JOURNAL OF MATERIALS SCIENCE **21** (1986) 3292–3296

Interaction of Fecralloy with sodium disilicate glass

M. G. NICHOLAS
Atomic Energy Research Establishment, Harwell, Oxfordshire OX11 0RA, UK

Interactions of sodium disilicate glass with Fecralloy, Fe–6Cr–4Al–0.25Y, have been analysed in terms of the Pask chemical equilibrium theory. Sessile drops assumed contact angles of 38 to 47° at 900 to 1100° C on polished substrates following interactions that led to significant weight losses. Up to 7% of aluminium and much smaller amounts of iron, chromium manganese and yttrium were taken into the glass. On pre-oxidized substrates, coated with alumina, near-perfect wetting was achieved but once more aluminium was taken into the glass and weight losses suffered. These data can be interpreted as resulting from redox reactions between the aluminium in the alloy and the sodium monoxide in the glass.

1. Introduction

Interfacial phenomena produced by contact with sodium disilicate glass have been studied for a number of pure and alloyed metal workpiece systems. To some extent the glass has been used as a model material because of its simple composition, $Na_2O \cdot 2SiO_2$, but it also possesses potentially technologically useful characteristics. Thus it flows at about 800° C and has a thermal expansion coefficient of $13.6 \times 10^{-6}\,K^{-1}$, similar to that of steels and nickel-base alloys. In this paper, observations are described that relate to its interaction with Fecralloy*, Fe–6Cr–4Al–0.25Y, a complex material that has potential applications as an electrical feed-through and microcircuitry substrate that depend on the creation of high-integrity glass–metal interfaces.

Previous work [1–6], most notably by Pask and his co-workers, has shown the behaviour of sodium disilicate glass–metal systems to be critically dependent on the nature and extent of chemical reactions occurring at the melt–substrate interfaces. Of particular importance is the role of workpiece components that can participate in redox reactions causing the glass to lose weight by volatilization of sodium or, less commonly, silicon monoxide. While these reactions progress, wetting is enhanced but bonding remains poor until the interface region is saturated with the lowest valent stable oxide and, albeit localized, chemical equilibrium is established.

The generalizations formulated above are based on rather limited data and hence no certainty exists about predictions for uninvestigated materials such as Fecralloy. Chromium and iron and some of their binary alloys have been observed to cause redox reactions but the behaviour of Fecralloy in oxidizing environments, such as the glass melt, should be markedly influenced by the presence of aluminium and perhaps even the traces of yttrium. Whatever the redox behaviour, it seems probable that pre-oxidation of the Fecralloy to form a surface film of predominantly α-alumina should promote wetting since some of the oxide will dissolve in the glass and introduce Al^{3+} and Al^{2+} ions, which shorten the Si–O bond length [7] and decrease the energy of the system. Significant uptake of aluminium by a glass ceramic from oxidized Fecralloy [8] has been reported but no data are known for sodium disilicate glass. If the oxide is completely dissolved, the behaviour would be expected to revert to that of clean Fecralloy. To test the validity of these concepts, experiments were conducted with clean and oxidized Fecralloy workpieces over a range of temperatures and note taken of weight losses indicating redox reactions, wetting and bonding behaviour, and microstructural variations.

2. Materials and techniques

The substrates used in this work were annealed Harwell stock Fecralloy machined into 20 mm diameter, 3 mm thick discs, with surfaces polished to a metallographic standard using silicon carbide papers and 0.3 μm alumina powder. Some of the Fecralloy discs were used in this condition, but others were pre-oxidized in air for 7 or 70 h at 1115° C. All the workpieces were degreased by ultrasonic agitation in acetone, dried, and weighed immediately before being used in an experiment, as was the glass. The glass preparation has been described elsewhere [9] and that used in this work was supplied by Dr A. P. Tomsia of the University of California, Berkeley, as cubes weighing about 0.06 g.

Sessile drop tests were conducted with these samples using an evacuated furnace chamber [9] containing a tantalum tube resistance-heating element encircling an alumina platform on which the samples were placed. Two Fecralloy workpieces were used in each experiment, on one of which was located a glass cube while the other was used as a blank for subsequent weight-change measurements. The chamber was evacuated to

---

*Registered trademark of the United Kingdom Atomic Energy Authority.

0022–2461/86 $03.00 + .12

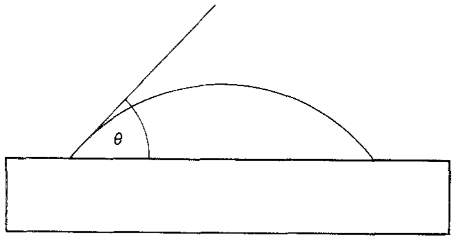

Figure 1 Schematic profile of a sessile drop identifying θ, the contact angle.

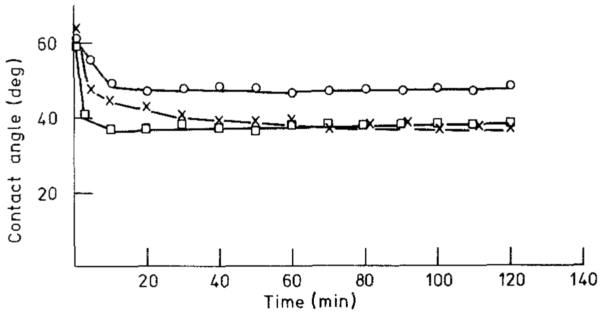

Figure 2 The contact angles assumed in vacuum by drops of sodium disilicate on polished Fecralloy workpieces at (x) 900, (□) 1000 and (○) 1100° C.

1 to 3 × 10^{-7} mbar (1 to 3 × 10^{-5} Pa) using a cold-trapped oil diffusion pump, and the samples were heated to the experimental temperatures at 0.5 K $\sec^{-1}$ and held for 2 h before the heater power was switched off and the experiment ended. Diametrically opposed parts permitted the samples to be illuminated and observed during the experiments, and the contact angles, defined in Fig. 1, assumed by the glass drops were measured with an accuracy of $\pm 1°$ at 10 min intervals during the experiments using a telescope fitted with a goniometer. Each experiment was duplicated, and the average reproducibility of contact angle data was $\pm 2.2°$.

The samples and blanks were weighed at the end of each experiment and note was taken also of any colour changes caused by the experiment when the samples were viewed using a bench microscope. Most of the glass–Fecralloy samples were mounted in clear epoxy resin, immersed in kerosene and cut using a diamond saw through the drop centres on planes normal to the glass–metal interfaces. The cross-sections revealed were prepared for metallographic and electron probe microanalyser examination by grinding on dry emery papers and vibratory polishing using oil-lubricated 6 and 1 μm diamond pastes.

3. Results

3.1. Polished samples

On heating, the glass became fluid enough to form a symmetrical drop profile at about 750° C and degas vigorously at 750 to 850° C, before assuming a contact angle of about 60° at 900° C. The glass continued to degas, albeit not vigorously, and the profile changed significantly during the first 30 min at 900° C to decrease the contact angle to about 40°, but thereafter little occurred except for occasional small transient distortions that may have been gentle gas release. During this final essentially quiescent stage lasting 90 min, the contact angle further decreased slightly to 38° (Table I and Fig. 2). At higher temperatures the initial angle was again about 60° but the final values were lower, 39° at 1000° C and 47° at 1100° C. During the experiments at 1100° C the observation windows became significantly clouded, but they remained clear at lower temperatures.

On removal from the furnace both the blanks and the glass–metal samples were found to have lost weight (Table I), particularly during the experiments conducted at 1100° C. (The glass itself experienced some weight loss, although to a much smaller extent as revealed by experiments using inert platinum substrates.) Taking account of the separate Fecralloy and glass losses, those induced by glass–Fecralloy reactions were found to increase significantly with temperature to extents that suggested approximate rates of 1 to 18 × $10^{-9}\,\mathrm{g\,mm^{-2}\,sec^{-1}}$ at 900 to 1100° C.

All the glass drops were bonded to the Fecralloy workpieces and those heated to 900 and 1000° C had assumed a light yellow-brown hue while those that had been heated to 1100° C were tinged a light green. The drop peripheries were smooth but there was evidence of grain-boundary grooving of the Fecralloy both within and without the drop contact areas, and of faceting of samples that had been heated to 1100° C.

Optical examination of the cross-sectioned samples revealed little apart from identifying small bubbles

TABLE I Summary of wetting and weight-loss data

Workpiece condition	Temperature (° C)	Contact angle (deg)		Contact area (mm²)*	Weight loss (g)			Loss due to glass–metal interaction	
		10 min	120 min		Blank	Glass	Sample	% of Na_2O	Approximate reaction-induced weight-loss rate ($\mathrm{g\,mm^2\,sec^{-1}}$)†
Polished	900	50	38	34.9	0.00009	0.00004	0.00048	2.1	1.4 × 10^{-9}
	1000	37	39	39.2	0.00049	0.00020	0.00162	4.2	3.3 × 10^{-9}
	1100	44	47	34.2	0.01073	0.00055	0.01576	25.7	18.2 × 10^{-9}
Polished, oxidized, 2.4 μm	900	31	6	80.6	0.00007	0.00004	0.0031	1.2	0.3 × 10^{-9}
	1000	24	4	100.8	0.00004	0.00020	0.00089	3.8	0.9 × 10^{-9}
	1100	6	2	167.9	0.00005	0.00055	0.00669	36.0	5.0 × 10^{-9}
Polished, oxidized, 6.4 μm	1000	22	2	197.2	0.00008	0.00020	0.00091	3.4	0.4 × 10^{-9}

*After 120 min.

†(Sample loss − blank loss − glass loss)/(7200 × final contact area).

TABLE II Contamination of glass produced by contact with Fecralloy

Exposure temperature (°C)	Fecralloy condition	Approximate uptake rate (10^{-9} g mm^{-2} sec^{-1})*			
		Al	Fe	Cr	Y
900	Polished	0.6 (1.7) 0.7†	0.06†	0.02†	0.002†
1000		0.9 (5.0)	0.3 (0.3)	0	–
1100		2.1 (14.4) 2.4†	1.0 (10)	0.3†	0.02†
900	Oxidized, 2.4 μm	0.2 (2.1)	0	0	–
1000		0.4 (2.5)	0.03	0	–
1100		1.4 (1.6)	0.14	0	–
1000	Oxidized, 6.4 μm	0.2 (1.2)	0	0	–

*(Contaminant concentration × drop weight)/(7200 × final contact area).

†Obtained by optical emission spectroscopy, other data being derived from electron microprobe analyses. Bracketed data refer to locations near the workpiece interfaces.

present within glass that had been heated to 1100° C. There was no evidence of phase separation within the glass or reaction zones at the glass–metal interfaces. It was noteworthy, however, that the process of cutting, grinding and polishing had caused fairly extensive fracturing within the glass of samples that had been heated to 900 or 1000° C.

Electron probe microanalyses and inductively coupled plasma optical emission spectroscopy of selected samples revealed that significant contamination of the glass had occurred. The uptake of aluminium was most marked, but transfer of iron and chromium was also significant and even that of yttrium was detectable (Table II). Increasing the exposure temperature from 900 to 1100° C trebled the uptake of aluminium and increased that of the other contaminants at least ten-fold. Spot analyses using the electron probe microanalyser revealed enhanced contamination near the metal interface for aluminium but not for iron.

3.2. Oxidized polished substrates

Pre-oxidation of the polished Fecralloy samples for 7 or 70 h at 1115° C caused average weight gains of 0.022 and 0.063 g, equivalent to alumina film thicknesses of about 2.4 and 6.4 μm, confirmed by optical microscopy. Glass cubes used with these substrates in sessile drop tests behaved during the heat-up period as had those on polished substrates, becoming fluid at about 750° C and degassing vigorously at 750 to 850° C. In experiments using substrates with an oxide film thickness of 2.4 μm, an initial contact angle of 46° was assumed at 900° C and then decreased progressively to 6° during the 120 min hold-time without any noticeable profile distortions. At 1000° C, the initial contact angle was lower at 30° and the subsequent decrease to 4° somewhat more rapid, while at 1100° C the initial angle was only 25° and the subsequent decrease to less than 2° was far more rapid (Table I and Fig. 3). Reflecting these low final angles, the glass contact areas were far greater than those formed with polished substrates (Table I). An experiment conducted at 1000° C with substrates covered with 6.4 μm oxide films yielded wetting behaviour similar to that reported above for the less oxidized material (Table I and Fig. 3).

Once more, both blanks and glass–metal samples were found to have lost weight as a result of being heated, but to a lesser extent than had the polished Fecralloy samples. The data suggested that contact between the materials had induced weight losses at rates of approximately 0.3 to 0.5 × 10^{-9} g mm^{-2} sec^{-1} at 900 to 1100° C. The samples cooled from 1100° C were adherent. However, when samples were cooled from 900 or 1000° C the glass drops completely separated from the steel workpieces except for a narrow peripheral annulus, or partially separated with retained material being severely cracked.

Unlike glass heated in contact with polished substrates, the drops assumed a pale grey hue during the course of experiments conducted at all three temperatures. The drop peripheries were smooth but grain-boundary grooving of the Fecralloy surface within and without the glass contact areas was observed for all the samples. Optical microscopy of cross-sectioned samples confirmed that the oxide films formed by the Fecralloy pre-treatment had remained intact and apparently unthinned within the glass contact zone. The glass–metal separation referred to above occurred at the oxide–metal interfaces. While providing information about this oxide layer, these examinations did not reveal any bubbles, phase separation within the glass, or identifiable structure features at the glass–oxide interfaces.

Electron microprobe microanalyses once more revealed substantial contamination of the glass by aluminium (Table II), although the rate of uptake was less than with polished substrates. Once more the rate increased with temperature and spot analyses showed that aluminium contamination was greater near the metal interface.

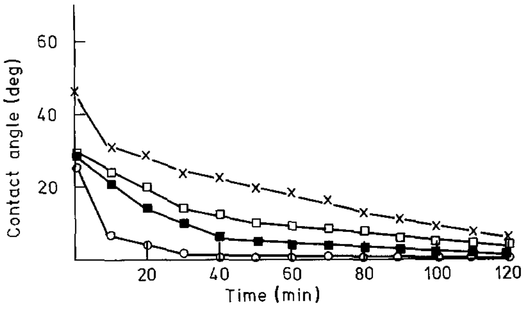

Figure 3 The contact angles assumed in vacuum by drops of sodium disilicate on polished and oxidized Fecralloy workpieces at (x) 900, (□) 1000 and (○) 1100° C. The workpiece oxide thickness was 2.4 μm except for one experiment (■) with a thickness of 6.4 μm conducted at 1000° C.

4. Discussion

The data obtained in this brief study are neither definitive nor comprehensive, but do permit some tentative conclusions to be drawn about the nature of the physical and chemical interactions between sodium disilicate glass and Fecralloy. Thus the compilation by Hultgren *et al.* [10] includes values for the activity coefficients of chromium and aluminium in iron which predict activities of about 1.0, 0.1 to 0.2, and 0.0001 to 0.0002 to be calculated for iron, chromium and aluminium, respectively, at the temperatures used in this study if it is assumed that the solutes are not interactive. No data have been found for yttrium and therefore possible effects involving it have had to be ignored. While the activity of aluminium is low relative to that of the other components, the free energy of formation of Al_2O_3 is so much more negative than that of other possible products (Fig. 4) [11–13], that its formation should dominate the redox reaction

$$\alpha M + \beta Na_2O \rightarrow M_\alpha O_\beta + 2\beta Na\uparrow \qquad (1)$$

when the alloy is in contact with the sodium disilicate glass. It should be noted, however, that this conclusion is based on the assumption that the stability of the glassy oxides does not differ significantly from that of their crystalline form.

Chemical analyses of glass exposed to polished Fecralloy revealed the presence of aluminium and some iron and chromium. The concentrations of aluminium were particularly large near the workpiece interfaces but iron was more uniformly distributed in accord with the observation by Tomsia [14] that the fabrication of a uniform glass by unstirred melting is easy for the Na_2O–SiO_2–Fe_2O_3 system. The yellow coloration assumed by the glass exposed at 900 to 1000° C suggests that the iron was present as Fe^{3+} ions, and therefore that some of the weight loss was due to reactions forming $Fe_2O_3(gl)$. Glass exposed at 1100° C was pale green, suggesting that Cr^{3+} ions were present and that the reactions forming $Cr_2O_3(gl)$ occurred. However, the dominant reaction revealed by the glass analyses was with aluminium:

$$2Al + 3Na_2O(g) \rightarrow Al_2O_3(gl) + 6Na\uparrow \qquad (2)$$

which will have played the major role in causing the weight losses, and those reported in Table I can be related reasonably well to at least the 900 and 1000° C glass contamination data cited in Table II by assuming the losses to be due to redox reactions producing sesquioxides.

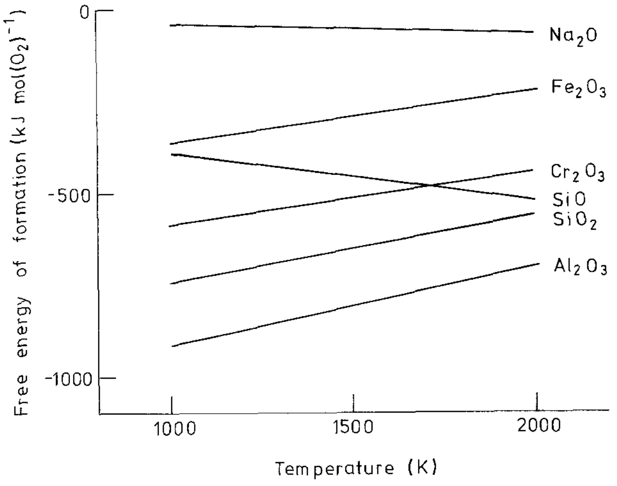

Figure 4 Thermodynamic stability of oxides potentially relevant to Fecralloy–glass interactions.

The Fecralloy blanks and the glass itself also suffered weight losses and it may be worthwhile commenting on these effects, even though they are not of major importance. For example, the weight losses experienced by the blank samples increased with temperature in good accord with the vapour pressure of chromium [15], although the actual losses were several times less than that theoretically achievable with the pure clean metal, possibly due to the presence of a thin oxide film on the alloy surfaces. In contrast, the weight losses of the glass were greater than could be accounted for by simple vaporization [12] and may have been enhanced by the loss of retained water, which would also account for the degassing effects observed at 750 to 850° C.

The behaviour of the glass with oxidized polished substrates differed from that discussed above, principally in terms of bonding and wettability. Thus, while all the drops remained uncracked and adherent on polished substrates, on which stable profiles and unchanging contact angles had been assumed, they separated from the oxidized workpieces except when a hold temperature of 1100° C was used and a stable, completely wetting configuration was achieved. An even more obvious difference was the enhanced wettability on the oxidized substrates that approached perfection when contact times were prolonged (Table I and Fig. 3). These substrates were coated with substantial alumina films as compared to the thin iron oxide present on polished workpieces, and the better wetting when contact was first made may reflect the greater ionicity of Al–O as compared to Fe–O bonds [16, 17] and hence the easier achievement of a low-energy interface with an ionic glass melt. The alumina films were still intact after exposure to the glass at even the highest temperature, and hence the contact angle decreases might be due to partial solution of alumina and the establishment of a localized chemical equilibrium. Any such saturation must be very localized since the alumina films were not only intact but unthinned, yet thinning of about a micrometre would be needed to account for the observed aluminium uptakes. An even more important discrepancy is that mere solution cannot account for the observed weight losses, but it can be argued that these were caused by redox reactions with metallic aluminium that had diffused through the alumina to cause vaporization of sodium and establish an equilibrium Al^{3+} activity in the glass. However, while the smaller weight losses and aluminium contamination of the glass in contact with Fecralloy coated with the thicker oxide are consistent with this hypothesis, quantitative proof cannot be offered. Diffusion data for aluminium in alumina are known only for lattice diffusion at 1670 to 1950° C [18], and uncertain extrapolations to temperatures of interest yield estimated rates too slow to account for the weight loss and contamination data, but in practice it is probable that grain-boundary diffusion dominates the mass transport process.

The purpose of the work was to evaluate the applicability of the concepts developed by Pask and his co-workers, and while many details remain obscure the main observations are in accord with their predictions. Thus wetting of the Fecralloy substrates was associated with redox reactions with the Na_2O component of the glass which caused weight losses through sodium evaporation, and bonding was poor unless chemical equilibrium was achieved, as indicated by stable contact angle values. The conclusion that can be drawn from this study, therefore, is that the substantial body of work on simple, model, systems conducted in an attempt to gain fundamental insights is of value in work directed to the exploitation and understanding of technologically important, chemically complex, systems.

Acknowledgements

The bulk of the work described in this report was performed during a visit to the Department of Materials Science and Mineral Engineering, the University of California, Berkeley, and thanks are given for the advice and help of many faculty members, particularly Professor J. A. Pask and Dr A. P. Tomsia. Thanks are also due to Dr D. Sewell and Mr A. G. Morton of A.E.R.E., Harwell, for their chemical analyses.

References

1. J. A. PASK and R. M. FULRATH, *J. Amer. Ceram. Soc.* **45** (1962) 592.
2. J. A. PASK, in "Modern Aspects of the Vitreous State", Vol. 3, edited by J. D. McKenzie (Butterworths, London, 1964) p. 1.
3. J. A. PASK and M. P. BOROM, "Physical Chemistry of Glass–Metal Interfaces", UCRL-118/6 REV (University of California, 1965).
4. B. W. KING, H. P. TRIPP and W. H. DUCKWORTH, *J. Amer. Ceram. Soc.* **42** (1959) 504.
5. V. K. BHAT and C. R. MANNING, *ibid.* **56** (1973) 455.
6. L. H. VAN VLACK, *Metals. Eng. Q.* (Nov. 1965) 7.
7. J. V. SMITH and S. W. BAILEY, *Acta Crystallogr.* **16** (1963) 801.
8. R. W. JONES, *Fortschr. Deutschen Keramischen Gesellschaft* **1** (1985) 99.
9. A. P. TOMSIA and J. A. PASK, *J. Amer. Ceram. Soc.* **69** (1981) 523.
10. R. HULTGREN, P. D. DESAI and D. T. HAWKINS, "Selected Value of Thermodynamic Properties of Binary Alloys" (ASM, Metals Park, Ohio, 1973).
11. C. T. LYNCH (ed.), "Handbook of Materials Science", Vol. 2 (CRC Press, Cleveland, 1975) p. 339.
12. O. V. MAZURIN, M. V. STRELTSINA and T. P. SHVAIKO-SHVAIKOVSKAYA, "Handbook of Glass Data, Part A" (Elsevier, 1983) p. 169.
13. A. P. TOMSIA, Z. FEIPENG and J. A. PASK, *Bull. Amer. Ceram. Soc.* **63** (3) (1984) 473.
14. A. P. TOMSIA, private communication (1984).
15. E. A. BRANDES (ed.), "Metals Reference Book", 6th Edn (Butterworths, London, 1983) p. 8.
16. L. PAULING, "The Nature of the Chemical Bond" 2nd edn. (Cornell University Press, 1939) p. 98.
17. H. O. PRITCHARD and H. A. S. KINNER, *Chem. Rev.* **55** (1955) 745.
18. A. E. PALADINO and W. D. KINGERY, *Chem. Phys.* **37** (1962) 957.

Received 14 October
and accepted 21 November 1985