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Wetting of refractory materials by molten metallides

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The sessile-drop technique has been used to investigate the wetting *in vacuo* by a series of intermetallic compounds ($TiAl_3$, $TiSi_2$, TiNi, $TiNi_3$, $TiCr_2$, Cr_3Si_2, Fe_2Al_5, FeSi, Fe_2Si_5, CoSi, "$CoSi_3$", Ni_3Al, Ni_2Si), by silicon and by a nickel alloy (713LC), of single-crystal Al_2O_3, single-crystal SiC, polycrystalline Si_3N_4, pyrolytic BN, and in some cases only, tungsten. Measurements of contact angle were made at fixed temperatures within the range 1200 to 1600°C. Qualitative observations were made of the interaction and degree of bonding between the constituents. The results of the various experiments are compared and contrasted.

1. Introduction

In previous communications from this Laboratory [1, 2] the results of experiments have been described in which the sessile-drop technique has been used to investigate the wetting of aluminium oxide by molten aluminium and certain other metals. The same technique has now been used for an investigation of the wetting by a series of metallides, by silicon and by the nickel alloy 713LC of single-crystal alumina, single-crystal silicon carbide, polycrystalline silicon nitride, pyrolytic boron nitride and tungsten. This work formed part of an investigation into the feasibility of producing composite materials consisting of intermetallic compounds reinforced with fibres. The metallides investigated consisted of silicides and aluminides of metals in the first transition group together with a few intermetallic compounds of elements within this group; those investigated were: $TiAl_3$, $TiSi_2$, TiNi, $TiNi_3$, $TiCr_2$, Cr_3Si_2, Fe_2Al_5, FeSi, Fe_2Si_5, CoSi, "$CoSi_3$",* Ni_3Al and Ni_2Si.

The present investigations have been less detailed than the earlier ones [1, 2] and have been limited to a single temperature in each instance. However, the experiments covered a wide range of materials and the results are reported here since very little previous work seems to have appeared in the literature on the wettability of refractory materials by molten intermetallic compounds.

2. Experimental

The intermetallic compounds used in these experiments were prepared in our laboratory, with the exception of $TiSi_2$ and Cr_3Si_2 which were obtained from Alfa Inorganics Inc, Beverly, Mass, USA, and of TiNi which was obtained from Mond Nickel Co. The nickel alloy 713LC† was supplied by NGTE Pyestock.

All the ceramic plaque materials were cut and polished by Agate Products Limited. The single-crystal Al_2O_3 samples were 18 mm square × 1.5 mm thick, cut from Verneuil boules supplied by H. Djevahirdjian, Switzerland, and with both principal faces optically polished. Plaques 12 mm square × 3 mm thick were cut from large plates of polycrystalline Si_3N_4 (supplied by Hoffmann Manufacturing Co) and of pyrolytic BN (supplied by Union Carbide Corporation). The SiC material was obtained as large masses of single-crystal platelets from Arendal Smeltwerk, Norway, through Tennant Trading Ltd, London. Individual crystals of irregular profile were cut from lumps and one principal face polished. The

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*The phase diagram given by Smithells [3] indicates a compound with this formula melting at 1306°C, but Hansen [4] points out that there is evidence which casts doubt on its existence. X-ray analysis showed the material produced at NPL to be a mixture of $CoSi_2$ and Si.

†Nominal analysis: 12.5% Cr, 6.1% Al, 0.8% Ti, 4.2% Mo, 2.2% Nb, 0.1% C, 0.1% Zr, 2.5% max Fe, balance Ni.

tungsten was in the form of discs 12 mm diameter × 3 mm thick cut from bars.

The wetting experiments were carried out under vacuum in the sessile-drop apparatus as described previously [1]. To be consistent within the present experiments, however, none of the samples was etched prior to placing in the furnace since many of the materials were porous so that it would have been difficult to remove all traces of the etchant.

The profiles of the molten liquid drops were photographically recorded on 35 mm film and contact angles determined by measuring projected images of the negatives. In systems which gave good wetting the liquid drop often spread over the surface in a random manner so that truly meaningful values for contact angles could not be measured. Consequently, contact angles below 40° were simply recorded as "less than 40°" with the implication that very good wetting occurred in these instances. Visual observation of the plaque after the experiment gave a qualitative indication of chemical reaction and compatibility between the materials. Severe interactions were manifestly apparent in some instances but minor degradation of the substrate at the interface would not necessarily have been observable.

3. Results

The results, except for the wetting experiments with tungsten discs, are summarized in Table I. Reaction rings were observed on some of the alumina plaques: these were similar to those observed previously with aluminium and aluminium alloys on alumina and may indicate the formation of a volatile reaction product [1]. The bond strength of the solidified drop to the plaque was assessed by twisting one relative to the other. Sometimes failure occurred within the plaque, leaving the drop with a layer of plaque material firmly adhering to the base. These samples were classified as being bonded, but this merely means that the interfacial bond strength was greater than the shear strength of the plaque materials.

The experiments in which the wetting properties of a limited number of the intermetallic compounds (TiNi, Ni_3Al, $TiAl_3$, FeSi, Fe_2Al_5, $TiSi_2$ and Ni_2Si) to tungsten discs were investigated at temperatures in the range 1200 to 1500°C all resulted in very good wetting being obtained (contact angle less than 40°).

TABLE I Wetting of single-crystal Al_2O_3, single-crystal SiC, polycrystalline Si_3N_4 and pyrolytic BN by various materials

Plaque material	Al_2O_3			SiC			Si_3N_4			BN		
Drop material	Temp. (°C)	θ (deg)	Comment	Temp. (°C)	θ (deg)	Comment	Temp. (°C)	θ (deg)	Comment	Temp. (°C)	θ (deg)	Comment
$TiAl_3$	1500	82	w c f	1450	<40	b d	1400	50	b c	1450	45	b d
$TiSi_2$	1560	80	x c n	1500	<40	b c	1500	<40	b c	1515	<40	w c
TiNi	1300	<40	b c n	1500	82	w c	1300	<40	b c	1300	<40	x c
$TiNi_3$	1500	60	x c n	1500	50	b c	1450	66	b c	1500	96	w c
$TiCr_2$	1500	<40	x c n	1500	<40	x c	1500	<40	x c	1500	<40	x c
Cr_3Si_2	1550	100	x c m	1460	<40	b c	1500	80	b c	1460	118	w c
Fe_2Al_5	1400	67	w c n	1300	58	b c	1300	66	b c	1300	45	w c
FeSi	1500	85	x c n	1420	<40	w c	1500	76	x c	1550	66	x c
Fe_2Si_5	1450	90	x c f	1350	<40	w c	1450	66	b c	1500	82	b c
CoSi	1600	99	s c f	1500	<40	b c	1470	62	b c	1500	63	x c
"$CoSi_3$"	1500	80	s c n	1400	60	x c	1400	<40	b c	1450	116	x c
Ni_3Al	1550	83	x c f	1550	<40	b c	1550	75	b c	1600	<40	x c
Ni_2Si	1400	87	x c n	1320	90	x c	1450	108	b c	1600	97	x c
Si	1550	94	b c m	1450	<40	b c	1500	<40	b c	1500	105	b c
713LC	1500	90	x c n	1350	<40	b c	1400	<40	b d	1500	54	w c

Key to comments: x: no bond, w: weak bond, b: bonded, s: bulk of drop did not adhere to plaque but small areas at periphery firmly bonded, c: apparent compatibility, d: doubtful compatibility, n: no reaction rings, f: few reaction rings, m: many reaction rings.

4. Discussion

It was found that in general, alumina was unreactive with, and not well wetted by, silicides, silicon or aluminides. Only compounds which contain titanium were found to wet alumina to any extent. These results may perhaps be compared with those of Kurkjian and Kingery [5], of Ritter and Burton [6] and of Sutton and Feingold [7] who found that additions of titanium promoted the wetting of alumina by nickel. The observed decrease in metal-alumina interfacial energy was assumed to be due to a selective adsorption of titanium atoms at the interface, the process being of a chemisorptive nature, resulting in the formation of strong metal-oxygen bonds. Armstrong *et al* [8] detected an interfacial reaction product α-Ti_2O_3 in similar experiments and it was found that titanium diffused into the bulk alumina. The results obtained with the intermetallics containing iron may be compared with those of Kingery [9] who studied the effect on the wettability of alumina by iron with additions of silicon. Kingery found that the interfacial energy decreased with increasing amount of solute (contact angles range from 137° for 0.06% Si down to 115° for 8.7% Si). This he attributed to the greater stability of Si–O bonds compared with Fe–O. In general, electropositive solute bonds, which form more stable metal–oxygen bonds than the solvent, tend to be surface-active, resulting in a decrease in contact angle.

In the present experiments it was found that silicon and the silicides investigated, except possibly Ni_2Si, wetted silicon carbide. Aluminides gave low contact angles but aluminium carbide (Al_4C_3), which is unstable in the presence of water, may be formed at the interface. Titanium compounds, with the exception of TiNi, gave low contact angles.

With silicon nitride the effects of silicides were varied. Very low contact angles were given by "$CoSi_3$", $TiSi_2$ and Si while the remaining silicides wetted to a lesser extent and Ni_2Si did not wet at all. Aluminides gave moderate wetting while titanium-containing compounds gave moderate to good wetting. These results may be compared with those of Calow and Barclay [10] who found that silicon nitride whiskers showed degradation after short periods at 1200°C in nickel and iron matrices, (although this degradation was found to be due to physical changes in the ceramic whiskers rather than chemical reaction), and those of Ginsberg and Krock [11] who patented an alloy comprising 90% Ni, 7.5% Ti and 2.5% Si which has good wetting characteristics with silicon nitride. In the latter instance titanium was chosen because of its ability to lower the surface energy between the liquid and solid phase and the silicon was added to slake the affinity of titanium for silicon, thus reducing the degree of reaction on the silicon nitride.

With boron nitride, silicon and the silicides (except $TiSi_2$) did not give good wetting. Compounds of both aluminium and titanium (except $TiNi_3$) yielded low contact angles.

The compound $TiCr_2$ is interesting in that it gives low contact angles with all four ceramics, does not bond to any and also appears to be unreactive. With silicon carbide and silicon nitride, it is the only titanium compound that does not bond. This lack of bonding could be due to physical changes brought about by the solid state transformation which occurs at the ordering temperature (1370°C).

The nickel alloy 713LC shows good wetting with silicon carbide, silicon nitride and boron nitride but not with alumina, even though it contains elements such as Ti, Cr and Al which have been reported to promote wetting with nickel [12]. The series of experiments with tungsten plaques demonstrated that this metal is readily wetted by all the intermetallic compounds which were tried.

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