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TECHNICAL NOTE

A microscopic examination of Ti-doped Fe_2O_3–glass coatings on mild steel

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1. Introduction

Previous work by Johnson and Tseung [1, 2] showed that a 3 at% Ti-doped Fe_2O_3–glass coating on mild steel was of potential interest as an inexpensive, corrosion-resistant and conducting chlorine anode. The main problem was the presence of some open porosity (about 0·5%) in the coating and this could not afford complete protection of the mild steel substrate. This note presents some preliminary results on the microstructure of glass coatings and their interaction with the mild steel substrate.

The solid-state reaction between glass and mild steel is now considered. Previous work [3] on the adhesion of enamel coatings to mild steel showed that maximum metal–coating adherence was achieved when the interface was saturated with the oxide of the lowest valency cation of the substrate metal. In this case, the oxide is FeO and the lowest valency cation Fe^{2+}. Thus, we would expect to find a thin layer of FeO at the glass Fe_2O_3–metal interface as a result of the reaction:

$$Fe + Fe_2O_3 = 3FeO$$

Since the solubility limits of FeO, Fe_3O_4 and Fe_2O_3 in glass are 42, 23 and 19 wt%, respectively [3], the coating would consist of iron oxide phases (FeO and semiconducting Ti-doped Fe_2O_3) as well as a glass phase containing dissolved iron oxides.

Ideally, the microstructure would comprise a maximum amount of continuous, semiconducting Ti-doped Fe_2O_3 and a minimum amount of continuous glassy phase containing dissolved iron oxides to ensure that the coating porosity is reduced to a minimum, without interconnecting pores. This is more likely to be achieved if the volume fraction of Fe_2O_3 (after allowing for Fe_2O_3 dissolution in the glassy matrix) is higher than the volume fraction of the glassy phase. Therefore, the concentration of glass in the coating was limited to 30 wt% (density of glass = 2·46 g cm^{-3}; density of Fe_2O_3 = 5·24 g cm^{-3}).

2. Experimental

The Fe_2O_3–glass mixture was prepared by the method used in earlier work [1]. Three coating compositions were investigated – 10, 20 and 30 wt% glass. The coatings were applied uniformly onto the surfaces of mild steel sheet or 40 mesh mild steel screen, either by powder compaction or painting on a toluene/paraffin wax slurry. Firing of electrodes was carried out under a nitrogen atmosphere at various temperatures and for different times. For phase identification, both optical and EDAX techniques were used. Optical activity is expected for the anisotropic Fe_2O_3-rich phase, but not expected for the isotropic glass.

3. Results and discussion

Fig. 1 gives the interfacial microstructure of 10 wt% glass–oxide powder, pressed onto steel sheet and heated for 2 h at 1290° C. Between the metal and the bulk coating, there was a thin grey layer which was Ti- and Fe-rich (consequently electrically conducting). Using the same heat treatment, 40 mesh screen was encapsulated but the iron underwent massive dissolution at this temperature, as shown in Fig. 2.

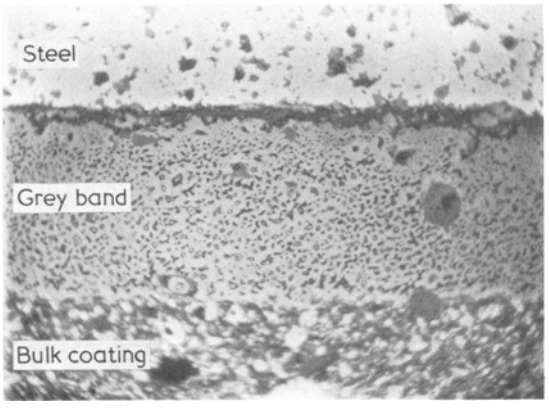

Fig. 1. Interfacial region of 10 wt% glass coating on mild steel sheet, heated for 2 h at 1290° C (× 127).

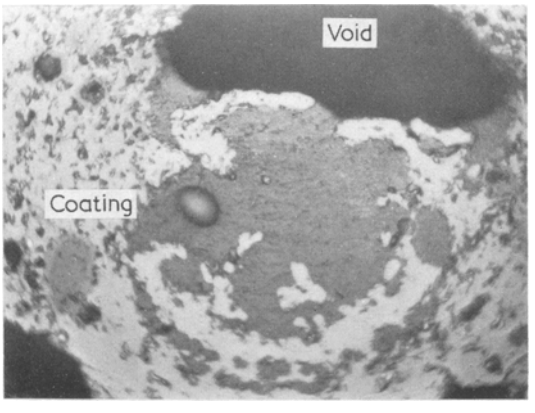

Fig. 2. Interfacial region of 10 wt% glass coating on 40 mesh mild steel screen, heated for 2 h at 1290° C (× 127).

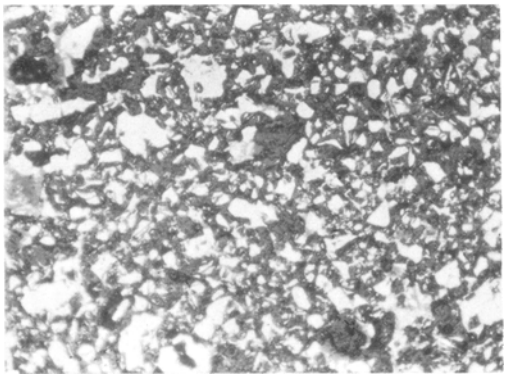

Fig. 3. Detail of 10 wt% glass coating microstructure away from interface, heated for 2 h at 1290° C (× 260).

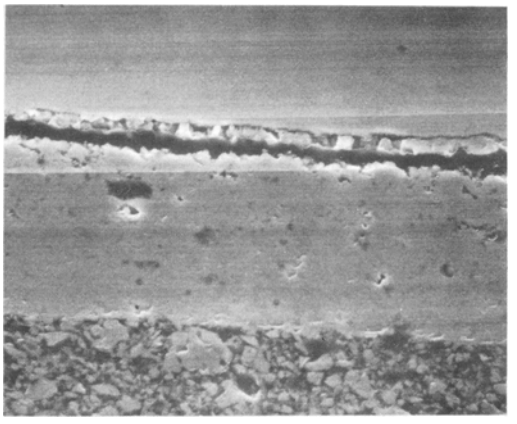

Fig. 4. Scanning electron picture of interface in Fig. 1 (60 kV, × 124).

Fig. 5. Interfacial region of 20 wt% glass coating painted on 40 mesh mild steel screen and heated for 1 h at 1200° C (× 170).

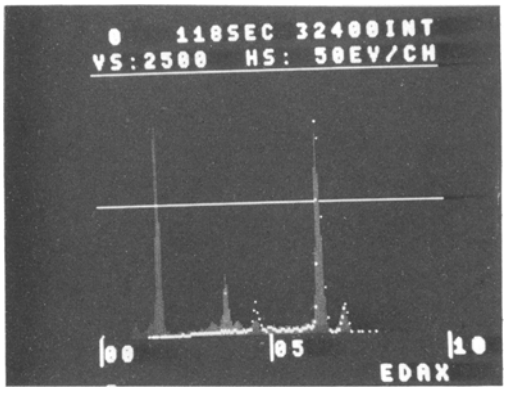

Fig. 6. EDAX analysis of 20 wt% glass coating away from interface. Dotted portion, oxide phase; line portion, glassy phase.

A more detailed micrograph of the coating is given in Fig. 3, the volume fractions of oxide: glass being 73:27 (light and dark phases, respectively). Iron dissolution was greatly reduced when heating was carried out at 1200° C for 1 h. Fig. 4 is a 60 kV scanning electron picture of a 40 mesh specimen. EDAX analysis on the grey edge above the void just outside the wire showed the presence of Fe and Ti. It is relevant to note that an electrically-conducting (Fe-, Ti-rich) filament made contact between the wire and coating.

Fig. 5 shows the interfacial region of a 20 wt% glass coated on a 40 mesh screen electrode by heating for 1 h at 1200° C. At least 50 vol.% of this region comprised conducting oxide (light phase), thus giving a potentially high conductivity electrode.

The coating remote from the interface was examined by EDAX. The minor (dark) glass phase gave the following analysis ratio – Na: 150, Si:200, K:75, Ca:500, Ti:75, Fe:1900, as shown in Fig. 6. The major (light) oxide phase contained iron and titanium only, in the ratio Fe:Ti, 2000: 300.

The interfacial region of a 30 wt% glass coating on sheet steel is given in Fig. 7. Despite the fact that the bulk coating has a resistivity of 1 Ωm [1], the morphology of the interface shows a large vol.% of glassy (non-conducting, dark) phase in direct contact with the metal substrate, generally undesirable for high conductivity applications. A scanning electron picture (Fig. 8) shows the dark glassy phase entirely surrounding the metal, away from which are the oxide (conducting) islands.

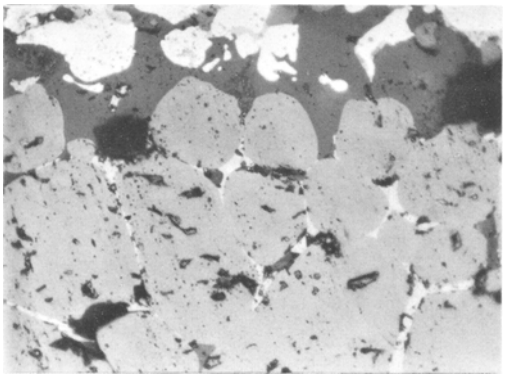

Fig. 7. Interfacial region of 30 wt% glass coating painted on mild steel. Heated for 1 h at 1200° C (× 270).

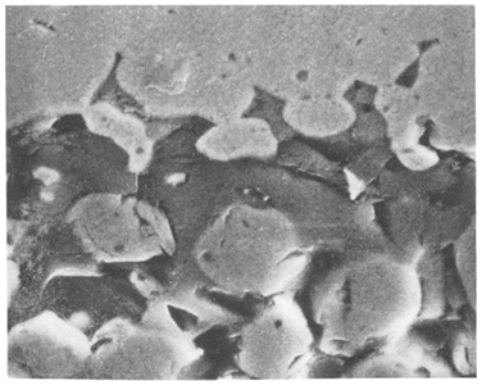

Fig. 8. Scanning electron picture as Fig. 7 (× 210).

4. Conclusions

Microstructural studies indicated that for the 10 and 20 wt% glass coatings, a thin dense conducting layer of iron oxide containing titanium was formed at the metal–coating interface. In the case of the 30 wt% glass coating, however, an insulating layer surrounded the metal, which is an undesirable situation.

Analysis of the coating composition has been useful as this, together with conductivity and corrosion studies, may provide the key to the success of the semiconducting oxide–glass coating concept.

Acknowledgement

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References

[1] A. S. W. Johnson and A. C. C. Tseung, UK Patent No. 1448989.
[2] *Idem, J. Appl. Electrochem.* 7 (1977) 445.
[3] B. W. King, H. P. Trip and W. H. Duckworth, *J. Amer. Ceram. Soc.* **42** (1959) 504.