THE WETTING OF REFRACTORY CARBIDES, BORIDES, AND NITRIDES BY MOLTEN METALS

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Carbides, borides, and nitrides of the transition metals in groups IV-VI of the periodic system of elements are distinguished by high chemical stability, melting points of about 3000° C or higher, and other special properties [1]. Consequently, they are being used increasingly for constructional and refractory components and parts intended for operation in corrosive media and in contact with molten metals, alloys, and slats. Among the more important characteristics of refractory compounds is the wetting of their powders or components made from these compounds by molten metals. Thus, good wettability is essential for the formation of cermets and for welding materials in the presence of a liquid phase; the minimum wetting by molten materials, or the absence of it, is necessary in the case of refractories intended for operation in contact with molten media.

In the course of an investigation into the reaction of refractory compounds with molten metals, the author determined the wetting of the surface of parts from titanium, zirconium, chromium, molybdenum, and tungsten carbides and borides, titanium, zirconium, boron, and silicon nitrides, and molybdenum disilicide by molten copper, cadmium, aluminum, silicon, tin, bismuth, manganese, iron, cobalt, and nickel.

Wetting was determined by the sessile drop method [2] and was measured by the angle of contact formed by the tangent to a drop of liquid at its point of contact with a solid surface. A small lump, about 0.3 cm^3 in volume of a metal being investigated was placed on the surface of a hotpressed disk from one of the refractory compounds, which had previously been thoroughly polished and washed with alcohol. The metal was melted on the disk in a tube furnace with a tungsten wire heating element in a protective gas (argon) atmosphere or in a vacuum of 10^{-2}-10^{-4} mm Hg. The test metal on the refractory compound disk was illuminated through windows in the furnace chamber along the chamber axis with a beam of light, and its picture was projected through a photographic objective at 6-fold magnification onto a film. The tests were conducted at the melting temperatures or with some overheating in the case of low-melting metals and metals capable of formation of tough oxide films: 1000° C for aluminum, 450° C for cadmium, 350° C for tin, 450 ° C for lead, and 370 ° C for bismuth. The outline of the drop was photographed 10-15 min after the melting of the metal. The experimentally determined angles of contact θ are presented in the table.

After remaining in contact with each other, the metals and the refractory compound support plates were examined by the methods of metallographic and chemical or spectral analyses to determine changes in their phase and chemical compositions. Attention was paid to the predominant changes in the phase and chemical compositions of one of the materials, the metal or the support plate. Such changes pointed to the preferential migration of elements from one material into the other.

The investigation demonstrated that the wetting of refractory compounds by metals is directly related to the character of their chemical reaction, this in turn being determined by their electronic and crystalline structures. Thus, metals with filled d-electron shells (nontransition metals) exhibit poor wetting of carbides; metals with unfilled d-shells vigorously react with carbides and readily wet their surface. The wetting of carbides by metals improves with decreasing acceptor capacity or the carbide-forming transition metal in the series TiC, ZrC, Cr_3C_2, Mo_2C, and WC. The wetting of borides by a given metal improves with increasing atomic number of the boride-forming metal within the group of the periodic system of elements, i.e., with decreasing criterion of incompleteness of their electron shells, expressed as 1/Nn (N is the principal quantum number of the element, and n the number of electrons in the incomplete d-shell of this element) [3, 5].

The angle of contact is affected by the direction of preferential migration of atoms (see table), which depends on the character of chemical reaction of the contacting materials. When chemical reaction is either absent or only slight, the surface of the refractory compound is not wetted by the molten metal, i.e., the angle of contact is

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Angles of Contact between Refractory Compounds and Molten Metals, Classified According to Preferential Direction of Transport of Elements in Contacting Materials

No reaction		Transport of element from refractory compounds into melt		Transport of metal atoms into refractory compounds		Reciprocal transport	
Me—MeX	θ, deg	Me←MeX	θ, deg	Me→MeX	θ, deg	Me←→MeX	θ, deg
Cu—ZrB_2	138	Cu—TiC	127	Cu—Mo_2C	79	Cu—Cr_3C_2	86
Cu—TiN	136	Cu—ZrC	135	Cu—WC	31	Cu—$MoSi_2$	87
Cu—ZrN	120	Cu—TiB_2	136	Cu—CrB_2	25	Al,Cr_3C_2	85
Cu—BN	125	Al—TiC	117	Cu—Mo_2B_5	127	Al—Mo_2C	69
Cu—Si_3N_4	134	Al—ZrC	97	Cu—W_2B_5	60	Al—WC	69
Al—TiB_2	114	Al—BN	157	Al—TiN	0	Al—ZrB_2	107
Al—Si_3N_4	126	Mn—BN	119	Al—ZrN	27	Al—CrB_2	58
Si—BN	134	Mn—Si_3N_4	74	Al—$MoSi_2$	0	Al—Mo_2B_5	Solid phase
Fe—ZrB_2	122	Fe—BN	112	Si—Cr_3C_2	0	Al—W_2B_5	» »
Cd, Sn, Pb, Bi		Fe—Si_3N_4	90*	Si—Mo_2C	0	Si—TiC	68
do not wet cardides		Co—BN	112	Si—WC	30	Si—ZrC	57
borides, nitrides, or		Co—Si_3N_4	90*	Si—TiB_2	34	Si—Mo_2B_5	60
silicides. Angle of		Ni—BN	118	Si—ZrB_2	44	Si—W_2B_5	75
contact greater than		Ni—Si_3N_4	90*	Si—CrB_2	44	Mn—TiC	68
90°				Si—TiN	22	Mn—ZrC	70
				Si—ZrN	45	Mn—TiB_2	75
				Mn—Cr_3C_2	0	Mn—ZrB_2	56
				Mn—Mo_2C	0	Mn—TiN	74
				Mn—WC	0	Mn—ZrN	76
				Mn—Mo_2B_5	0	Fe—TiC	40
				Mn—CrB_2	0	Fe—ZrC	50
				Si—$MoSi_2$	0	Fe—TiB_2	118
				Mn—W_2B_5	22	Fe—CrB_2	25
				Mn—$MoSi_2$	0	Co—TiC	79
				Fe—Cr_3C_2	0	Co—ZrC	86
				Fe—Mo_2C	0	Co—TiB_2	25
				Fe—WC	0	Co—ZrB_2	50
				Fe—$MoSi_2$	0	Co—CrB_2	76
				Co—Cr_3C_2	0	Co—Mo_2B_5	85
				Co—Mo_2C	0	Co—W_2B_5	97
				Co—WC	0	Ni—TiC	15
				Co—TiN	84	Ni—ZrC	43
				Co—ZrN	90	Ni—TiB_2	64
				Co—$MoSi_2$	0	Ni—ZrB_2	78
				Ni—Cr_3C_2	0	Ni—CrB_2	40
				Ni—Mo_2C	0	Ni—Mo_2B_5	75
				Ni—WC	0	Ni—W_2B_5	64
				Ni—TiN	113		
				Ni—ZrN	0		
				Ni—$MoSi_2$	0		

*The nitrogen evolved from Si_3N_4 as a result of reaction with the metal causes metal spattering, and the drop is very mobile.

greater than 90°. In the case of reaction between a solid support plate and a liquid metal, wetting is not observed only when there is a preferential migration of elements from the refractory compound into the melt, for example, in the pairs TiC-Cu, TiC-Al, BN-Fe, Si_3N_4-Fe, etc.

Rise in temperature activates the diffusion of elements from a melt into a refractory compound. It cannot be ruled out that the oxide film on the surface of a molten metal becomes less firm under these conditions; this, too, might be expected to intensify the transport (reactive diffusion) of elements from the melt into the support plate material, i.e., improve wetting. Al-TiC may be cited as an example: the angle of contact between the molten metal and the support material at 1200° C decreases to 30-40°. In the case of preferential migration of a molten metal into the structure of a refractory compound, the angle of contact ranges between 45 and 0°, and wetting of the refractory compound is observed.

Many pairs of contacting materials exhibit reciprocal transport of atoms of the molten metal into the structure of the refractory compound and of elements of the latter into the melt. Wetting in such a case does take place, but the angle of contact in the majority of cases lies between 45 and 90°. Deviations from these rules shown by some pairs of materials must be attributed to slow reaction of the given contacting materials, i.e., to the measurement of the angle of contact before equilibrium has been established.

From the observations described in this report, it may be concluded that the wetting of a hard surface by molten metal may be influenced both by changing temperature and by introducing into one of the materials (support or melt) additions which intensify or weaken the migration of atoms in the required direction.

SUMMARY

The investigation has shown that the wetting of refractory compounds by metals is directly linked with the character of their chemical reaction, as well as with the direction of preferential transport of elements, from the melt to the refractory support or vice versa. The wetting of a support material by a melt can be controlled by means of additions to one of the contacting materials, which either intensify or weaken the transport of atoms participating in reaction, in the required direction.

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