Micro/macro observations of a metal/ceramic reaction

It has been known for some time that a surface reaction takes place between the noble metals and a number of refractory oxides, and that this reaction can be utilized in the formation of practical, macroscopic metal–ceramic bonds [1, 2]. The direct evidence for the reaction derives from observations at magnifications of the order of ×250 000 in the transmission electron microscope (TEM). It is the purpose of this comunication to relate the microscopic and the macroscropic observations and thereby to obtain approximate analyses of the cation concentration in the reaction zone.

In the first set of experiments, crushed single crystals of MgO were heated to the appropriate temperature in the TEM, and the formation of the characteristic reaction "necks" (by reaction between the MgO and the metal of the specimen grid) was observed directly. The crystalline fragments used were very large compared to the smoke cubes used in previous observations [3, 4], and the reaction rate was seen to approach zero, in agreement with macroscopic observations [5, 6]. The furnace grids were then transferred to a scanning electron microscope (SEM) and it was found that reaction zones could be identified by their characteristic shape (Fig. 1 and 2). It was thus possible to carry out X-ray microprobe analysis on the reaction zone itself. The SEM was operated at an accelerating voltage of 16 keV. This low electron energy, combined with the particularly favourable orientation of the reaction zone with respect to the palladium metal grid and the X-ray detector, allowed very high spatial resolution for X-ray maps of palladium ($L\alpha, L\beta$, 2.84, 2.99 keV) and magnesium ($K\alpha, K\beta$, 1.25, 1.29 keV). In Fig. 3 the resolution of the X-ray maps appears to be 0.1 μm, i.e. about one-tenth of the diameter of the neck joining the MgO crystal to the palladium grid. A point analysis at the centre of this neck showed no significant Mg peak above background, indicating that at least 95% of the cations were Pd. Bremsstrahlung and absorption in the detector window make the detection of the light cation less sensitive.

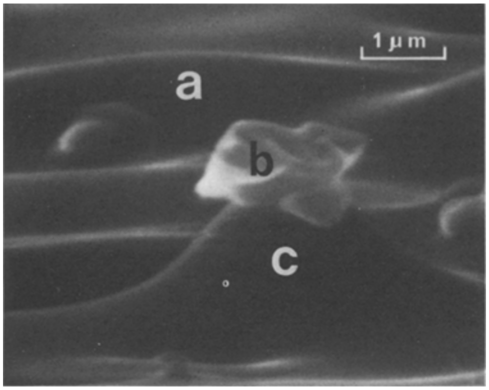

Figure 2 Enlargement of outlined area of Fig. 1 showing palladium grid (a), MgO (b) and reaction zone (c).

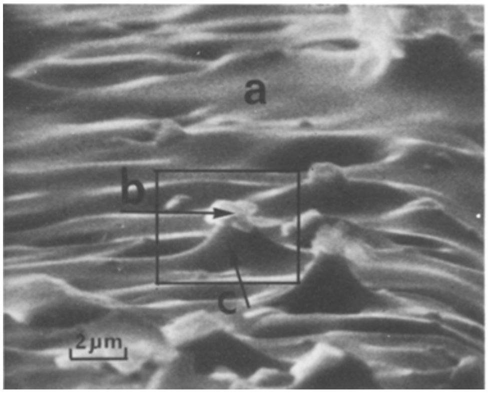

Figure 1 Scanning electron micrograph of a palladium grid (a) which has reacted with MgO (b), thus allowing identification of the "neck"-shaped reaction zones (c). Outlined area is shown enlarged in Fig. 2.

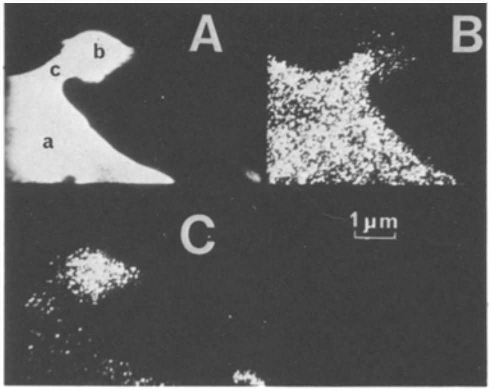

Figure 3 Composite micrograph showing: (A) the electron image of the palladium grid (a), MgO (b) and reaction zone (c); (B) the palladium X-ray image and (C), the magnesium X-ray image. Evidence in (B) indicates that approximately 95% of the cations in the reaction zone are palladium.

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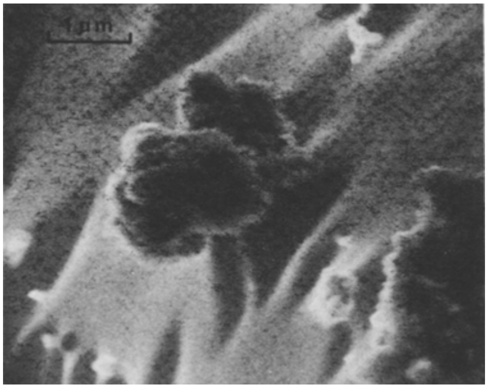

Figure 4 Scanning electron micrograph of the Pt/Al_2O_3 reaction carried out in air. The reaction zone is evident but the oxide has sintered.

In the second set of experiments the reactions were carried out in air, and the specimens then transferred to the SEM. The same characteristic necks were observed, and hence reaction zones could be identified.

Typical results for the Pt/Al_2O_3 reaction are shown in Fig. 4, where the ceramic is commercial Linde B. The images show an important practical feature, namely that the Al_2O_3 begins to sinter throughout the reaction. The combined sintering-metal/ceramic reaction has been observed directly in the TEM at high magnification, and will be reported in detail elsewhere.

References

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