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Wetting of refractory titanium hard metals by sodium disilicate glass

I. J. McCOLM, C. DIMBYLOW*
School of Materials Science, University of Bradford, Bradford, UK

The sessile drop technique has been used to investigate the wetting *in vacuo* of a series of polycrystalline titanium monoxides by sodium disilicate glass. To a lesser extent the wetting behaviour of titanium metal, titanium nitride and titanium carbide have also been investigated. Measurements of contact angle were made at 1000° C. Qualitative observations were made of the interaction and degree of bonding between the glass and the substrates and a relationship between the valency electron concentration of the substrate and the degree of wetting and bonding is obtained. Some microhardness data on the arc cast substrates and information on the chemical reactivity of the powdered substrates with the glass are also given.

1. Introduction

There are many reports on the use of the sessile drop technique to investigate the wetting of oxides by liquid metals and of metals by glasses, for example [1-4]. It is customary to investigate variations in atmosphere, glass composition, or variations in the substrate by alloy formation. It was felt that another dimension in the study of the parameters affecting glass to metal bonding might be available by using as substrates non-stoichiometric compounds with metallic properties whose crystal structures remain basically constant through a wide stoichiometric range. Titanium monoxide has a composition range extending from $TiO_{0.67}$ to $TiO_{1.25}$ within a NaCl type B_1 structure about 980°C [5]. Variations of composition within this range are accompanied by changes in concentration of metallic delocalised electrons in the band system describing the bonding in these compounds and can be related to the valency electron concentration using the Denker model [6]. The object of the work reported here is to examine the effect of substrate stoichiometry and valency electron concentration on the contact angle and degree of bonding between a simple sodium disilicate glass and cubic special ceramic substrates containing titanium. Microhardness of a series of titanium oxides and the reactions between the substrates and the glass has also been investigated.

2. Experimental

All the ceramic plaque materials used in this work were prepared in this laboratory using an arc furnace and methods already described in [7]. The TiO_x specimens were made from TiO_2 (Johnson and Mathey spectrographically pure) and Ti metal (> 99.9 Koch-Light Ltd). Each preparation was examined by X-rays in an 11.4 cm Debye-Scherrer camera. TiC and TiN were made from the elements and the glass was supplied by Crossfield Chemicals Ltd.

The sessile drop apparatus was a horizontal resistance tube furnace enclosing a fused quartz tube with an optical flat end, which could be operated at 10^{-6} Torr. The molten liquid drops were examined via a telescope system focused through the optical end of the tube. Direct measurements to $\pm \frac{1}{2}°$ were made using a calibrated eyepiece fitted with a protractor and photographs were taken from time to time from which the contact angles could also be measured.

For an experiment the plaque material was cut into a strip 3.0 cm × 1.0 cm × 1.0 cm of which one long face was metallurgically polished to a finish of 1 μm diamond grit. A piece of the glass weighing 100 mg was placed on the polished surface and the apparatus evacuated to 10^{-6} Torr before the furnace, ready at 1000°C, was moved into place. The experiment was timed from the onset of melting and readings of pressure, temperature and contact angle with time

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*Present address: Central Dockyards Laboratory, H.M. Naval Base, Portsmouth, UK.

were taken as well as noting any obvious reactions occurring between substrate and glass. Generally a constant angle was achieved after 15 min but readings were continued up to 30 min from the onset of melting.

Visual observation of the plaque during and after the experiment and of the cooler parts of the reaction tube gave an indication of chemical reactions between the materials. The appearance and colour of the specimens was noted and the adherence of the glass bead was estimated qualitatively by attempting to shear it from the substrate. Adherence was classified as good if the glass could not be moved, or if the glass or substrate broke in preference to the interfacial bond. Whenever possible adherent specimens were mounted in perspex, sectioned perpendicular to the interface, polished to a $\frac{1}{4}$ µm diamond paste finish and examined optically.

To further the studies concerning substrate-glass reactivity, powdered mixtures were heated in sealed evacuated silica ampules for several hours at 1000°C with one end projecting from the furnace. This end was air cooled and was where any sublimate collected. The sublimate was examined chemically.

After polishing and before using in a wetting experiment the microhardness of each substrate surface was determined using a Leitz miniload microhardness tester with a load of 100 g.

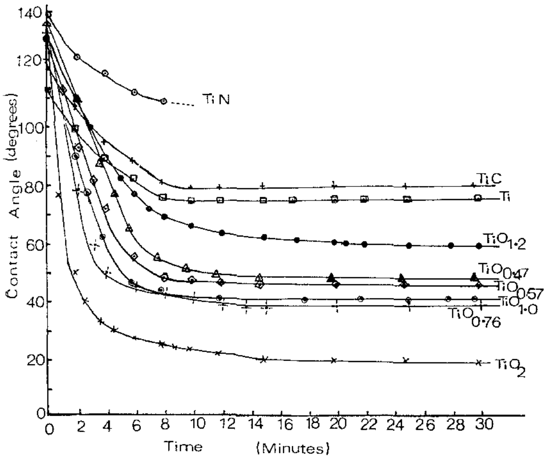

Figure 1 Plot of contact angle against time for 100 mg $Na_2Si_2O_5$ at 1000°C.

3. Results

A plot of contact angle versus time for the substrates is shown as Fig. 1 where it can be seen that after 15 min in all cases a constant angle is attained. When the contact angle was less than 40° excellent adherence was achieved which applies only to $TiO_{1\cdot0}$ and $TiO_{0\cdot76}$. In the case of $TiO_{1\cdot00}$ the bond between glass and ceramic was so strong that contraction stresses on cooling produce large cracks in the glass and substrate but not in the interfacial bond region. This effect is shown in Fig. 2.

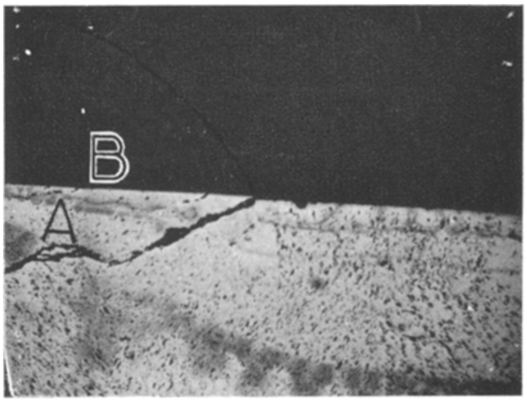

Figure 2 Section of $Na_2Si_2O_5$ [B] glass bead on $TiO_{1\cdot00}$ substrate [A] showing cracks developed on cooling in both the glass and the substrate (× 65).

While the contact angles do not decrease linearly as the substrate oxygen content increases the hardness measurements on the polished substrates show a linear increase in hardness for the TiO_x specimens up to $TiO_{1\cdot0}$. This is shown in Fig. 3 as a plot of microhardness against valency electron concentration.

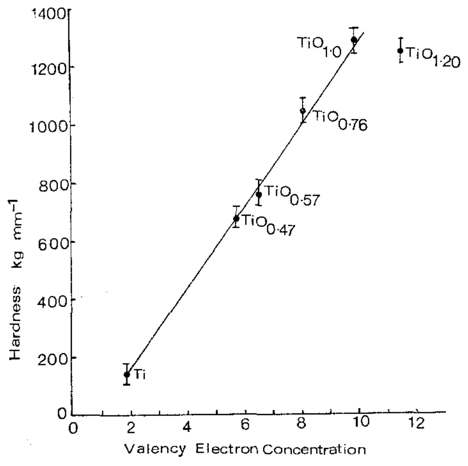

Figure 3 Plot of Vickers pyramid hardness against valency electron concentration for titanium oxide substrates, 100 g load.

3.1. Ti metal

In this system the contact angle at 30 min was 74° with resultant weak interfacial bonding such that contraction stresses on cooling were sufficient to cleanly shear the glass from the metal. The surface of the metal was very clean and shiny but the underside of the glass bead was black and contrasted markedly with the transparent clear glass. An X-ray of the powdered black layer indicated the presence of TiO, Ti_2O_3 and Ti_4O_7 amongst the glassy matrix.

A yellow-brown sublimate in the cooler parts of the furnace was collected and found to be a mixture of sodium and silicon. A sealed tube reaction between Ti and $Na_2Si_2O_5$ powder at 1000° showed that after 30 min 2.1% of the Na in the glass was evolved together with an amount of Si that was not estimated because it was not possible to concentrate it sufficiently by sublimation.

3.2. $TiO_{0.47}$

The contact angle reached 47° after 30 min and there was little to suggest sodium evolution during this time. There was only weak bonding with the bead easily removed cleanly from the substrate. Patchy mottled areas of blue-black colour were apparent on the underside of the glass bead.

3.3. $TiO_{0.57}$

A slightly lower contact angle of 45° was achieved but no bonding and very little reaction.

3.4. $TiO_{0.76}$

A strong glass to ceramic bond was formed after 30 min and the lowest contact angle of 36° was obtained. Although some sodium was evolved the reaction was only slight. An experiment with the powdered materials showed that $< 0.1\%$ of the available sodium was replaced after 30 min.

The adherence of the glass bead was sufficient to allow a cross-section to be prepared and examined microscopically. A pink coloured intermediate layer of near uniform thickness was found between the $TiO_{0.76}$ and the glass. Fig. 4 shows the depth of the layer as a slightly darker colour than the substrate.

3.5. $TiO_{1.0}$

Very strong bonding was achieved coupled with a low contact angle of 38°. Little sodium was evolved and an intermediate layer was again in evidence.

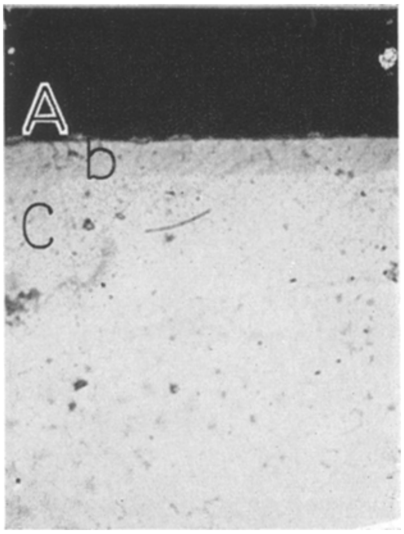

Figure 4 Polished section of $Na_2Si_2O_5$ [A] on $TiO_{0.76}$ substrate [C] showing the interfacial layer [b] (× 280).

3.6. $TiO_{1.0}$

In all tests this sytem behaved like the low oxygen content $x < 0.7$ substrates with no adherence of the glass and a high contact angle of 59°.

3.7. $TiN_{1.0}$

Reaction between the substrate and glass was obvious and extensive with considerable amounts of sodium, nitrogen and silicon being evolved. This made contact angle measurements impossible beyond 8 min at 1000°C but resulted in an adherent glass-TiN composite with a room temperature contact angle of 27°. The glass bead was deep blue in colour.

A separate reaction of the mixed powders at 1000°C showed that 11.3% of the available sodium was replaced after 30 min.

3.8. $TiC_{1.0}$

This system was very reactive with much gas and sodium being evolved. A high contact angle of 78° and no adhesion were obtained. The surface of the plaque where the bead had been was found to be very rich in Ti metal. A reaction between powdered TiC and the glass at 1000°C produced a deposit of 8.5% of the available sodium in 30 min.

4. Discussion

Denker [6] has described a model of bonding in cubic refractory hard metals that might be relevant to the results of this work. In this model cohesion is discussed in a general way which relates the intrinsic mechanical, electrical and chemical properties to the valency electron concentration V.E.C. V.E.C. is α times the total number of outer or valency electrons of the cation, in this case Ti^{2+}, plus β times the total number of valency electrons of the anion X^{2-}. In the original work α and β are the real fraction of Ti and X sites occupied in $M_\alpha X_\beta$ as determined from pyknometric and X-ray densities. For the results presented here we make the simplifying assumption that the TiX_x samples are defective only in the anion sublattice. This leads to the unreal situation in $TiO_{1\cdot 2}$ in which β will be greater than unity and give a V.E.C. of 11.6 while fully dense $TiO_{1\cdot 0}$ would have a V.E.C. of 10. The occupancy of atomic positions and average numbers of valency electrons have been determined for $TiO_{1\cdot 0}$ and $TiO_{1\cdot 2}$ [6] and it is known that both Ti^{2+} and O^{2-} sites have vacancies to the extent of 14.3% in both cases for $TiO_{1\cdot 0}$ and 21.0 and 5.2% respectively for $TiO_{1\cdot 2}$. Thus the average V.E.C. does increase from $TiO_{1\cdot 0}$ to $TiO_{1\cdot 2}$ but not as sharply as the simplification used here suggests.

In this theory of bonding maximum stability is achieved by that crystal structure in which nearly all the bonding orbitals are occupied and anti-bonding orbitals are vacant which occurs for a V.E.C. between 8 and 9 valency electrons per TiX molecule.

Fig. 5 shows that the contact angle reaches a minimum and the strength of the interfacial bond is at a maximum for $TiO_{0\cdot 76}$ with a V.E.C. of 8.1. The general shape of the curve suggests a relationship between wetting and the bond strength of the ceramic substrate as expressed by the V.E.C.

The three samples that produced the lowest angles and excellent adhesion had V.E.C.s in the range 8 to 10 on the simple model assumed here. A more accurate derivation of V.E.C. for $TiO_{0\cdot 80}$, $TiO_{1\cdot 0}$ and $TiO_{1\cdot 2}$ is given in [6] with values 8.15, 8.55 and 8.85 respectively and thus it appears that the contact angle is at a minimum at 8 where covalent bonding forces in TiO_x are at a maximum. Hence the reaction leading to wetting and adhesion is sensitive to the covalent bond strength of the substrate in these materials and not on a continually increasing oxygen content.

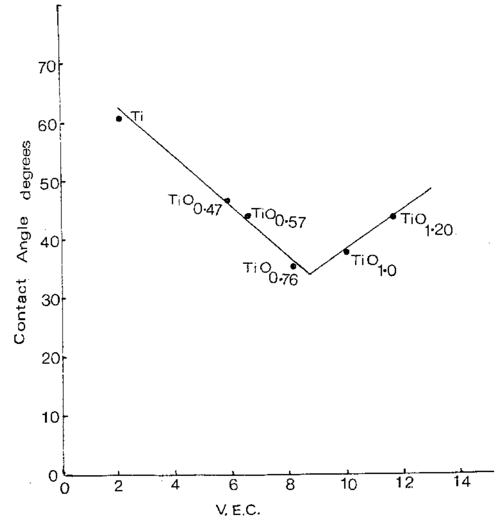

Figure 5 Relationship between the measured contact angle at 1000° C of molten $Na_2Si_2O_5$ on a range of substrates and the calculated valency electron concentration.

The surface hardness of the oxide plaques is seen in Fig. 3 to increase linearly as the non-metal component increases and does not reflect the maximum covalent bond strength at $TiO_{0\cdot 78}$. It is interesting to see that the metal will fit onto the linear part well giving it a V.E.C. of 2 which corresponds in the model to $TiO_{0\cdot 0}$. There is a suggestion in the hardness results that a maximum in yield stress occurs near the stoichiometric composition. This carries a suggestion that the movement of dislocations is governed by the constitutional vacancy content of the lattice rather than covalent bond strength and is, therefore, not in direct conflict with the bond strength model.

A feature of all the sessile drop experiments was the production of a pinkish-grey deposit of sodium on the reaction tube walls. This deposit was heaviest when Ti substrates or substrates leading to free Ti were used. Maximum adherence of glass to metal occurs when the glass at the interface is saturated with the oxide of the lowest valency cation of the substrate metal [8-10]. If such saturation does not exist reactions can occur at the interface that introduce the required oxide into the glass and this is clearly what is happening in these systems at 1000° C. In the case of Ti metal reduction of Na^+ in the glass is the principal reaction which can be conveniently expressed as

$$Ti + Na_2O_{(glass)} = TiO_{(glass)} + 2Na_{(g)}$$

In the time given for the experiment the glass did not saturate and adhesion was poor. The sodium evolution was more extensive in the case of TiN where the reaction

$$2TiN + 2Na_2O_{(glass)} = 2TiO + 4Na_{(g)} + N_2$$

occurs to cause more rapid saturation of the glass and good glass to substrate bonding.

In the case of the TiO_x substrates one might expect no sodium evolution as straightforward dissolution occurs. The fact that some sodium was evolved and a thin pink coloured intermediate layer was detected suggests that as well as physical dissolution some Ti^{2+} diffusion into the glass takes place where oxidation to Ti^{4+} occurs and incorporation in the Si—O network would account for small amounts of Si and Na evolved in the experiments. Charge compensation could occur in the substrate by the appearance of Ti^{3+} which would account for the colour of the interfacial layer.

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