

Fig. 5—Influence of titanium content on the temperature for 60 pct reduction in area.

potential of this elemental addition, thus increasing the amount of titanium required to completely suppress intergranular brittleness.

Titanium at lower concentrations, while not completely suppressing intergranular brittleness, does tend to minimize its deleterious effects. Rellick and McMahon¹ have noted that certain furnace cooled Fe-Ti alloys exhibited far greater ductility at -195°C than that

observed in either Fe-C or Fe-Al alloys. This ductility increase is probably due to the general affinity of titanium for carbon which leads to the elimination of the coarse carbides contained in the latter alloys. Indeed, a similar effect has been observed in the present investigation, Fig. 6. Although the temperature for 60 pct reduction in area is not a "true transition temperature" it does illustrate the same general behavior previously reported.^{1,2} It appears that the observed minimum occurs when the increased ductility associated with the elimination of the coarse carbides and the partial suppression of intergranular brittleness is counterbalanced by increased titanium solid-solution hardening.

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Morphology of Aluminum Oxide Particles in Nickel

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THIS communication reports the high-temperature equilibrium morphology of aluminum oxide particles in a nickel matrix. The composite specimens were prepared by a vapor deposition technique and by the internal oxidation method.

Several methods have been attempted to produce aluminum oxide dispersion free from clustering.¹ The vapor deposition technique was found to be favorable. High-purity nickel (99.999 pct) was deposited onto a (0001) face of Linde sapphire single crystal by electron beam evaporation in a bell jar at a vacuum better than 1×10^{-5} torr. Prior to the deposition, the sapphire substrate was cleaned sequentially with hydrochloric acid, acetone, and methyl alcohol. Temperature of the substrate was held at 600°C during the deposition. The deposited nickel films were polycrystalline with a typical grain size of 1 μ m. When the deposited film reached a thickness of approximately half a micron, it was then exposed to an aerosol suspension of α -alu-

mina particles. The suspension was produced by mechanically vibrating a jar containing Linde-A alumina powder (nominal size 0.3 μ). Particles smaller than the nominal size were adsorbed on the surface of the nickel film. A second layer of nickel was then deposited to produce a sandwich containing the alumina

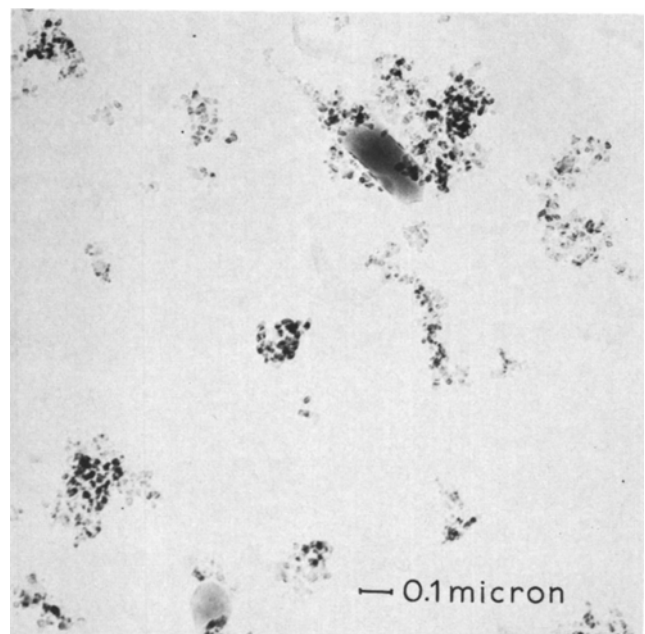


Fig. 1— α -Al₂O₃ (Linde-A) particles before annealing.

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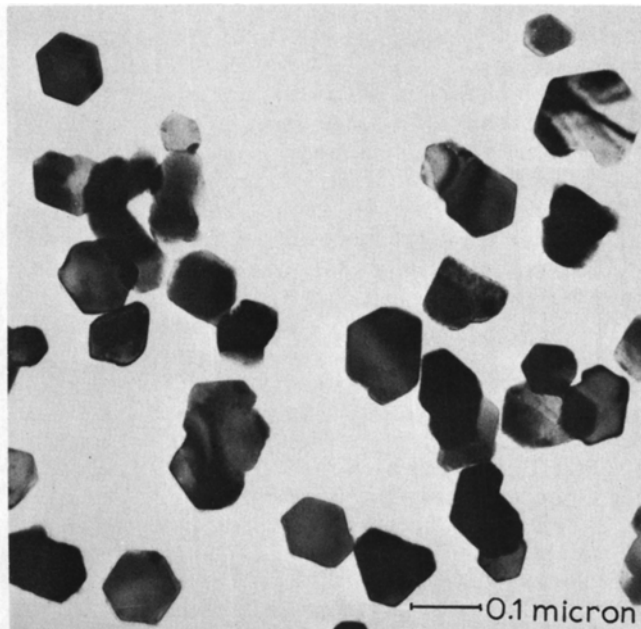


Fig. 2— α - Al_2O_3 particles from a sandwich specimen annealed at 1400°C for 25 hr.

particles. During the deposition of the second nickel layer, the substrate was tilted frequently to vary the incident angle of nickel vapor, thus avoiding the possible formation of voids around the particles. The above procedure of depositing successive layers of nickel and alumina particles was continued until a specimen of the desired thickness was produced.

The equilibrium shape of the α -alumina particle was achieved by annealing the specimen in a nickel crucible containing high-purity nickel powder in a vacuum furnace at 1400°C , in a vacuum better than 10^{-6} torr, and for times longer than 25 hr. Extraction replicas of oxide particles were then examined with an AEI-100KV transmission electron microscope. Fig. 1 shows the oxide particles before annealing. The size of the oxide particles is very small, 100\AA or less. The two large particles shown in Fig. 1 are oxide particles of nominal size ($0.3\ \mu$) which were also introduced into the aerosol suspension but with much less frequency. By annealing, the aluminum oxide particles grew to a size of approximately $0.1\ \mu$, and developed mostly into a hexagonal thin platelike shape which consists of (0001) basal plane bounded by $[10\bar{1}0]$ edges as shown in Fig. 2. No appreciable change in the morphology of alumina particles was observed by the addition of 2 at. pct Al to the nickel matrix. This Ni-Al alloy sandwich specimen was prepared by using Ni-Al alloy as a vapor source during the deposition.

Alumina dispersion were also produced by the internal oxidation of Ni-Al alloys (0.1 to 0.5 at. pct Al). Small disks 20 mils thick were cut from the alloy bars by electro-spark cutting, polished with a chemical polishing solution, rinsed with distilled water and alcohol, and dried. The chemical polishing solution used consisted of 65 ml of acetic acid, 34 ml of nitric acid, and 1 ml of hydrochloric acid. The disks were then placed in an unsealed nickel capsule containing a powder mixture of $8\ \text{NiO} + 1\ \text{Ni} + 1\ \text{Al}_2\text{O}_3$. This capsule was then sealed in an evacuated quartz tube (10^{-5} torr), and heated at 1000°C for 24 hr in a resistance heated

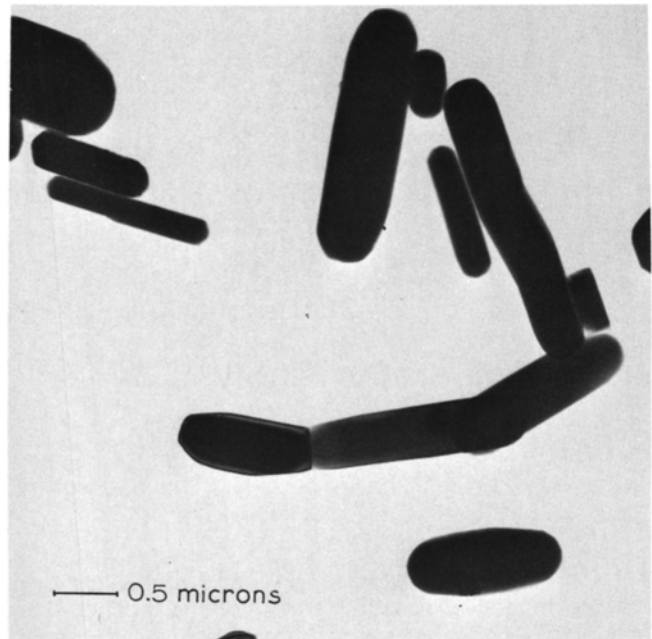


Fig. 3—Alumina particles from Ni-0.45 pct Al alloy specimen which was internally oxidized at 1000°C for 24 hr, and then annealed at 1400°C for 50 hr.

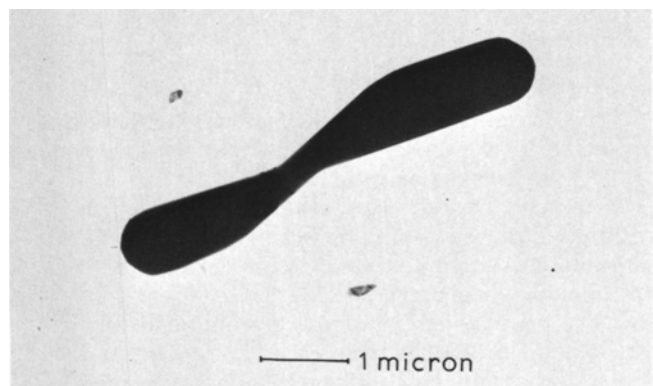


Fig. 4—Waist formation in an alumina particle obtained from Ni-0.2 at. pct alloy specimen which was internally oxidized at 1000°C for 24 hr, and then annealed at 1400°C for 50 hr.

furnace. The internally oxidized specimens were examined in the same way as described above. The morphology of oxide particles obtained by this method was different from that of the sandwich specimen. The oxide particles in this case were mostly in an elongated polyhedron shape as shown in Fig. 3. Waist formation in a particle was sometimes observed, Fig. 4, as had been reported by Stapley and Beevers² in their alumina whisker-nickel composite. An X-ray powder diffraction pattern of the oxide particles obtained from internal oxidation was identical with that of Linde α -alumina, except that it showed extra very weak lines. However, a selected area electron diffraction pattern revealed a more complicated structure than that of α -alumina. This difference in structure could correspond to a difference in composition and lead to the different equilibrium morphology from that of α -alumina.

In summary, from the hexagonal platelike equilibrium morphology of the α -alumina particles in the annealed nickel sandwich specimen, it was concluded that the (0001) crystal plane of α -alumina in a nickel

matrix at 1400°C is a singular surface on which the cusp of the γ -plot of the Wulff diagram appears.³

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Comments on the Analysis of Thermal Grooving Data

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IN a previous publication¹ it was pointed out that the data developed by N. A. Gjostein² for the thermal grooving of copper could be interpreted as volume diffusion instead of a combination of volume diffusion and surface diffusion. Such interpretation resulted in volume diffusion coefficients which are in agreement with coefficients determined from tracer diffusion studies.³ This reanalysis was justified on the basis of an incubation period during which the thermal groove attained an equilibrium profile.

In his comments on this discussion, Gjostein⁴ disagreed with the reanalysis and made objections which can be summarized as follows:

1) No groove width is necessary to describe an initial groove of equilibrium shape since mathematically no allowance must be made for an infinitely narrow equilibrium-shaped groove.

2) The negative or positive intercept results from incremental widths contributed by an additional diffusion process to the dominant one characterized by the exponent.

3) Data at 1020°C show the same shape tendencies theoretically described for incremental width contributions.

4) Surface contamination can change the transport rate by several orders of magnitude, thus indicating surface diffusion.

The reasons that these objections are not considered conclusive are as follows:

1) A considerable number of atomic steps must be present across the groove profile before the profile contour is smoothly defined and not dominated by the steps and curvature of individual atoms. Further descriptions of the necessity of considering atomistic behavior during initial profile formation were presented in the original note.

2) If the two processes having $\frac{1}{3}$ and $\frac{1}{4}$ exponential rates each made a substantial contribution to groove growth with the $\frac{1}{4}$ one strongly dominant initially and

the other dominant finally, then the data would consistently plot concave upward on a $t^{1/4}$ plot and concave downward on a $t^{1/3}$ plot. This is not the case. Individual data points from studies of many materials consistently result in the same shape of curve (nearly straight line) whether plotted $t^{1/4}$ or $t^{1/3}$. Long-time annealing data points which fall below the best fit straight line on $t^{1/3}$ plots also fall below on $t^{1/4}$ plots lending support to the model of a dominant mechanism.

3) At no time previous to these objections has there been the suggestion that curvature must be considered in analyzing the data. Least-squares fits have been used as the best approximation. On the 1020°C data replots, a straight line (with negative intercept at $t^{1/4}$ and positive intercept at $t^{1/3}$) fits the data as well as the curves which were drawn and forced through the origin in Ref. 4. Rechecking of Gjostein's data at other temperatures shows that data at other temperatures do not even approximate the shapes proposed to explain the intercept problems. Of course, it is agreed that, initially, multiple processes do contribute substantially and a curvature will result which gives a positive intercept when the straight line portion is extrapolated back to $t = 0$. Justification has been given for the high activation energy obtained for surface diffusion being in the same range as for volume diffusion. This is extremely inconsistent with the observation that there is a substantial contribution from volume diffusion at higher temperatures. Unless there is a difference in activation energy between surface diffusion, and volume of diffusion, temperature will not favor one or the other as a mechanism. Surface diffusion should logically have a much lower activation energy.

4) Gjostein himself² has been reluctant to attribute the high thermal grooving activation energies to contamination. However, in the event of contamination surface diffusion would be retarded and volume diffusion would be left unchanged. The most important point is that both processes are being driven by surface tension, and if the role of contamination is to decrease surface tension, then both transport processes would be affected. Comparison of accepted metal and ceramic surface tension values indicates that the reduction of surface tension in the presence of absorbed impurities is very substantial and could easily explain the effect that the changing oxygen partial pressure has on copper thermal grooving rates. In fact, the surface tension may become low enough to increase the tangent at the root to the point that the low angle assumptions are no longer valid. This, combined with the presence of a second "phase" on the surface, may make the whole procedure of grooving copper in the presence of oxygen very questionable. For instance—for bare copper with a 160 deg dihedral angle and $\gamma_s = 1850$ erg per sq cm, γ_{GB} is 640 erg per sq cm. If copper oxide is formed on the surface, ($\gamma_s(\text{oxide}) \sim 900$ erg per sq cm), the dihedral angle becomes 138 deg giving a small angle of 21 deg which is outside the range which makes the low angle assumption valid.

In order to elucidate the actual mechanisms of groove growth, some additional investigations of the thermal grooving of copper were conducted.

In this investigation the smooth, flat surface was produced by grinding with successively finer diamond grits ranging from 600 mesh to $\frac{1}{4}$ μm in diameter. The samples were electropolished to remove the

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