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EXPERIMENTAL STUDY OF HAFNIUM–SILICON PHASE DIAGRAM

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Abstract – The currently accepted Hf–Si phase diagram indicates the stability of the phases liquid L, Hf_{SS} and Si_{SS} as well as of the silicides Hf_2Si, Hf_3Si_2, Hf_5Si_4, HfSi and $HfSi_2$. However, some proposals reported in the literature suggest also the stability of the fase Hf_5Si_3. The Hf–Si system have been experimentally studied in the entire composition range. Samples were prepared by arc-melting Hf (min. 99,8%) and Si (99,998%) in water-cooled copper crucible under argon. Selected samples were heat treated under argon atmosphere for 120 h at 1200ºC or for 6 h at 1600ºC and analysed in scanning electron microscope and X-Ray difractometer. The results confirm the stability of the phases and the invariant transformation as proposed in the accepted phase diagram as well as the stability of the fase Hf_5Si_3.

Me-Si-B (Me – metal) alloys have been intensively studied due to their potential for the development of high temperature structural materials [1]. Considering that these materials are highly demanded in service, multicomponent based alloys seems to be the only possibility to satisfy all the requirements for structural integrity. In this sense, phase diagram information becomes extremely important. In this work, the experimental study of Hf–Si phase diagram has been carried out.

The currently accepted Hf–Si phase diagram is shown in Figure 1, based on the assessment of Gokhale e Abbaschian [2]. This diagram indicates the stability of the phases liquid L, Hf_{SS} and Si_{SS} as well as the intermediate phases Hf_2Si, Hf_3Si_2, Hf_5Si_4, HfSi and $HfSi_2$. However, some proposals reported in the literature suggest also the stability of the fase Hf_5Si_3 [3, 4]. Samples with compositions in all extension of the Hf–Si diagram were prepared. Mixtures of Hf (min. 99.8%) and Si (min. 99.998%) were cold pressed, arc-melted under argon atmosphere in water-cooled copper crucible with non-consumable tungsten electrode and titanium getter. The mass losses associated to the melting steps, supposing that all of them were either from Hf or Si volatilization, allowed calculate the composition adopted for each alloy, expressed by the mean value of composition interval. Selected samples were heat treated at 1200ºC for 120 hours or 1600°C for 6 hours. The alloys were characterized by scanning electron microscope (SEM) in back-scattered electron mode (BSE) and X–ray diffraction (XRD) at room temperature, under Cu-Kα radiation with Ni filter. For the SEM analysis, the alloys were prepared following standard metallographic procedures: hot mounting in resin; grinding in the sequence #220-#4000 SiC paper; and polishing with colloidal silica suspension (OP-S). For the XRD experiment ($10º < 2\theta < 90º$; 0.05º 2θ step and 2s integration time) the samples were mechanically ground and sieved to below 80 mesh. The phases were identified based on the simulated diffractions patterns obtained from the PCW program [5] using crystallographic data compiled by Villars and Calvert [6].

The results, summarized on the Table I, Figure 2, confirm the stability of the phases and the invariant transformation proposed in the accepted phase diagram [1]. However, showed the stability of the phase Hf_5Si_3, Figure 3.

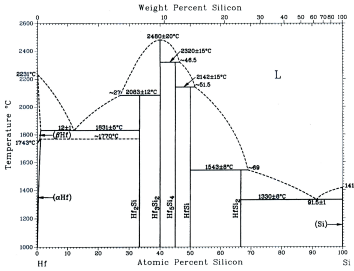

Figure 1 – The currently accepted Hf–Si phase diagram – assessment of Gokhale e Abbaschian [2].

Adopted composition	Observed phases (AC)	Observed reactions (AC)	Observed phases (HT)	Originary reactions (HT)
Hf90Si10	Hf_{SS}, Hf_2Si	$L \leftrightarrow Hf_{SS} + Hf_2Si$	Hf_{SS}, Hf_2Si	$L \leftrightarrow Hf_{SS} + Hf_2Si$
Hf88Si12	Hf_{SS} e Hf_2Si*			
Hf64Si36	Hf_2Si, Hf_5Si_3*	$L + Hf_5Si_3 \leftrightarrow Hf_2Si$	Hf_2Si, Hf_5Si_3	$Hf_5Si_3 \leftrightarrow Hf_2Si + Hf_5Si_3$
Hf62Si38	Hf_2Si, Hf_5Si_3, Hf_5Si_3*	$L + Hf_5Si_3 \leftrightarrow Hf_5Si_3$	Hf_2Si, Hf_5Si_3	
Hf55Si45	Hf_5Si_3*, Hf_5Si_4, HfSi	$L + Hf_5Si_3 \leftrightarrow Hf_5Si_4$	Hf_5Si_3, Hf_5Si_4, HfSi (1)	$L + Hf_5Si_3 \leftrightarrow Hf_5Si_4$
Hf50Si50	Hf_5Si_4*, HfSi, $HfSi_2$	$L + Hf_5Si_4 \leftrightarrow HfSi$	Hf_5Si_4, HfSi	$L + Hf_5Si_4 \leftrightarrow HfSi$
Hf48Si52			HfSi	
Hf32Si68	HfSi*, $HfSi_2$, Si_{SS}	$L + HfSi \leftrightarrow HfSi_2$	HfSi, $HfSi_2$, Si_{SS} (1)	$L + HfSi \leftrightarrow HfSi_2$
Hf30Si70	HfSi*, $HfSi_2$, Si_{SS}		HfSi, $HfSi_2$, Si_{SS} (1)	
Hf09Si91	$HfSi_2$, Si_{SS}	$L \leftrightarrow HfSi_2 + Si_{SS}$	$HfSi_2$, Si_{SS}	$L \leftrightarrow HfSi_2 + Si_{SS}$
Hf07Si93	$HfSi_2$, Si_{SS}*		$HfSi_2$, Si_{SS}	

* – primary; (1) non-equilibrium.

Figure 2 – Table I – Composition, phases and reactions observed at as cast (AC) and heat treated (HT) alloys.

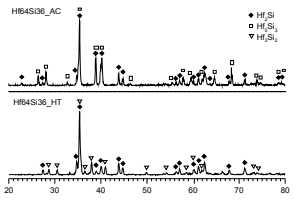

Figure 3 – XRD results of the Hf64Si36 alloy as cast (AC) and heat treated (HT) at 1600ºC for 6 hours.

[1] Zhao, J.C.; Westbrook, J.H. Ultrahigh-temperature materials for jet engines. MRS Bull, 622-30, 2003.
[2] Gokhale, A. B., Abbaschian, G. J. The Hf-Si (Hafnium-Silicon) System. Bulletin of Alloy Phase Diagrams, 10, 4, 390-393, 1989.
[3] Todorov N.; Shurin, A.K.. Phase equilibria in alloys of hafnium with silicon. Metallofizika, Kiev, 33,100-102, 1971.
[4] Yang, Y.; Chang, Y.A.; Zhao, J.-C.; Bewlay, B.P. Thermo. Mod. of the Nb–Hf–Si Tern. Syst.. Intermetallics, 11, 407-415, 2003.
[5] Krans W, Nolze G. POWDERCELL. Journal of Applied Crystallography, 29, 301-303, 1996.
[6] Villars P, Calvert LD. Pearson's handbook of crystallographic data for intermetallic phases, Materials Park, ASM International, 1991.