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Observations of a Metal-Oxide Interface

THE partial spalling that occurs when a metal is cooled after high temperature oxidation has made it possible to make direct observations of the metal-oxide interface. Scanning electron microscopy, with its large depth of focus and perspective view, has permitted this interface to be studied at high magnification in the centre of specimens away from the edges.

A high purity iron-chromium binary alloy (Cr 28 per cent) was oxidized in pure oxygen at atmospheric pressure for 6 h at 950°C. The surface was prepared before oxidation by mechanical polishing, electropolishing and brief cathodic etching. The oxide formed was chromic oxide with a small percentage of iron present, as reported by Wood and Whittle¹. On cooling after oxidation, spalling was first observed at temperatures less than 500°C, occurring violently at alloy grain boundaries, as reported previously by Howes². More extensive spalling occurred as room temperature was approached. The spalling is due to the differential contraction between the oxide and the alloy, and the broken oxide faces examined indicated brittle fracture rather than plastic deformation.

Fig. 1 shows the structure of the oxide surface, the structure of the oxide through its thickness, the face of the alloy as it existed under the oxide and the structure of the interface between the alloy and oxide. The presence of

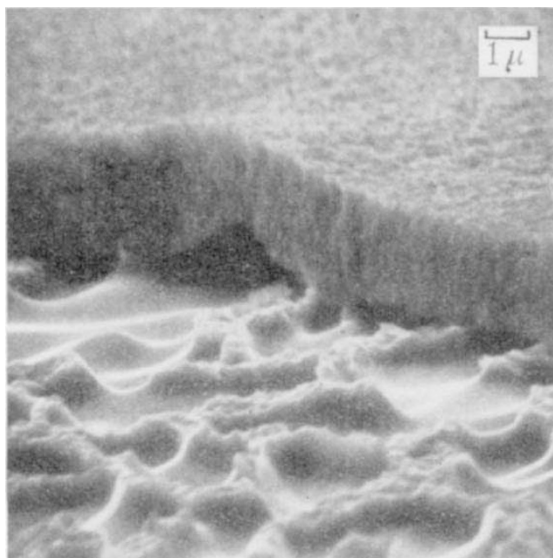


Fig. 1. The broken face of the oxide and the alloy-oxide interface.

voids at the interface is clearly seen, and they explain the corrugated nature of the alloy face—the rough upper levels are regions where contact had been maintained between the oxide and alloy and the smooth depressions are where voids have developed.

This direct evidence of void formation at the interface verifies the outward diffusion of chromium involved in the oxidation mechanism. The considerable reduction, however, in the contact area between the oxide and alloy raises questions of how the chromium then enters the oxide, and the significance of weight gain kinetic data. It seems probable that as contact diminishes, chromium transport across the voids after evaporation, or by surface diffusion around the voids, becomes appreciable.

This investigation is continuing and will be reported more fully elsewhere.

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Tetragonal and Hexagonal Iron-Manganese Carbides

DURING recent studies of the iron-manganese-carbon system, specimens, each weighing approximately 5 g, were carefully prepared according to predetermined compositions. The components were 500-mesh powders of 99.995 per cent pure iron and spectroscopically pure carbon and a 200-mesh powder of 99.995 per cent pure manganese. The component powders were intimately mixed by shaking, then each specimen was packed into a pure alumina crucible the end of which was closed, but not sealed, with high purity alumina cement. Each specimen was then sintered at 960°C for 110 h in a silica capsule containing helium at approximately 0.25 at m. (such time having been previously found sufficient for equilibrium to be attained¹).

Debye-Scherrer X-ray photographs were taken of at least two samples from different parts of each specimen using a 114.6 mm diam. camera. The exposure time was two hours using filtered chromium radiation, at a tube voltage of 30 kV and a tube current of 10 m.amp. For several of the specimens, it was found that photographs of samples taken from near the end of the specimen were somewhat different from those taken from the main body of the specimen, indicating the presence of composition gradients in the specimen. The presence of such gradients was confirmed by chemical analysis of two different portions of the sample.

Two specimens yielded unusual X-ray powder patterns from the main body of the specimen. The powder patterns did not indicate the presence of free iron or manganese and were not compatible with a pattern which was taken of a specimen the nominal composition by weight of which was 10 per cent iron, 90 per cent manganese (the nominal ratio of iron to manganese in all the specimens), which was prepared under identical conditions to all the other specimens. The patterns could be indexed with the aid of Bunn charts, and the crystal classes of the structures present are shown in Table 1 together with the nominal

Table 1

| Specimen No. | Carbon percentage by weight from analysis | | Nominal carbon percentage by weight | Nominal iron percentage by weight | Nominal manganese percentage by weight | Crystal class of structures present |
|--------------|---|-----------------|-------------------------------------|-----------------------------------|--|-------------------------------------|
| | Determination 1 | Determination 2 | | | | |
| 3 | 4.90 | 5.2 | 6.0 | 9.4 ₆ | 84.6 ₆ | Tetragonal |
| 4 | 5.73 | 4.4 | 6.3 | 9.3 ₇ | 84.3 ₃ | Tetragonal + hexagonal |