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H. W. NEWKIRK
D. K. SMITH
Lawrence Radiation Laboratory
University of California
Livermore, California, USA
E. S. MEIERAN
D. A. MATTERN
Fairchild Semiconductor Research and
Development Laboratory
Palo Alto, California, USA

Discussion on the Letter "Grain Boundary 'Pest' in the Intermetallic Compound NiAl" by P. A. Turner, R. T. Pascoe, and C. W. A. Newey (J. Matls. Sci. 1 (1966) 113*)*

The present authors published the results of an investigation [1] on oxygen-induced grain-boundary hardening in NiAl in 1965. It was shown in this work, as in the case of NiGa [2] quoted by Turner *et al*, that grain-boundary hardening occurred both at a free surface and at grain boundaries. The hardening observed by Turner *et al* in the 54 at. % alloy, and attributed by them to the result of stresses caused by the oxidation of Al_2O to Al_2O_3, apparently was observed only at grain boundaries and not at the surface of the sample. While we do not claim that the mechanism suggested by Turner *et al* cannot occur, in our studies [1] of alloys containing up to 51.3 at. % Al we have seen no convincing evidence of the type shown in their micrographs. On the contrary, we have looked very carefully for evidence of grain-boundary precipitates, and have never observed any phase which could be related to the occurrence of grain-boundary hardening or embrittlement. Our experiments included electron microscopy by replica and by transmission. The hypothesis of grain-boundary splitting or opening followed by a progressive oxygen penetration would require microscopic evidence of such grain-boundary parting, along with the continual presence of the oxidised particles; this simply was not observed in our work. It may be that the difference in composition, 51.3 versus 54 at. % Al, is responsible.

In any case, the equivalence of bulk hardening at a free surface and grain-boundary hardening in the precipitate-free, less aluminium-rich alloys forces one to look elsewhere for an explanation for the oxygen embrittlement in our alloys. The mechanism of oxygen-atom-vacancy interaction, which deposits vacancies either at a free surface or at a grain boundary but then leaves the oxygen atom stranded nearby, appears to explain all of the observed phenomena as outlined by Seybolt, Westbrook, and Turnbull [3]. Finally, it might be pointed out that, if the authors' proposed Al_2O to Al_2O_3 transformation does occur under some circumstances, it would bring about a local impoverishment in dissolved oxygen near the precipitation site, e.g. the grain boundary, and hence soften that region via the Seybolt, Westbrook, and Turnbull mechanism. This would seem to be a more tenable explanation for the softening observed by Turner *et al* concomitant with transformation of their precipitate than an implied difference in the hardening between Al_2O and Al_2O_3 dispersions.

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A. U. SEYBOLT
J. H. WESTBROOK
G E Research and Development Center
Schenectady, New York, USA

Reply to the Discussion (J. Matls. Sci. 2 (1967) 196*) on the Letter "Grain Boundary 'Pest' in the Intermetallic Compound NiAl" (J. Matls. Sci.* 1 (1966) 113*)*

The purpose of our letter was to propose a mechanism for the occurrence of the pest, in NiAl containing 54 at. % Al, in terms of the observation of precipitates at the grain boundaries which underwent a morphological change on exposure to the atmosphere at room temperature. Grain-boundary hardening was mentioned because it and the pest appear to be related, since the pest is found in materials which also exhibit grain-boundary hardening. However, this does not mean that the pest is a natural consequence of grain-boundary hardening, and we do not know of any evidence in the literature which suggests that the NiAl composition used by Seybolt and Westbrook (51.3 at. % Al) is susceptible to the pest. Seybolt and Westbrook have not attempted, even in their discussion of our letter, to account for the pest phenomenon in terms of their proposed grain-boundary hardening mechanism.

We have in fact obtained microscopic evidence for progressive oxygen penetration down a grain boundary during pesting. Pested samples were examined after removal of successive layers from the surface exposed to air. We found that the longer the exposure time the greater was the depth of the layer which had to be removed before unoxidised particles were detected at the boundary. We consider that Seybolt and Westbrook's proposal, that the grain-boundary softening which occurs when the particles oxidise is due to a local impoverishment in dissolved oxygen, is unlikely; because softening which is detectable by the microhardness technique would require massive matrix diffusion in relatively short times at room temperature.

In the light of the experimental evidence available for NiAl containing 51.3 and 54 at. % Al, it is not unreasonable to conclude that the operative grain-boundary hardening mechanism depends upon composition (this may, for example, lead to an uptake of different concentrations of oxygen on heat treatment, which could be present as either oxide and/or solute), and, in the latter composition, that both the hardening and the pest result from the presence of grain-boundary precipitates. This view is supported by the fact that hardness traverses across grain boundaries, at points where no precipitates were observed, did not reveal hardening.

The important point to be clarified by further studies is whether pesting occurs only when precipitates, which undergo the type of transformation observed in NiAl, are present at grain boundaries; or, alternatively, whether alloys which exhibit grain-boundary hardening in the absence of grain-boundary precipitation are also susceptible to the pest.

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P. A. TURNER
Bell Telephone Laboratories
Murray Hill, New Jersey, USA
R. T. PASCOE
Metal Physics Section
Aeronautical Research Laboratories
Fisherman's Bend, Melbourne, Australia
C. W. A. NEWEY
Metallurgy Department
Imperial College
London SW7, UK

A Method for the Etching of Pyrolytic Silicon Carbide

Silicon carbide prepared by the pyrolytic decomposition of methyltrichlorosilane vapour upon uranium carbide spheres in a fluidised bed has variations in structure dependent upon deposition rate. To examine this in detail, a suitable etch was required. The following single-stage electrolytic etches were tried; some