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Interface chemistry and bonding strength for diffusion-bonded Fe/Fe–FeO/Al_2O_3 systems

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The samples for this study were made by oxidizing the interface region of an Fe/Al_2O_3 system containing either wüstite or Fe–FeO composite (I) as interlayer. The bonded materials of Fe/FeO/Al_2O_3 and Fe/I/Al_2O_3 were prepared by hot-pressing. For analysis of the boundary region electron probe microanalysis (EPMA), transmission electron microscopy and X-ray diffraction were used; at the FeO/Al_2O_3 and I/Al_2O_3 interfaces a newly formed reaction layer of about 6 μm in thickness containing iron, aluminium and oxygen could be identified, but EPMA failed to reveal the Fe/FeO interface. Therefore, the interface of iron single crystals with FeO scale was investigated by Auger electron spectroscopy and X-ray photoelectron spectroscopy, and at the Fe/FeO interface formation of a transition layer with a thickness of several hundred nanometres was observed. Through the Fe/I interface, interdiffusion of iron occured. Fe/I/Fe and Al_2O_3/I/Al_2O_3 bonded materials had tensile strengths of 150 and 130 MPa, respectively, when an interlayer of Fe–25 mol% FeO was applied between both bonding pairs.

1. Introduction

The metal–ceramic bonded materials draw wide interest as new materials which possess both the reliability of metals as well as the resistance against heat, wear and corrosion of ceramics. Depending on the materials to be bonded, different bonding methods like the active metal method [1], the metallizing method [2] and hot isostatic pressing (HIP) [3] have already been proposed. In this paper we report another, newly developed bonding method for the iron and Al_2O_3 bonding pair, and some results on the interface chemistry and the tensile strength of this bonding pair.

It is well known that in the progress of the high-temperature oxidation of iron, a wüstite layer is first formed on the iron metal, then magnetite, and at last haematite exposed to the oxidizing atmosphere. It is also a well-known fact that the thicker the wüstite layer becomes, the stronger the scale that can be formed.

On the other hand, from the phase diagram of the alumina system, it can be seen that alumina can easily form a complete oxide with other oxides. Therefore, a good solid-state bonding can be expected between iron and alumina, if wüstite is inserted between them.

2. Experimental details

2.1. Materials

The base metal was pure iron, and alumina was prepared by hot-pressing alumina powder of 99.99% purity. Wüstite for interlayers was made by the reduction of haematite. According to the X-ray diffraction, this wüstite contains traces of iron. These materials, as Fig. 1 shows, are stacked on the carbon dies. Fabrication of the bonded materials of iron and alumina was carried out by hot-pressing at about 1450 K for 36 ksec in a vacuum of 10^{-3} Pa under a pressure of 29.3 MPa. For tensile strength measurements, the specimens of bonded materials Fe/FeO/Fe and Al_2O_3/FeO/Al_2O_3 were prepared by hot-pressing. To prove the effect of FeO content on the bonding strength, the fraction of FeO in the interlayer of the Fe–FeO system was varied.

The samples for this study were made by oxidizing (0 0 1) iron single crystals at 1120 K in wet hydrogen with a dew point of 350 K. After the FeO scale was formed on the iron crystal, it was rapidly cooled, so that no magnetite could be formed on the FeO layer. The FeO layer on the iron crystal was found to be oriented such that the (0 0 1) plane of iron was parallel to the (0 0 1) plane of FeO, and the [1 1 0] direction of iron corresponded to the [2 0 0] of FeO.

2.2. Measurements

The bonded material Fe/FeO/Al_2O_3 was cut through perpendicular to the bonding interface, and subsequently the boundary region was analysed by electron probe microanalysis (EPMA). Fig. 2 is an SEM image showing the interface between iron and wüstite (Fe/FeO). Obviously no trace of a reaction layer can be detected, and the bonding effect between iron and wüstite was proved to be good. The structure of the boundary region between the reaction layer and the wüstite interlayer was studied in a transmission electron microscope (TEM).

EPMA was not able to resolve the iron–wüstite interface of the bonding materials, and for further investigation Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used. Samples for this investigation were prepared by oxidizing the iron single crystals with the surface parallel to the (0 0 1) plane. AES and XPS analysis and

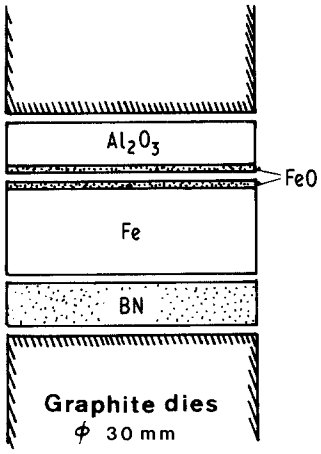

Figure 1 Schematic representation of a sandwich Fe/FeO/Al_2O_3 specimen prepared in graphite dies by hot-pressing.

argon etching were carried out successively from the top of the scale surface to the iron base metal.

The mechanical properties of the transition layer at the Fe/FeO interface and the new reaction layer at the FeO/Al_2O_3 interface were investigated. For tensile strength measurements, specimens of bonded materials Fe/FeO/Fe and Al_2O_3/FeO/Al_2O_3 were prepared by hot-pressing. It was found that all specimens were broken not at the interface, but at the brittle wüstite region within the interlayer.

Therefore, it is necessary to improve the brittle nature of the interlayer material. For this purpose dual-phased composite material with a different FeO content, that is, the Fe–FeO system instead of the wüstite single phase, was investigated.

3. Results and discussion

3.1. Interface chemistry

3.1.1. Fe/FeO/Al_2O_3 system

In Fig. 3 at the wüstite/alumina (FeO/Al_2O_3) interface, there is to be seen a newly formed reaction layer which is of about 6 μ thick and contains iron, aluminium and oxygen. It was proved that this reaction layer contributes to the bonding of wüstite and alumina.

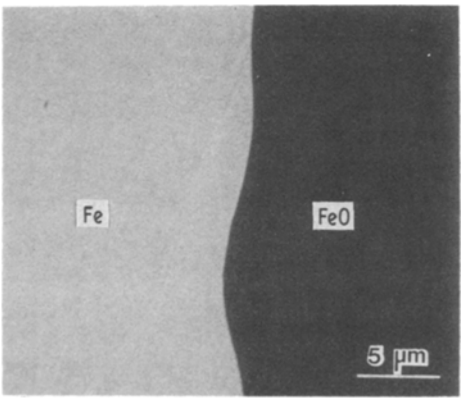

Figure 2 SEM (back-scattering mode) micrograph at the Fe/FeO boundary region.

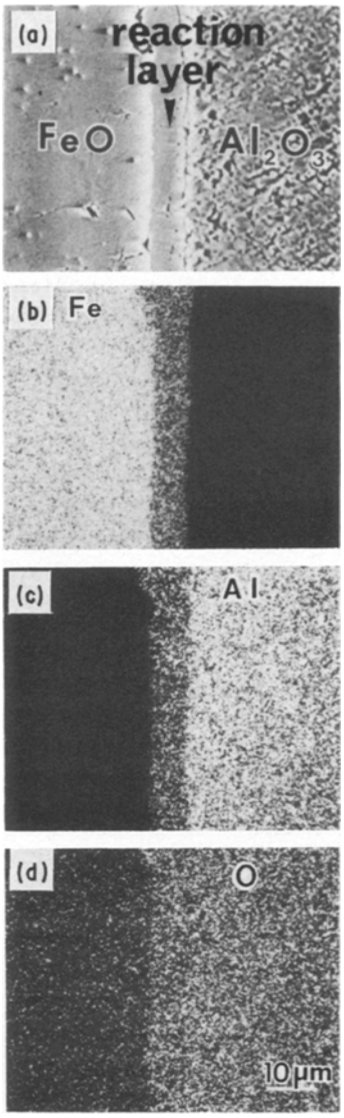

Figure 3 SEM and X-ray image micrographs for the FeO/Al_2O_3 boundary region: (a) SEM, (b) iron, (c) aluminium and (d) oxygen.

Fig. 4 shows a TEM image as well as diffraction patterns. In Figs 4a and b, arrow 1 indicates the reaction layer, arrow 2 the boundary region and arrow 3 the wüstite region. Correspondingly, the first diffraction pattern of Fig. 4c, taken from the area of arrow 1, indicates only a halo pattern, the second one a mixture of the halo and diffraction spots. The third pattern shows only spots from a wüstite crystal. To study the structure of the reaction layer, the X-ray diffraction pattern was taken and it could be interpreted as a mixture of the broad reflection from the spinel structure with the lattice parameter 0.8171 nm and the very weak reflection from aluminium oxide solid solution. The value of this parameter is slightly larger than that of $FeAl_2O_4$ spinel structure, that is 0.8119 nm. Referring to the phase diagram, it can be assumed that the reaction layer has the structure of $Fe(Fe, Al)_2O_4$. Taking the results of the electron diffraction and the X-ray analysis into account, it can be concluded that the reaction layer is composed of microcrystals with a predominant spinel structure $Fe(Fe, Al)_2O_4$.

3.1.2. AES and XPS analysis of the scale on the iron crystal

Fig. 5 shows the results of AES and XPS. The intensity ratio I_O/I_{Fe} is plotted against the distance from the

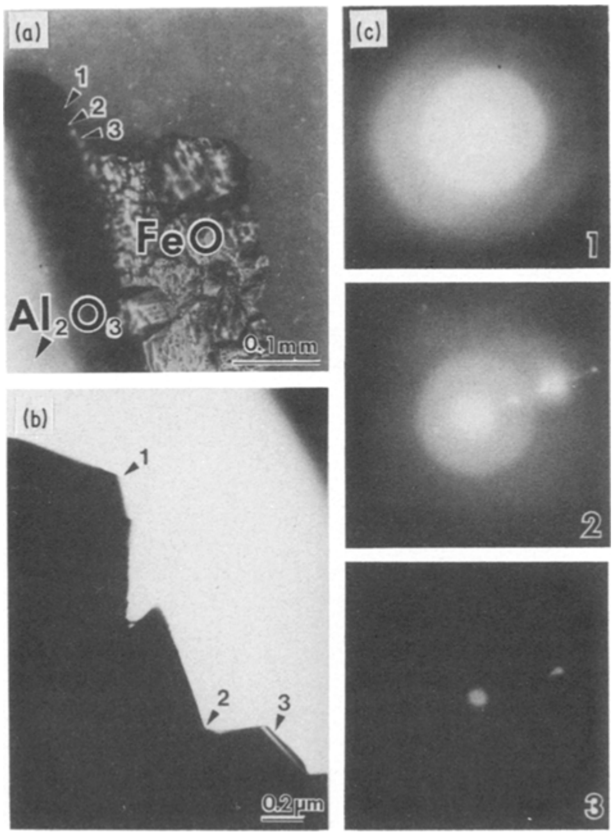

Figure 4 Micrographs and electron diffraction patterns of the Al_2O_3/FeO boundary region. (a) Photomicrograph, (b) TEM and (c) electron diffraction patterns; (1) reaction layer, (2) boundary, (3) FeO.

outer surface of the scale. This intensity ratio was obtained from the AES peak heights of $O_{(510)}$ and $Fe_{(703)}$. The chemical shift ΔE is the difference between the bonding energy of Fe $2p_{3/2}$ and that of the formed scale. This result suggests that a haematite was formed at the outermost surface, under which were magnetite and finally wüstite. Under wüstite, there is a region with a linearly decreasing intensity ratio, and subsequently it decreases exponentially to the value for pure iron. The thickness of the region with the constant linear gradient depends on the thickness of the wüstite layer, and it will be called the transition layer and denoted by T. The transition layer is about 190 nm thick and plays an essential role in the bonding of iron and wüstite.

3.1.3. Fe/Fe–FeO/Al_2O_3 systems

EPMA photographs in Fig. 6 show the distribution of each element around the boundary. The bonding of iron base metal to the composite layer is very good and, as shown in Fig. 6, this arises from the interdiffusion of iron atoms between the base metal and the composite material. On the other hand, at the boundary between the composite layer and the alumina plate, a new reaction layer has been formed. This layer contains iron, aluminium and oxygen, and this is similar to the previous sandwiched specimens which have wüstite as an interlayer. The existence of this reaction layer may contribute to the better bonding.

3.2. Tensile strength

The mechanical strength of the interface was studied as a function of compositional changes in the Fe–FeO system. The tensile strength of hot-pressed sandwiches is shown in Fig. 7. In the case of Fe/I/Fe, with increase of FeO ratio in the composite interlayer (I) the strength decreases very rapidly, until a constant value of about 100 MPa between 50 and 80 mol % FeO is reached. In the case of $Al_2O_3/I/Al_2O_3$ the strength is much lower, and of about 10 MPa at about 10 mol % FeO. For this composition, no more FeO in the composite interlayer could be detected after hot-pressing. This fact suggests that one-way diffusion of iron and oxygen ions occurs from the wüstite phase into the alumina side. Then the strength is raised up to the maximum strength of about 130 MPa at 25 mol % FeO and then it drops down to a constant value of about 80 MPa between 40 and 80 mol %. On the other hand, the tensile strength of the interlayer itself depends on the FeO content and shows similar

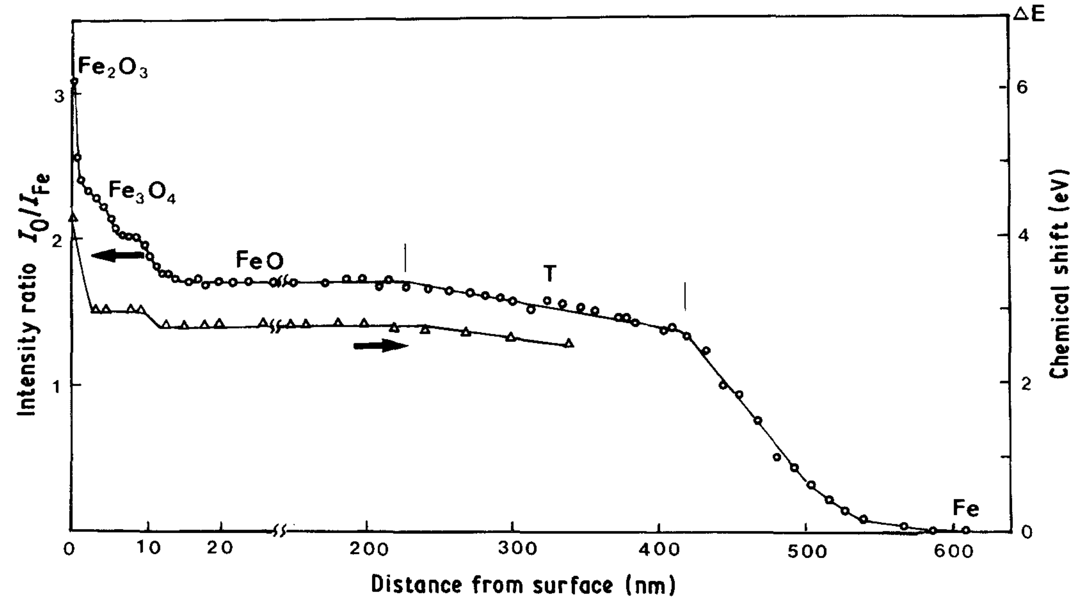

Figure 5 Ratio of the Auger peak heights $I_{O(510)}/I_{Fe(703)}$ and the chemical shifts ΔE of Fe ($2p_{3/2}$) in relation to the distance from the surface of oxidized iron. T = transition layer.

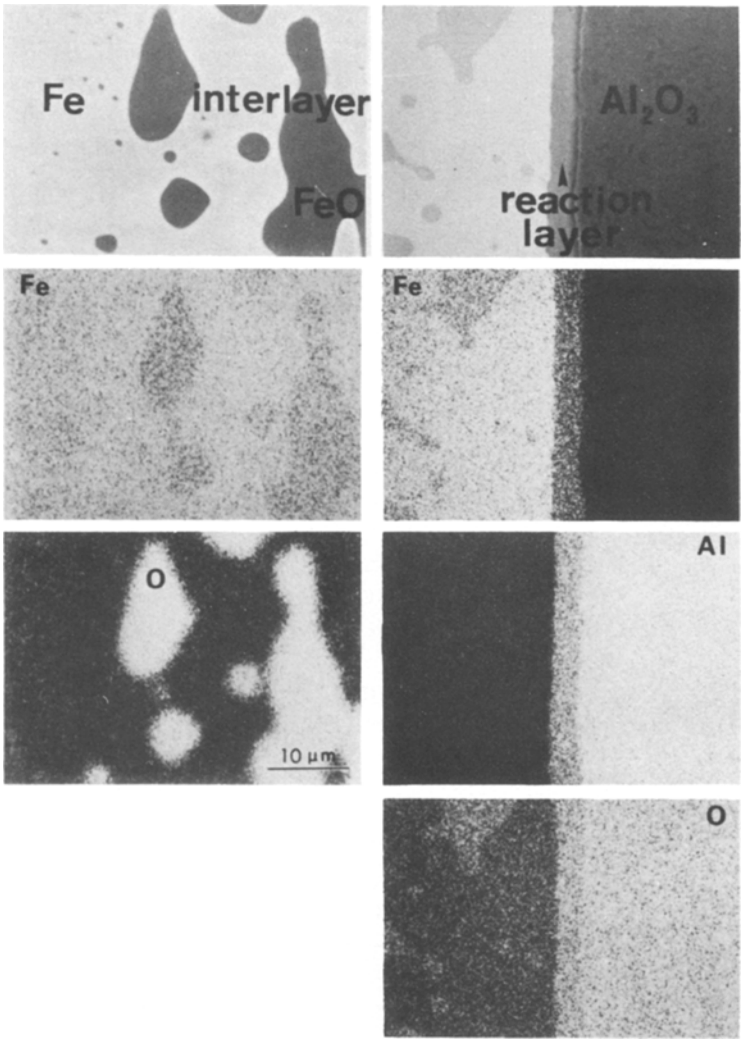

Figure 6 SEM and X-ray image micrographs for the boundary region of Fe/Fe–FeO/Al_2O_3 with a composite interlayer Fe–25 mol % FeO.

behaviour to the one observed in the Fe–FeO composite materials.

4. Conclusion

In specimens with a composite interlayer, fracture occurred in the first place within the composite material along the Fe/FeO interface. However, the strength of the Fe/FeO interface depends on the ratio of iron to wüstite in the composite material. It is possible to give more ductility to the interlayer by making a composite of iron and wüstite. The strength at 25 mol % FeO falls between 150 and 130 MPa and this is the optimum content of FeO in the interlayer of the Fe/I/Al_2O_3 bonded materials.

The mechanism of the solid-state bonding can be summarized as follows: the first stage is the

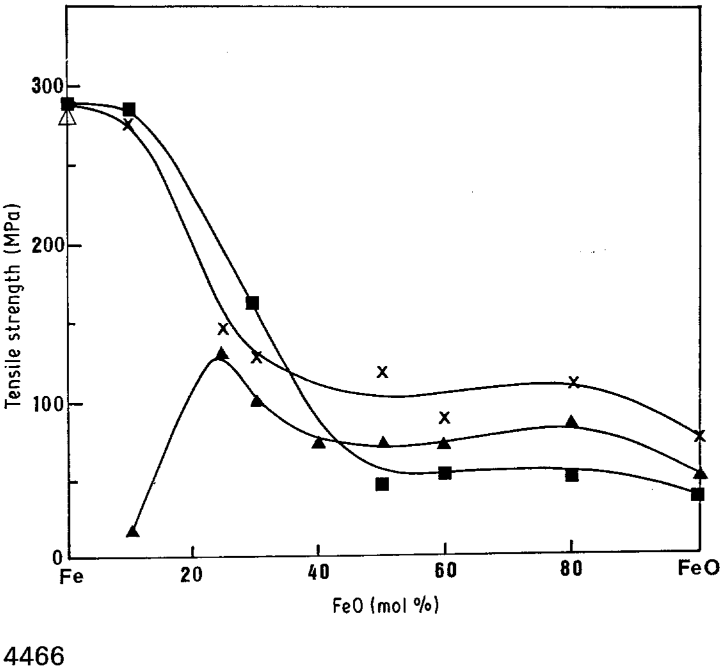

Figure 7 Composition dependence of tensile strength: (x) Fe/Fe–FeO/Fe, (▲) Al_2O_3/Fe–FeO/Al_2O_3 and (■) composite materials Fe–FeO.

interdiffusion of iron at the Fe/I interface, the second the formation of a transition layer with a thickness of several hundred nanometres at the Fe/FeO interface in the interlayer composite material, and the third stage the appearance of a reaction layer about 6 μm thick at the I/Al_2O_3 interface.

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