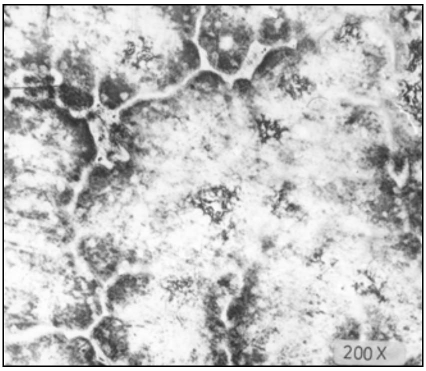
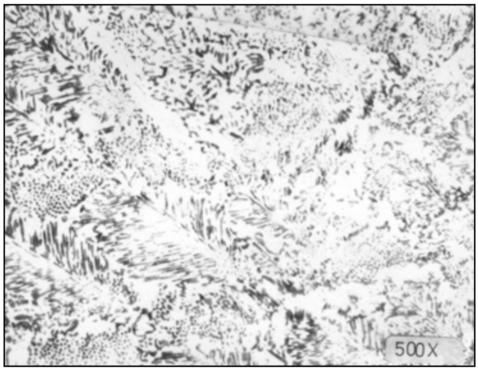


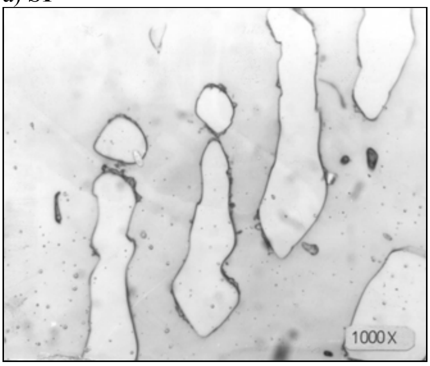
Figure 1. Phase diagram of the Os-Hf system according to [16] with signed investigated samples



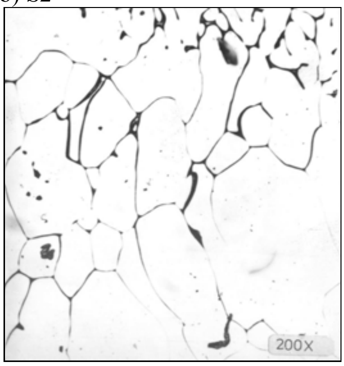
a) **S1**



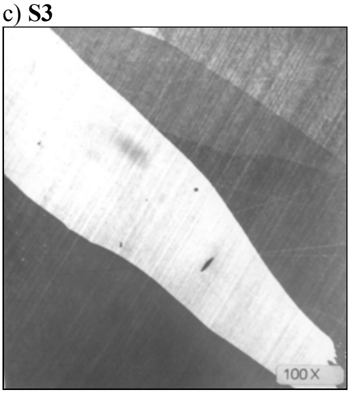
b) **S2**



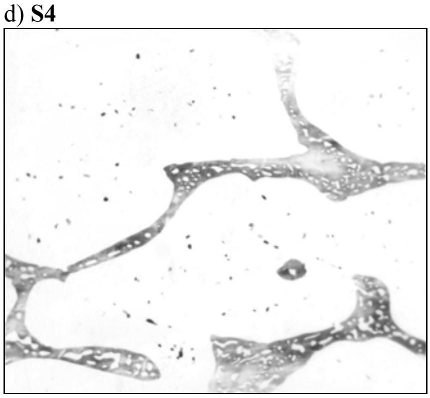
c) **S3**



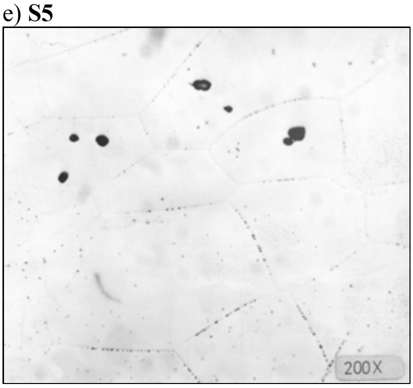
d) **S4**



e) **S5**



f) **S6** (500x)



g) **S7**

Figure 2. Characteristic microphotographs of selected samples in the Os-Hf system

a) S1; b) S2; c) S3; d) S4; e) S5; f) S6; g) S7

Characteristic microphotographs presented in Fig.2 and three intermediate phases - compounds (Table 2) existing in examined system [9-11] and confirmed by the experiments in this work, are in accordance with the Os-Hf phase diagram (Fig.1) - referent data by Eremenko et al. [13] and Okamoto [16]. Three more compounds - ξ-$Hf_{71}Os_{29}$; Θ-$Hf_{77}Os_{23}$; $Hf_{54}Os_{17}$ - reported earlier to possibly exist in investigated binary system [9,13], were not identified.

Table 2. Intermediate phases existing in the Os-Hf system confirmed by the experiments

Intermediate phase	Crystal system	Structure type	Refs.	Composition (at% Hf)
λ-$HfOs_2$	hexagonal	MgZn	[9]	29-38
δ-HfOs	cubic	CsCl	[10]	49-54
η-Hf_2Os	cubic	Ti_2Ni	[13]	67

Intermediate phases, λ and δ, melt congruently, while γ melts incongruently ($\gamma \leftrightarrow L+\delta$) at 1660°C (1620°C according to [13]). Other reactions which occur in this system are: L↔ λ+<Os> at 2600°C (2525°C according to [13]), L↔λ+δ at 2520°C (2550°C according to [13]), L↔(β-Hf)+γ at 1580°C (1600°C according to [13]) and <β-Hf>↔<L-Hf>+γ at 1225°C (1220°C according to [13]).

Having in mind experimental difficulties - the temperatures at which selected samples were synthesized, as well as economic point of view and the price of metals used, the results presented in this work may be of significant assistance in additional research or assessments of the Os-Hf phase diagram in the future.

5. CONSLUSIONS

Some new experimental data for the Os-Hf alloys are presented in the paper. Metallographic results obtained during the investigation were used as the basis for additional considerations of the Os-Hf system constitution, which could be important for further, more detailed investigation of examined alloy system, important for application under specific conditions of high temperatures and corrosive atmosphere.

6. ACKNOWLEDGEMENT

The authors of the paper acknowledge financial support under the projects OI172037 and TR34023, Ministry of Education, Science and Technological Development of the Republic of Serbia.

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