THE CHROMIUM-MELT RESISTANCE OF SUPERDUTY REFRACTORY MATERIALS

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The relatively low melting point of chromium (about 1900°C) offers scope for using superduty refractory materials for the crucibles and casting molds for smelting chromium and its alloys. First attempts to cast high-purity chromium ingots in ceramic crucibles showed, however, that the metal is contaminated by its reaction with the refractory.

The search for superduty materials stable to a chromium melt has been the subject of a large volume of experimentation [1-6]. The published data are highly contradictory. Some workers recommend crucibles of ZrO_2 [1], BeO [2], and ThO_2 [3] for smelting chromium. Tests have been carried out [4] also with Al_2O_3, MgO, CaO, certain spinels, and graphite as material for the smelting crucible.

In recent years, synthetic methods have yielded new materials of high refractoriness so that an investigation of their stability relative to a chromium melt is relevant.

The need for such an investigation is reinforced by the fact that the literature contains almost no information about the interaction with refractories of a chromium melt containing an alloying additive in the form of rare-earth metals (REM) like Al, Ti, Zr, Hf, V, Nb, and Ta. The addition of these elements to electrolytic chromium is known [7, 8] to improve the heat resistance and low-temperature plasticity of the metal.

The refractory materials used in the experiments were powders of oxides (Al_2O_3, ZrO_2, MgO, and BeO), carbides (TiC and ZrC), borides (TiB_2 and ZrB_2), and silicides ($MoSi_2$ and W_5Si_3). The melting point of these materials is above 2000°C. Having regard to the strong influence of contaminants on the chemical and thermodynamic stability of these materials, the experiments were carried out with powders of maximum purity. The powders consisted of 20% grain size fraction 1-10μ, 30-40% fraction 10-30μ, 20-30% fraction 30-50μ, 10-15% fraction 50-100μ, and about 10% fraction coarser than 100μ.

The powders were used for slip-casting or molding crucibles of a capacity up to 1 kg molten chromium. The crucibles were fired at 1850-2000°C after which their porosity was 4-8%.

The smeltings were carried out in a laboratory-size induction furnace in purified argon. The charge consisted of electrolytic hydrogen-refined chromium of grade ÉRKh containing not more than 0.006% N, C,

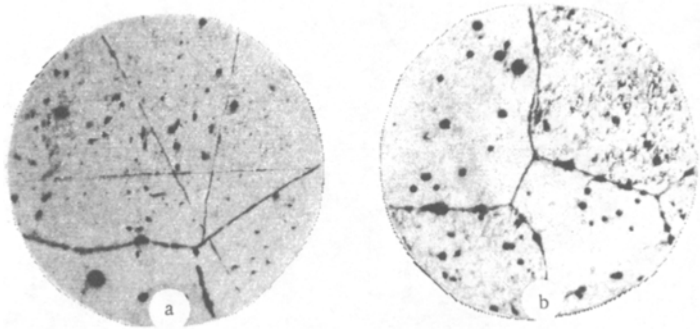

Fig. 1. The microstructure of chromium smelted in crucibles of BeO (a) and ZrO_2 (b). ×200. Reflected light.

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TABLE 1. Characteristics of the Interaction of Chromium with Refractories

Crucible material	Melt No.*	Thickness of contact zone mm	Crucible erosion	Neocrystallization	Contamination of surface layer of metal: contaminant	Contamination of surface layer of metal: content, wt.%
Al_2O_3	1	<0,5	Insignificant		O_2	0,02—0,03
	2	4,0	Very severe†	R_2O_3	Al	0,01
					O_2	0,26
MgO	1	4,0	Very severe†	Spinel of type $MgCr_2O_4$	N	$1\cdot10^{-3}$—$2\cdot10^{-3}$
ZrO_2	1	<1,0	Insignificant	Not noted	Zr	0,016
					O_2	0,03
	2	4,0	Very severe†	R_2O_3	O_2	⩽0,3
BeO	1	<0,3	Quite insignificant	Not noted	O_2	0,01
	2	3,5	Very severe†	R_2O_3	O_2	⩽0,14
TiC	1	~1,0	Slight	Mutual solubility	C	0,08—0,1
TiB_2	1	1,5	Slight	Mixed Y, La, Ti, and Cr borides of types Cr_2TiB_2 and Cr_2TiB_4	B	⩽0,12
	2	1,5—2,0	»		B	~0,1
ZrC	1	<0,5	Quite insignificant	No interaction	C	~0,02
	2	<0,5	The same		C	0,023—0,03
$BN+B_4C$	1	2,5—3,0	Severe	Chromium carbides, borides, and nitride	N	⩽0,1
					C	~0,1
$MoSi_2$	1	5,0	Very severe†	Solid solutions, binary and ternary silicides	Si	~2,0
W_5Si_3	1	5,0	Very severe†	Solid solutions, binary and ternary silicides	Si	~1,1
C	1	1,5	Severe	Chromium carbides	C	~0,1

*Melt No. 1 consisted of 100% Cr, melt No. 2 of 100% Cr + 1% (on 100%) Y(La).

†The crucible was destroyed.

and O; and REM of a purity of not less than 99.7%; The molten metal remained in the crucible for 5 min.

The suitability of the materials concerned for the fabrication of crucibles and casting molds for chromium and its alloys was assessed from the degree of the reaction of the chromium melt with the refractory, and from the mechanical (primarily ductile) properties of the cast metal. These properties are highly sensitive to contaminants.

The degree of the reaction of the melt with the crucible material was determined by x-ray and petrographic analyses of the refractory and chemical and metallographic analyses of the surface layer of the ingot. The thickness of the contact zone was determined by inspection and petrographic analysis.

The mechanical properties of the cast metal were expressed in terms of the cold-shortness temperature T_s, the hardness H_V, and microhardness H_μ.

The cold-shortness temperature T_s was represented by the lowest temperature at which a specimen measuring 1 × 4 × 30 mm will be deflected 90° in a three-point bending test. In cases where the brittleness was so high that specimens for the T_s test could not be produced, the plastic properties were assessed from the H_μ and H_V values. An increase in the hardness by 25-30 kg/mm² corresponds to an average increase by 50°C in T_s.

The results of the investigation of the chemical stability of the refractory materials relative to a chromium melt are set out in Table 1. The stability to the action of a melt of unalloyed chromium was found to be highest for crucibles fabricated from BeO and ZrC.

TABLE 2. The Ductile Properties of the Chromium and Its Alloys

Crucible material	Melt No.*	Ductile properties		Crucible material	Melt No.*	Ductile properties	
		T_s, °C	H_V, kg/mm²			T_s, °C	H_V, kg/mm²
"Cold" crucible	1	30	125	TiC	1	—	220
The same	2	10	115	TiB_2	1	—	227
» »	3	20	120	TiB_2	3	—	400
Al_2O_3	1	50	136	ZrC	1	—	132
Al_2O_3	2	—	132	ZrC	3	~100	128
MgO	1	20	120	$BN+B_4C$	1	>250	460
ZrO_2	1	90	151	$MoSi_2$	1	>200	142
ZrO_2	2	—	137—142	W_5Si_3	1	>200	137
BeO	1	30—35	126	C	1	>250	192
BeO	2	—	130	C	2	>200	—
BeO	3	—	135	C	3	>200	—

*Melt No. 1 consisted of 100% Cr, melt No. 2 of 100% Cr + 1% (on 100%) La, melt No. 3 of 100% Cr + 1% (on 100%) Y.

Petrographic and x-ray analyses showed that the contact layer of the crucibles of MgO, B_4C + BN, TiC, TiB_2, $MoSi_2$, and W_5Si_3 contained new phases of the spinel type and carbides, nitrides, silicides, and borides of chromium. The oxygen, nitrogen, carbon, silicon, and boron content of the surface layer of the ingots had increased and the volumetric concentration of these contaminants had also increased. An unexpected phenomenon was the considerable decrease in the concentration of dissolved nitrogen in ingots smelted in crucibles of MgO.

An investigation of the mechanical characteristics of the cast chromium showed that contamination of the metal with impurities and nonmetallic inclusions (Fig. 1) results in much degraded ductility (Table 2). The ductility was satisfactory only for ingots of chromium smelted in BeO crucibles. The hardness of chromium smelted in the MgO crucible was lower in spite of the vigorous interaction of the metal with the crucible, the explanation evidently being the fact that the solid solution was devoid of nitrogen and the matrix had been alloyed with MgO particles. The beneficial effect of MgO on the ductility of chromium has been reported elsewhere [9].

The addition of rare-earth metals to the chromium as deoxidizing agents results in a sharp increase in the interaction of the metal with the refractory as a result of the increase in the chemical reactivity of the melt, more particularly when the melt contains more than 0.5 wt.% REM which is obviously above the solubility limit and creates conditions which favor direct contact between the REM and the refractory as a result of phase separation in the melt. Most crucibles were destroyed under these conditions, the exception being the crucibles of zirconium carbide.

An analysis of the composition of the contact layer showed that the rare-earth metals reduce Al_2O_3, ZrO_2, MgO, and BeO although thermodynamic calculations show that a redox reaction is unlikely in this case. The fact that Al_2O_3, ZrO_2, MgO, and BeO are reduced by rare-earth elements was observed also in smelting steel deoxidized with REM [10].

The high resistance of zirconium carbide to the action of a Cr—REM melt can be explained on the grounds that the free energy of the formation of the components is significantly higher than for $Cr_{23}C_6$ and Y(La)C, and that the solubility of the components in the molten chromium is insignificant [11, 12]. The ductility of ingots of chromium and of chromium—REM alloys smelted in crucibles of ZrC is nevertheless not satisfactory (see Table 2).

The refractory materials investigated here are therefore unsuited for the fabrication of crucibles for smelting chromium to which an REM has been added for the purpose of deoxidizing the metal and increasing its heat resistance. Published data [13, 14] suggest that crucibles fabricated from REM oxides might be suitable. The most suitable crucibles for smelting unalloyed chromium are those made of BeO and Al_2O_3 as well as crucibles of ThO_2 [3].

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