MELTING POINT IN SYSTEMS ZrC–HfC, TaC–ZrC, TaC–HfC

R. A. Andrievskii, N. S. Strel'nikova,
N. I. Poltoratskii, E. D. Kharkhardin,
and V. S. Smirnov

It was noted earlier [1] that in systems TaC–ZrC and TaC–HfC there are alloys with a melting point of about 4000°C which exceeds the melting point of the individual carbides. Later investigations [2, 3] demonstrated the presence of anomalies of the physical properties (including the melting point) for the composition 4TaC · 1HfC and in the system ZrC–HfC. The authors [2, 3] emphasize, of course, that the determination of the melting point in their investigation was of a preliminary nature. Other works appeared [4-7] that were devoted to a study of the evaluation, thermal expansion, and the emissivity in these systems.

It was of interest to reproduce the data of works [1-3] on the melting points in systems ZrC–HfC, TaC–ZrC, and TaC–HfC. For the investigation we selected the same compositions which, according to earlier data, demonstrated the highest melting points. The carbides were prepared by reducing the oxides of the metals in a vacuum (10^{-3} mm Hg) at a temperature up to 2000°C. To create a closer contact during reduction the charge was pressed under a pressure up to 200 dkN/cm^2, which was also used in works [2, 3]. From the thus prepared powders specimens were fabricated by the hot pressing method (T-2200°C, τ-15 min, P-200 dkN/cm^2), which were then additionally annealed at a temperature of 2500°C for 1 h. The porosity of the specimens did not exceed 5%. X-ray structural* and microstructural analyses of the samples showed that they were single-phase (Table 1). The values of the lattice parameters of the carbides and their solid solutions generally agreed nicely with the data in the literature (for example, [2, 3]).

The melting point was measured by the Pirani-Alterum method on specimens measuring 3 × 4 × 15 mm heated by passage of a current. The size of the hole for recording melting was selecting in conformity with recommendations in [7, 8] and was 0.3-0.4 in diameter and 2 mm deep. We used an OMP-054 micropyrometer. The experiments were carried out in a medium of thoroughly scrubbed helium. Testing of the device and determination of the correction for radiation absorption by the peephole was accomplished by measuring the melting points of pure refractory metals (tungsten, molybdenum, tantalum). Table 2 gives the results of determing the melting point of the investigated compositions.

We see from the table data that the composition 8TaC · 1ZrC and 4TaC · 1HfC are characterized by high melting points (3890 and 3990°C, respectively) which exceed the melting points of the individual carbides. Thus, the data in [1-3] for these systems are confirmed. In system ZrC–HfC we did not note the maximum that was detected in works [2, 3]; in contrast, the melting point of the alloys proved to be lower than that of the carbides of zirconium and hafnium. It has been suggested that this drop of the melting point in the aforementioned alloys can be due to some specimens of the system ZrC–HfC containing appreciable quantities of free carbon (Table 1), and this leads to the formation of the eutectic (Zr, Hf) C + C. An investigation of the structures of the middle part of the specimens after melting revealed the presence of eutectic segregations (Fig. 1, a); for other alloys only pure grain boundaries were observed (Fig. 1, b), or, sometimes, boundary segregations (Fig. 1, c) whose chemical and phase composition could not be determined. However, later determinations of the melting point in specimens of the system ZrC–HfC not containing free carbon (within the limits of sensitivity of chemical analysis) confirmed its low value in these alloys.

Table 2 shows the change in the content of bound carbon and of the lattice parameter in the middle part of the specimens after determining the melting point. As we see from these results, the content of bound carbon appreciably decreases. Analyses also showed that the content of the metallic components

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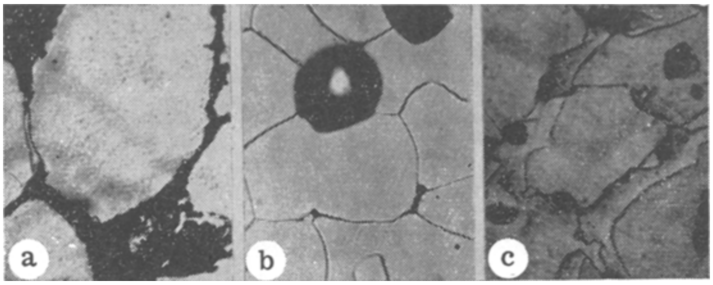
*Copper and cobalt radiation (RKU-86 camera) was used.

Presented at the Fifth All-Union Inter Institute Seminar of the Physical Properties and Electron Structure of the Transition Metals and Their High-Melting Compounds and Alloys, Kiev, April 5-9, 1966. Institute of Materials Science, Academy of Sciences UkrSSR. Translated from Poroshkovaya Metallurgiya, No. 1(49), pp. 85-88, January, 1967. Original article submitted August 10, 1966.



Microstructures of carbide alloys after determing melting points: a) 4ZrC−1HfC; b) 4TaC−1HfC; c) 8TaC−1ZrC.

TABLE 1. Chemical Composition of Investigated Specimens (After Hot Pressing and Annealing)

Specimen	Chemical composition, mass. %								Stoichiometric formula
	C_{total}	C_{free}	C_{bound}	Ta	Hf	Zr	N	O	
ZrC	10,2	<0,05	10,2	—	—	88,3	0,005	*	$ZrC_{0,88}$
HfC	6,1	<0,05	6,1	—	93,8	—	0,005	*	$HfC_{0,97}$
TaC	6,1	<0,05	6,1	94,1	—	—	0,005	*	$TaC_{0,98}$
1ZrC—1HfC	10,5	1,8	8,7	—	*	*	0,23	0,09	$(Zr, Hf)C_{1,06}$
3ZrC—2HfC	9,9	0,24	9,66	—	*	*	0,13	0,33	$(Zr, Hf)C_{1,11}$
4ZrC—1HfC	10,0	0,18	9,82	—	*	*	0,05	0,10	$(Zr, Hf)C_{0,99}$
same	9,0	<0,05	9,00	—	*	*	*	*	$(Zr, Hf)C_{0,91}$
2TaC—1ZrC	5,9	0,12	5,78	77,7	—	17,0	0,05	0,08	$(Ta, Zr)C_{0,79}$
4TaC—1ZrC	6,7	0,05	6,65	85,1	—	9,2	0,05	0,09	$(Ta, Zr)C_{0,98}$
8TaC—1ZrC	6,7	0,05	6,65	88,2	—	5,2	0,17	0,10	$(Ta, Zr)C_{1,02}$
3TaC—1HfC	5,3	0,13	5,17	72,8	24,0	—	0,43	0,10	$(Ta, Hf)C_{0,83}$
4TaC—1HfC	6,4	0,14	6,26	80,6	13,0	—	0,51	0,15	$(Ta, Hf)C_{1,00}$
5TaC—1HfC	5,6	0,15	5,45	82,5	12,0	—	0,47	0,32	$(Ta, Hf)C_{0,88}$

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*Not determined.

TABLE 2. Melting Point at Change of Chemical Composition When Determining Melting Point

Composition	Interval of measured temperatures, °C	No. of measurements	Average temp., °C	C_{bound}		a, A	
				Before melting	After melting	Before melting	After melting
$ZrC_{0,88}$	3460—3490	5	3470	10,2	9,1	4,689	4,695
$HfC_{0,97}$	3700—3760	5	3750	6,0	5,8	4,640	4,639
$TaC_{0,98}$	3830—3880	5	3840	6,1	5,7	4,454	4,444
1ZrC—HfC	2930—3030	8	2980	8,7	7,5	4,663	4,664
3ZrC—HfC	3140—3180	6	3150	9,66	7,7	4,670	4,669
4ZrC—1HfC	3150—3220	8	3200	9,82	9,1	4,683	4,684
4ZrC—1HfC*	3180—3220	4	3200	9,00	†	†	†
2TaC—1ZrC	3760—3830	5	3800	5,8	5,3	4,522	4,524
4TaC—1ZrC	3810—3840	5	3830	6,65	5,3	4,495	4,492
8TaC—1ZrC	3880—3930	11	3890	6,35	5,9	4,470	4,466
3TaC—1HfC	3820—3920	4	3890	5,17	5,05	4,486	4,483
4TaC—1HfC	3970—4010	4	3990	6,45	3,54	4,473	4,468
5TaC—1HfC	3940—3960	5	3950	5,45	5,05	4,473	4,472

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*Results were obtained on specimens not containing free carbon.

†Not determined.

after determining the melting point decreases appreciably more slowly or even remains constant, and in some cases increases. Hence we can state when determining the melting point of carbides and their alloys there is preferential evaporation of carbon and a change of stoichiometry. Thus, the carbides of zirconium and tantalum changed stoichiometry from $ZrC_{0.88}$ and $TaC_{0.97}$ to $ZrC_{0.78}$ and $TaC_{0.93}$. This is also indicated by the change of the lattice parameter, which coincides with the results of investigating the dependence of the lattice parameter on the stoichiometry of zirconium, hafnium, and tantalum carbides [9–11]. For the most refractory compositions we can consider that the change of stoichiometry occurred from $(Ta_{0.8}Hf_{0.2})C_{0.88}$ to $(Ta_{0.8}Hf_{0.2})C_{0.80}$ and from $(Ta_{0.89}Zr_{0.11})C_{0.96}$ to $(Ta_{0.89}Zr_{0.11})C_{0.74}$.

It is known from results of determining the melting points in the region of homogeneity of ZrC, HfC, and TaC that maximum temperatures pertain to nonstoichiometric carbides: $ZrC_{0.8-0.9}$, $T_{mp} = 3410$–$3435°C$ [9]; $HfC_{0.9}$, $T_{mp} = 3820°C$ [10]; $TaC_{0.8}$, $T_{mp} = 4000°C$ [12].

The appreciable decarburization which we noted in the systems TaC−ZrC and TaC−HfC and the results of works [9, 10, 12] give us grounds to assume that the high meltings points for compositions 4TaC · 1HfC and 8TaC · 1ZrC which we and other authors [1-3] elicited, are a consequence of a shift in stoichiometry during the experiment. Zirconium and hafnium probably have an effect only on intensifying the evaporation of carbon, which leads, in accord with the data [12], to a rise of the melting point in comparison with that for the stoichiometric carbide of tantalum.

In works [2, 3] the high melting points for alloy TaC are related to the formation of a stable configuration d^5 in the metallic sublattice. Owing to the demonstrated appreciable decarburization of carbides and the shift of stoichiometry toward compositions corresponding to the highest melting point, the ideas in [3] cannot be accepted unconditionally. We also emphasize that in the metallic system Ta–Hf no anomalies were noted for tantalum-rich alloys* [13].

Our suggestion concerning the possible cause of the high melting points for alloys 4TaC · 1HfC and 8TaC · 1ZrC is in need of an additional experimental confirmation, in particular, a more thorough study of the regularities of carbon evaporation at premelting temperatures.

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*We can indicate that the mixing energies in systems ZrC−HfC [14] and TaC−HfC [15], which were estimated in the works by studying the short-range order and the phase diagrams, are, generally speaking, small: 1.5 kcal/mole for Zr−HfC and 0.3 kcal/mole for TaC−HfC. This indicates a slight deviation of these systems from ideal solid solutions.