

## MELT REFRACTORY METALS WITH INDUCTION HEATING

In the All-Union Scientific-Research Tube Institute's industrial induction electric furnaces heated to 2000-2300°C, cylindrical billets of high-melting alloys are placed on refractory supports. To select materials for the supports which do not react with molybdenum billets below 2000-2300°C, and to ensure their normal operation, we have investigated the reaction of molybdenum with zirconium and hafnium dioxides, stabilized with CaO and Y<sub>2</sub>O<sub>3</sub>, and its reactions with yttrium oxide and zirconium—hafnium solid solutions. The tests were performed by the contact method and by the active powder method at 2000-2300°C in vacuum under a pressure of 1.33·10<sup>-2</sup> Pa [1, 2]. The changes in the specimens after the tests were monitored by petrographic, x-ray structural, and chemical methods. Laboratory investigations confirmed for ZrO<sub>2</sub>, and established for HfO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>, the absence of visible reaction of these materials with molybdenum below 2000°C.

Above 2000°C, at the contact of monoclinic ZrO<sub>2</sub> and HfO<sub>2</sub> supports with molybdenum we observed a certain loss of oxygen, with consequent appearance of a cubic phase; this agrees with [1, 2]. According to microscopic investigations, above 2000°C a monoclinic phase appeared in CaO-stabilized ZrO<sub>2</sub> specimens at the contact with molybdenum; this is attributable to partial evaporation of CaO and destabilization of the cubic phase. The destabilized layer was too thin (less than 0.5 mm) to separate it for chemical analysis. Destabilization of the working layer was not observed in specimens of ZrO<sub>2</sub> stabilized with Y<sub>2</sub>O<sub>3</sub>, which form solid solutions; this agrees with [3].

On the basis of our data, supports for the tests were made on the basis of zirconium dioxide, completely or partly stabilized with CaO and Y<sub>2</sub>O<sub>3</sub>, and also on the basis of zirconium—hafnium solid solutions. The composition and properties of the supports are given in Table 1.

TABLE 1. Characteristics of Supports Investigated

Composition	Composition of support	Roasting parameters of support		Open porosity, %	Apparent density, g/cm <sup>3</sup>	Phase composition, %		Compressive strength, MPa	Shrinkage over diameter, %
		temp., °C	time, h			monoclinic phase	cubic phase		
1	Completely stabilized ZrO <sub>2</sub> with addition of monoclinic ZrO <sub>2</sub>	1750	6	21,1	4,45	45	55	40	1,17
2	Partly stabilized ZrO <sub>2</sub>	1750	6	24,2	4,34	8	92	49,7	0,17
3	Partly stabilized ZrO <sub>2</sub> based on phosphate binder (unroasted material)	300	—	10,3	4,73	30	70	Not determined	
4	Zirconium—hafnium solid solution	1750	6	6,3	6,90	100	—	Not det.	14,4
5	The same	2300*	1						
		1300	6						
		1600	4	16,2	6,23	100	—	52,3	6,7

\*Roasting in vacuum, in other cases roasting in air.

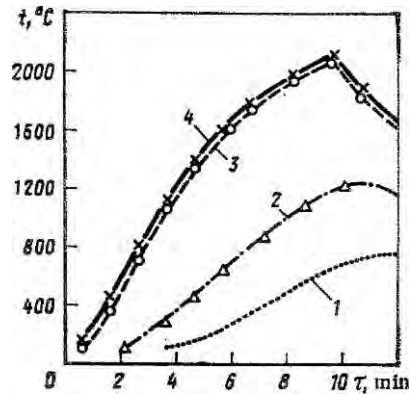


Fig. 1. Distribution of temperatures  $t$  vs duration of heating  $\tau$  of molybdenum billet to 2100°C: 1) in cold sector of support; 2) in middle sector of support; 3) at contact of support with billet; 4) in molybdenum billet.

The supports were prepared by the procedure described in a previous communication [4], and by hot pressing from finely dispersed masses (compaction temperature 1600°C, pressure 10 MPa).

Bearing in mind the capacity of the refractory materials, particularly zirconium dioxide, to yield oxygen at the contact with molybdenum, some of the zirconium dioxide supports were additionally roasted in a vacuum furnace at 2300°C under a pressure of  $1.33 \cdot 10^{-11}$  Pa for partial elimination of their oxygen [5]. For this purpose, certain zirconium dioxide supports were roasted in a coke filling and with addition of zirconium carbide to the mass.

The supports were tested in a 1 INZ-1.4-15/20D industrial induction furnace with heating of billets of high-melting alloys, 100 mm in diameter and 500-1000 mm long. The billets were heated to 2000-2300°C in argon (flow rate 6.7-7.2 m<sup>3</sup>/h) [4].

The period of contact of the support with the billet was 10-15 min.

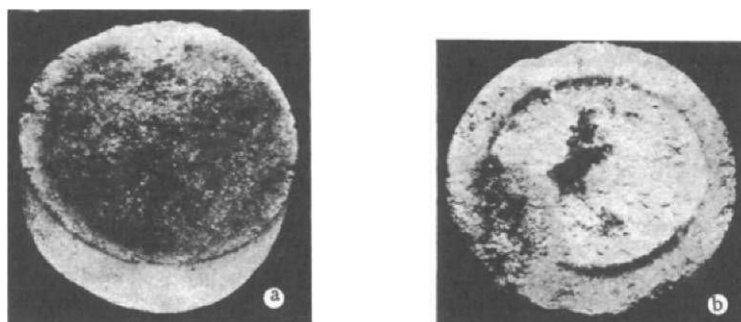
During heating of the billet to 2100°C the temperature drop in a zirconium dioxide support, 20 mm thick (see Table 1, composition No. 1), measured with a tungsten—rhenium thermocouple, was 1450°C (Fig. 1).

With heating to 2300°C, compact supports of zirconium—hafnium solid solutions did not adhere to the billets; they were readily detached from them and showed no visible changes. On the surface of the supports (Fig. 2a-b), at 2300°C we observed formation of a black deposit of molybdenum oxide only in certain places at the periphery. After a single heating to 2300°, supports of the other compositions (Nos, 2 and 3) adhered to the billets, forming at the periphery of the latter a bead of molybdenum oxides 2-3 mm high (Fig. 2c). As a result of the presence of molybdenum oxides, the content of which reached 8%, the working surface of the supports turned black. The depth of the working layer was 1 mm.

Supports made from, yttrium-oxide-stabilized hafnium and zirconium dioxides adhered most strongly to the billets (even at 2000°C).



Fig. 2. Supports of zirconium—hafnium solid solutions (a, b) and zirconium dioxide (c) after heating to 2300°C with molybdenum billet.



**Fig. 3. Structure of support of zirconium dioxide of composition No. 1 after four heatings to 2000°C with molybdenum billets (a) and seven heatings with tungsten billets (b).**

Thus the observed reaction of zirconium and hafnium dioxide supports with molybdenum billets in industrial induction furnaces is due to formation of molybdenum oxides, responsible for adhesion of the supports to the billets. The appearance of molybdenum oxides and their reaction with the refractory can probably occur even during extraction of the billet from the furnace, during which there is free access of atmospheric oxygen to the hot metal.

Tests on zirconium dioxide supports made on the basis of granular masses with a porosity of 30-32% did not give favorable results during heating of the billets to 2300°C. It is possible that the presence of residual air in the pores of the supports also promotes formation of molybdenum oxides and adhesion of the supports to the billets.

Reducing roasting of zirconium supports in a coke filling and in a vacuum furnace under a pressure of  $1.33 \cdot 10^{-2}$  Pa (i.e., preparation of supports with an oxygen deficiency) somewhat reduces the degree of their adhesion to the billets during heating to 2300°C but does not eliminate it altogether. Adhesion is not prevented by incorporation of 20% of boron carbide into the material, nor by the high degree of compaction attained by hot pressing, nor by covering the support with a layer of graphite.

For heating molybdenum billets to 2000°C, it is advisable to use calcium-oxide-stabilized zirconium dioxide supports, both roasted (compositions Nos. 1 and 2) and unroasted ones based on a phosphate binder (composition No. 3).

Such supports are fairly heat-resistant and can be used for from five to seven times with heating to 2000°C (Fig. 3). In their property indices, they meet the requirements of Technical Specification (TU) 14-8-98-74. Unroasted supports can be made from a tamped zirconium mass of PTsB-93 grade (TU 14-8-62-72) based on a phosphate binder at the site where they are used.

The character of the reaction of CaO-stabilized  $ZrO_2$  with molybdenum is described in [6]. After heating molybdenum billets in a vacuum induction furnace to 2000°C, zirconium dioxide supports turned dark brown, owing to partial loss of oxygen in vacuum. No signs of reaction with the billets were observed; after heating, the supports were in a satisfactory state.

After heating of the billets in a TVV-5 furnace to 2000°C, the color of the supports was unchanged, and, as in the case of heating in an induction furnace, signs of reaction with the billet were not observed; a silvery deposit of molybdenum oxides was observed only on their contact surface.

Thus, CaO-stabilized zirconium dioxide supports used for heating copper, aluminum, or steel billets to 1000-1250°C [7] can be recommended for heating to 2000°C billets of high-melting alloys based on tungsten and molybdenum, in a vacuum or inert medium.

#### CONCLUSIONS

The authors have selected compositions of refractory supports which ensure heating of billets of high-melting alloys to 2000-2300°C in industrial induction furnaces in argon or in vacuum.

For heating billets of high-melting alloys to 2000°C, they recommend supports of CaO-stabilized zirconium dioxide or partly stabilized zirconium dioxide based on a phosphate binder.

For heating billets to 2300°C, they recommend the use of compact supports of zirconium—hafnium solid solutions.

#### LITERATURE CITED

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#### USE OF SILICON CARBIDE REFRACTORIES IN GAS CARBURIZATION FURNACES

During the operation of furnaces with carbon-containing media, including gas carburization furnaces, the strength and thermophysical properties of the refractory structures (guides, muffles, semi muffles, radiation tubes) deteriorate far more intensely than in air furnaces. This is due to deposition of soot carbon in the pores of the refractory materials [1],

Previously [2, 3], we ascertained the factors influencing the resistance of refractory materials in carbon-containing media and established the requirements to be imposed on them: compressive strength at 500-1050°C not less than 50 MPa, coefficient of friction with alloys used for making hearths not less than 0.8 at 850-1050°C, service life not less than 20,000 h.

On the basis of the requirements imposed on carbon-containing materials, it was desirable to test in an endogas carbon-containing medium (40% H<sub>2</sub>, 34.8% N<sub>2</sub>, 20% CO, 5% CH<sub>4</sub>, 0.2% CO<sub>2</sub>) silicon carbide refractories differing in preparation procedure and properties (Table 1).

TABLE 1. Properties of Silicon Carbide Refractories

Refractory (specimen) No.	Refractory	Manufacturer	Open porosity.	Apparent density.	Compressive strength	Gas permeability coef
			*	g/cm <sup>3</sup>	MPa	ficient, nPm
1	Recrystallized	VNIASH	27.0	2.35	39	510
	Based on binder:					
2	aluminosilicate of Ka-3 grade according to COST 10153-70	Semiluki Refractory Plant	25.0	Notdet.	40	41.5
3	aluminosilicate of KATs grade according to TU 14-8-295-78	All-Union Institute of refractories	20.1	2.40	80	1.4
4	siliceous	The same	20.0	2.40	64	33.3
5	nitride	It w	23.8	2.43	108	0.83
6	oxynitride	** 1*	18.0	2.49	200	0.055
7	Poly crystalline.	Borvay Powder Metallurgy Plant	3.0	2.90	332	0.027

\* All-Union Institute of Refractories. All-Union Scientific-Research Institute of Electrothermal Equipment. Translated from *Ogneupory*, No. 12, pp. 29-31, December, 1979.