Letters

The grain boundary of $SrTiO_3$ boundary layer capacitor material

To explain the properties of capacitor materials of the boundary layer (BL) type a so-called two-layer model has been developed [1]. In this model it is proposed that the semiconducting matrix grains are separated by an insulating double layer. This double layer is assumed to be composed of a layer of oxidized matrix material and a second-phase layer. Recently, a series of new BL capacitor materials has been described [2]. By means of transmission electron microscopy we have investigated one of these new materials. The material investigated consists of a $SrTiO_3$ matrix into which Bi_2O_3 is diffused during a second firing step.

The samples, thinned by a mechanical lapping process ending with a syton polish step, were studied in a 120 kV transmission electron microscope (a Philips EM 400 machine) fitted with an energy dispersive X-ray spectrometer (EDAX). As observed for other ceramics (e.g. MnZn ferrite [3] and Sr-hexaferrite [4]), most of the intergranular phase, s, was shown to be located at the multiple grain junctions. By means of the dark-field imaging technique, it was found that most of the planar grain boundaries contained a very thin, generally amorphous, Bi-rich secondary phase.

In contrast with previously stated thicknesses of a few hundreds of nanometers for other BL capacitor materials [1], the thickness of the

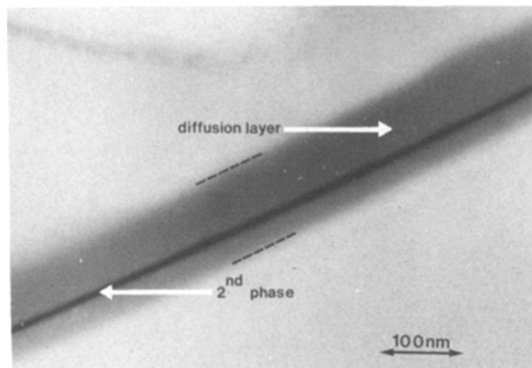

Figure 1 Bright-field electron micrograph of two grains separated by a secondary liquid-phase layer. The dark bands surrounding each grain, i.e. the diffusion layer, are indicated.

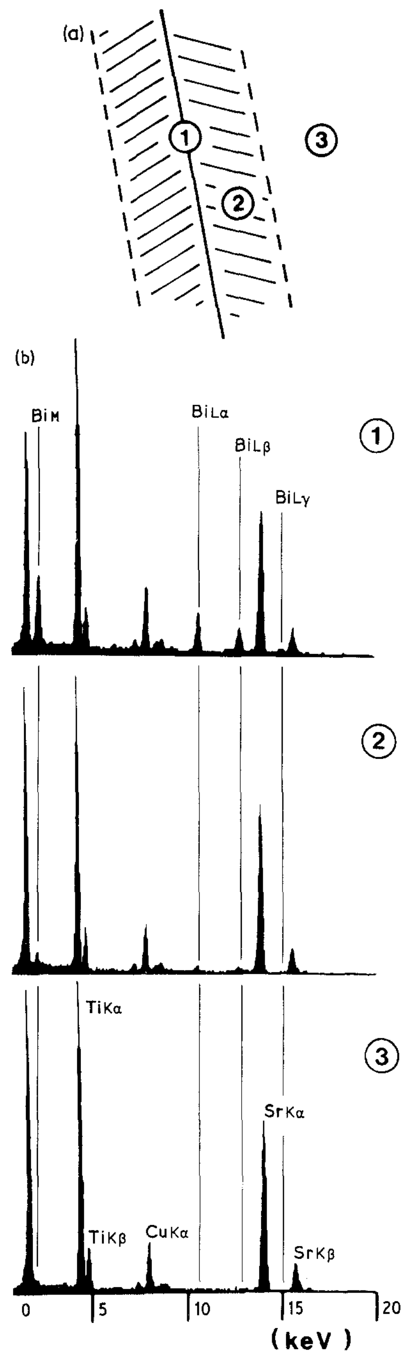

Figure 2 EDAX spectrum taken from three regions in the boundary layer. (a) Diagram of the boundary layer showing the regions from which the spectrum were taken (b) Region 1, EDAX spectrum of the grain-broundary region with the secondary Bi-rich phase; Region 2, EDAX spectrum of the Bi diffusion layer; Region 3, EDAX spectrum inside the $SrTiO_3$ grains; (spot size = 40 nm).

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secondary phase in the material investigated in this work was found to vary from 10 to 50 nm (Fig. 1).

Moreover, transmission electron microscope (TEM) observations revealed that each grain was surrounded by a dark band (Fig. 1), The dark area persisted when the objective aperture was removed. This indicated that the band is caused by absorption, which can be explained by the presence of the heavy element Bi in this region (here called the diffusion layer).

EDAX analysis confirms the presence of Bi (Fig. 2) in this region. After correction of the absorption coefficients, as discussed by Duncumb and Reed [5], the amount of Bi in the diffusion layer is estimated to be less than 2 at%. The width of the diffusion layer is found to vary greatly from boundary to boundary and probably depends on the crystallographic orientation of the grains. Whether, apart from this diffusion layer, another oxidation layer exists, or whether both layers are identical is not clear from the present data. However, it is obvious that the boundary layer model needs some modification, at least in the case of the boundary layer material investigated here.

References

1. S. WAKU, A. NISHIMURA, T. MURAKAMI, A. YAMAJI, T. EDAHIRO and M. UCHIDATE, *Rev. Elec. Comm. Lab.* **15** (1971) 665.
2. Y. TAKAHASHI, N. YAMAOKA, Y. YAMAOKA and S. KAKUBARI, Intergranular insulation-type polycrystalline ceramic semiconductive composition, US patent Number 3,933,688 (1976).
3. P. E. C. FRANKEN and W. T. STACY, *J. Amer. Ceram. Soc.* **63** (1980) 315.
4. F. KOOLS, M. KLERK, P. E. C. FRANKEN, F. J. A. den BROEDER and F. HABERY, *Sci. Ceram.* **10** (1980) 349.
5. P.DUNCUMB and S. J. B. REED, Proceedings of the Seminar on Quantitative Electron Probe Microanalysis, National Bureau of Standards, Washington D.C., 1967 NBS Special Publication Number 298 (National Bureau of Standards, Washington D.C. 1968).

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On the existence of initial damage in sheet metal

It is well established that ductile fracture of a material containing second-phase particles occurs by nucleation, growth and coalescence of voids generally associated with inclusions. Some theoretical models try to account for growth of cavities [1, 2], but the parameters controlling the nucleation of cavities during plastic deformation at low temperature ($T \leqslant 0.2 T_f$, T_f corresponding to the melting point) are still being discussed [3].

It is possible that a certain amount of plastic damage due to hot and cold rolling or ingot porosity exists before any plastic deformation of a sheet metal occurs. It could modify the evolution of the damage, suppressing the initial gap due to nucleation, but the existence of such initial damage is still being debated.

In this paper, some metallographic evidence of initial damage in tough pitch copper, 3003 aluminium alloy, aluminium-killed steel and interstitial free steel are noted (these materials are described by Schmitt *et al.* [4], Jalinier *et al.* [5, 6]). The influence of initial damage on the formability of the materials is studied taking into account the kinetics of the growth of the cavities in the metal.

Different experimental methods can be used to determine the amount of damage in a material. Some of these methods were discussed in a previous paper [5]. Most methods (e.g. relative density change measurements, hydrogen diffusion, positron annihilation) only provide information on the relative damage between a plastically deformed sample and an as-received one. An absolute method of determining initial damage is metallographic observation by optical or electron microscopy. The damage existing in the reference sample can be estimated by the measurement of the surface

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