in these cases the pits are triangular in section. The reagent is difficult to calibrate as a dislocation etchant by traditional means, as the garnet has no cleavage plane to allow matching of opposite surfaces, and the absence of low angle boundary T-junctions prevents calibration by measurement of the angular tilt around the point at which the boundaries intersect. However, the etch pits are considered to correspond to dislocations on the basis of the following observations:

(a) the pits line up in arrays typical of dislocation low angle boundaries as shown in fig. 2;
(b) prolonged etching produces an increase in the size of the pits but does not change their density or distribution;
(c) annealing at a temperature of 1500° C for 150 h produces a slight increase in the number of low-angle boundaries which suggest that dislocation movement has occurred.

The etch pit arrays observed in the garnet differ somewhat from those already described for other Czochralski-grown laser materials. For instance extensive arrays of low-angle boundaries are formed in both calcium fluoride and calcium tungstate and dislocations lying along slip bands are also observed [7]. In the present case, few low-angle boundaries are formed and there is no evidence of extensive slip. Crystals sectioned perpendicular to the growth axis, fig. 1, show randomly-distributed groups of dislocations. The same crystals sectioned parallel to the growth axis, fig. 2, show that these groups extend into bands in the direction of growth. These bands correspond to the strained regions described previously [4], where there is an enhanced neodymium incorporation due to the change in habit of the solid/liquid interface during growth from a planar to a cellular form. The growth striations delineating the interface shape can just be discerned in fig. 2.

Acknowledgements

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17 September 1965

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Grain Boundary "Pest" in the Intermetallic Compound NiAl

The "pest" phenomenon – the susceptibility to severe intergranular attack, which in the limit causes complete disintegration of a material – has been observed in a wide variety of intermetallic compounds, particularly silicides, beryllides and aluminides. The conditions under which it occurs are not clear. Westbrook and Wood [1] have shown that intergranular embrittlement in a wide variety of intermetallic compounds is associated with anomalous grain boundary hardening effects, resulting from the segregation of gaseous contaminants to the boundaries. Grain boundary hardening was only observed in compounds containing more than the stoichiometric proportion of the electropositive component. In a detailed study of NiGa, Seybolt and Westbrook [2] concluded that the hardening was due to the presence of dissolved oxygen, and they suggested that the hardening mechanisms might involve the lattice distortion produced by the formation of a Ga–O complex, e.g. an oxide, a sub-oxide or a cluster of oxygen atoms. Thus grain boundary hardening, which seems to be a necessary condition for the occurrence of the pest, can only be accounted for in a very tentative manner and, to date, no suggestions for a pest mechanism have been published. The purpose of this letter is to propose a mechanism for the pest which is based on some of the results of an investigation of the compound NiAl.

Specimens of NiAl containing 54 at. % Al, i.e. excess of Al, the electropositive component, were prepared from extruded rod supplied by the International Nickel Co (Mond) Ltd. NiAl is known to be very resistant to oxidation at temperatures below about 1100° C, but annealing in air for 2 h at 1400° C produced a white powdery deposit on the surface of the samples which was optically active under polarised light. Using an X-ray powder method, the deposit was shown to be predominantly α-Al_2O_3. Micro-hardness traverses, similar to those used by other investigators [1, 2], on the oxidised surfaces of these samples and on surfaces freshly prepared by mechanical polishing did not reveal any grain boundary hardening. However, upon subsequent annealing in air at 800° C and mechanical polishing, hardening effects were found which were similar in character and magnitude to those observed in NiAl by Westbrook and Wood [1]. (From the experiments carried out to date, it would seem that an anneal in air at an elevated temperature, about 1400° C, is an essential prerequisite for the occurrence of the pest.) Metallographic studies revealed the presence of precipitates predominantly at the grain boundaries and also, occasionally, within the grains; a typical example is shown in fig. 1. These precipitates are inactive under polarised light and have a micro-hardness of about 2000 kg/mm^2. Preliminary electron microprobe traces across the precipitates have shown that they contain considerably more Al than the bulk specimen. This information suggests that the precipitates are of the sub-oxide Al_2O, a conclusion which is supported by the X-ray investigation of Hoch and Johnston [3], who established that when Al and α-Al_2O_3 were heated together a cubic phase of composition Al_2O was produced which was unstable at room temperature.

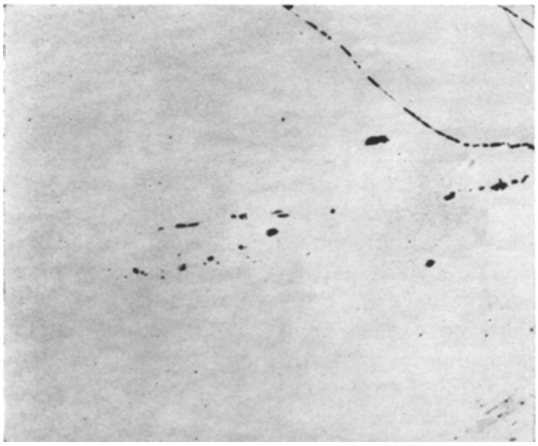

Figure 1 Distribution of precipitates (X152).

On exposure to the atmosphere at room temperature for a few days, the precipitates were observed to undergo a transformation. Initially, small regions of each particle became optically active under polarised light, and these areas spread until, eventually, the whole particle had transformed. This process is illustrated in figs. 2 and 3; the pested regions are the small very light areas within the grey particles. The darker grey appearance of these same particles in fig. 2 is merely a photographic effect. It was found that the transformation could be accelerated considerably in the presence of an oxidising

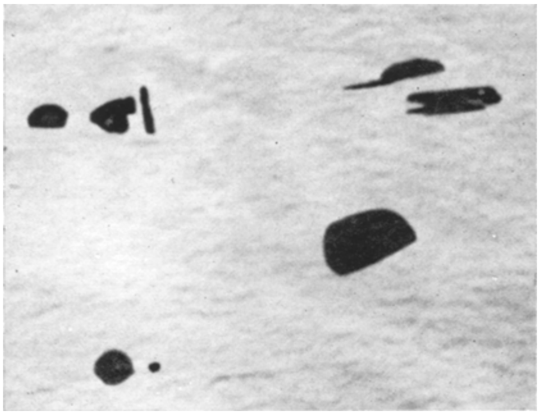

Figure 2 Al_2O precipitates before transformation (X1300).

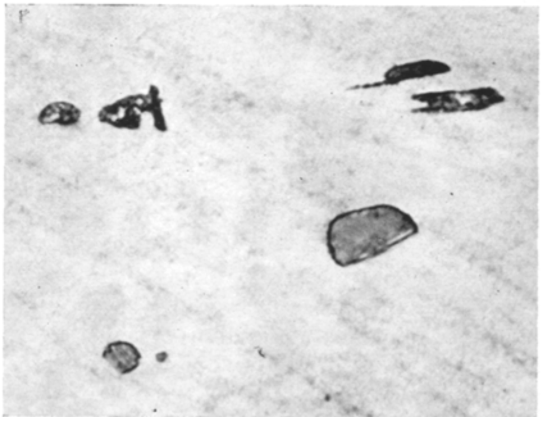

Figure 3 The same particles as shown in fig. 2 after 8 days exposure to the atmosphere at room temperature; the transformation to α—Al_2O_3 is more complete in the smaller particles (X1300).

agent, H_2O_2. The product of the transformation was white, powdery in form, optically active, and it could not be distinguished from the oxide layer present on the original surface. The initially flat surfaces of the Al_2O particles became so uneven that satisfactory electron microprobe traces could not be made; this feature indicates that a considerable volume expansion is involved in the transformation. It seems reasonable to assume that the product of the transformation is α-Al_2O_3. During the transformation the grain boundary hardening effects disappear and, in general, the grain boundary regions become softer than the grains.

These results indicate that the pest phenomenon is associated with the oxidation of Al_2O to α-Al_2O_3. This transformation probably occurs at internal boundaries by the diffusion of oxygen along the grain boundaries, and disintegration could then follow as a result of the internal strains produced by the volume expansion involved in the transformation. Such a process would open up the material along the grain boundaries and allow oxygen to diffuse further into the interior to continue the transformation.

A mechanism of this type is supported by the experimental observation that, when new surfaces were prepared in partially "pested" samples, precipitates in the bulk of the grains were still in the Al_2O form. The effect may be attributed to the extremely slow bulk diffusion of oxygen at room temperature, and would account for the striking feature of the pest observed by Westbrook and Wood [1] – that the individual grains in a "pested" sample could still undergo plastic deformation.

The factors which determine the formation of Al_2O and the mechanisms of grain boundary hardening will be discussed in detail in a later publication.

This work was supported in part by an SRC research grant and a Ministry of Aviation contract. One of us (R. T. Pascoe) is indebted to the Ministry of Aviation for the provision of a bursary.

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15 November 1965

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Book Reviews

Crystal Physics

G. S. Zhdanov

Pp ix+500 (Oliver and Boyd, 1965). Translated from the Russian by A. F. BROWN 80*s*

Professor Zhdanov's book is a course book intended for senior undergraduates in metal physics and solid state physics. The author has drawn on 20 years' experience of teaching these subjects in the USSR to produce a textbook that requires little prior knowledge of materials science. The initial chapters give an interesting and readable account of elementary quantum theory, atomic structure, interatomic forces, chemical bonding and the symmetry of atoms, molecules and crystals. This leads naturally to a simple discussion of the crystal structure and cohesive energy of crystals, the electron band theory of solids and the electrical and magnetic properties of materials. At this point the emphasis changes to a consideration of phase equilibria, crystal growth, thermal properties, diffusion, and finally the mechanical properties of solids. Thus the text ranges over much of what is to be expected from the title with no notable omission. Inevitably, and the author acknowledges this, the scope of the book is so wide that some subjects are inadequately covered. Thus the discussion of semiconductors, superconductors, and dislocation theory is so condensed as to be virtually useless to many students. This inadequacy is not effectively remedied by the list of review articles and books in the bibliography.