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Role of Nickel in Al-10 Percent Si Composites Containing Nickel-Coated Sapphire Whiskers

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The role of nickel in regard to whisker-matrix bonding in a composite of nickel-coated sapphire whiskers inserted into a matrix of aluminum-10 percent silicon alloy by means of liquid phase hot-pressing was investigated. The study was carried out with the aid of optical and electron microscopy, electron probe microanalysis, and microhardness measurements. Results show that most of the nickel is distributed within the matrix alloy.

Some of the nickel apparently interacts with the matrix and forms $NiAl_3$. The presence of $NiAl_3$ in this form increases the average hardness of the composite but apparently does not contribute significantly to strengthening of the alloy. Occasionally, clusters or clumps of nickel-rich material which also contains aluminum are found at or very near whisker-matrix interfaces. It is concluded that if any bonding of the nickel to the sapphire occurred, it was in these regions. Finally, a heat treatment to improve nickel to sapphire bonding and hence bonding of the entire composite is suggested.

Key Words: Al-10 percent Si alloy, electron probe microanalyzer, fiber composites, matrix-whisker bonding, Ni coated sapphire whiskers, optical metallography, sapphire whiskers.

1. Introduction

The availability of sapphire (α-Al_2O_3) fibers (whiskers) in the form of single crystals having very high strength has created extensive interest in the incorporation of whiskers in metallic matrices. It is hoped that such composites will combine the desirable properties of ductile metals with those of the ultrahigh-strength whiskers which would be oriented so as to provide reinforcement in the direction of the applied stresses. In one study [1],[1] 15 volume percent of 1 to 30 μm diam sapphire whiskers added to an aluminum-10 percent silicon matrix by liquid phase hot-pressing at 580 °C resulted in some cases in an increase of 60 percent in tensile strength coupled with a 50 percent increase in elastic modulus. The beneficial effects were still present up to 800 °F (426 °C); some specimens were stronger than any wrought commercial aluminum alloy at this temperature. However, strengthening from sample to sample occurred with less than satisfactory consistency. It was thought that this lack of consistency might be due to poor bonding of the whisker to the matrix.

In an effort to improve this bond between the matrix and the sapphire the specimens were prepared using nickel-coated fibers [1]. Nickel was chosen because it could be deposited with relative ease by the thermal decomposition of nickel tetracarbonyl, $Ni(CO)_4$. Hence, a matte of nickel-coated whiskers could be prepared; the matte could then be inserted into the matrix by liquid phase hot-pressing. Apparently, an NiO-Al_2O_3 spinel forms which serves to bond the Ni to Al_2O_3. In the absence of this spinel, adhesion of Ni to Al_2O_3 may be poor or not occur at all [2, 3]. The presence of the spinel is taken to indicate the probability of good Ni-to-fiber adhesion. In addition, bonding of the fiber matte to the matrix by diffusion during liquid phase hot-pressing is expected. Hence, better bonding of the nickel-coated whiskers to the matrix was expected as contrasted to uncoated whiskers.

Detailed studies concerning the adherence of Ni and Ni-base alloys to sapphire have been carried out [4, 5]. The contact angle between Ni and sapphire is 100°-a higher value than that for Al and sapphire. Adhesion of Ni to sapphire was studied for coatings applied under a pressure of 4×10^{-6} torr. The apparent shear strength at room temperature was high for pure Ni being about 18,000 psi (124.1 MN/m^2). This result is qualitative since the testing method did not ensure true shearing load [5]. Nevertheless, the beneficial effect of the Ni coating was clearly demonstrated.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Fracture tests usually showed that at least part of the failure was through the sapphire. In a few cases, fracture was entirely along the interface between the Ni and the sapphire [5]. Thus, good Ni to sapphire bonding should indeed offer improved composite strength.

However, we do not wish to imply that whisker-matrix adhesion is the limiting strength factor in the system. Other contributory factors include: (1) whisker orientation, length and aspect ratio, (2) matrix shear strength and shear modulus, (3) composite failure mode and (4) matrix hardening during composite loading. In the tests of strength which were conducted, each of the above factors was nearly the same. Hence, we believe that most significant differences observed were due to whisker-matrix adhesion effects.

Although some of the specimens containing nickel were stronger than those in which nickel was absent, the strengthening effect was not reproducible in all cases. The degree of strengthening was about the same for both coated and uncoated whiskers when (apparently) satisfactory bonding of the whiskers to the matrix occurred. Evidence of this was that tensile tests on both types of specimens gave similar results [1]. The present report concerns a further investigation into the distribution of the nickel in the composite.

2. Tests of the Composite Specimens

2.1. Optical Results

Metallographic examination of the as-pressed material was carried out. Typical microstructures are shown in figures 1 and 2 for Ni-coated and uncoated whiskers respectively. A great number of broken whiskers are seen; these are more or less randomly oriented. The chief difference is that specimens containing the Ni-coated whiskers exhibit an extra constituent which appears as pale blue dots under white light after etching in Keller's reagent; the color is enhanced in polarized light (fig. 1). No such constituent appeared in composites formed with uncoated whiskers (fig. 2).

In the study of Al-Ni alloys, the intermetallic compound $NiAl_3$ has been reported to appear blue after etching [6]. The presence of a dispersed "blue dot" constituent led to the suspicion that the Ni coating had been lost from the whiskers during processing.

In this regard, a pertinent question concerns the diffusivity of nickel in molten aluminum-silicon alloy at the pressure of 2000 psi used for liquid phase hot-pressing [1]. Unfortunately, there are very few data on diffusion in liquid metals other than for the alkali group. However, an approximate value of the diffusion coefficient of Ni in liquid Al, called $D_{Ni, Al}$, has been suggested as being 10^{-5} to 10^{-6} cm^2/sec [7]. The effect of 2000 psi (13.79 MN/m^2) pressure would be to reduce this value, but only by a factor of about two at most [8]. Therefore, we shall take $D_{Ni, Al}$ as being 10^{-6} cm^2/sec for the liquid phase hot-pressing step. For comparison, we note that the diffusion coefficient of Ni in solid Al has been reported as 10^{-11} cm^2/sec at 580 °C [9].

In order to determine the random walk distance, X for the nickel during liquid phase hot-pressing the relation is:

$$X = (Dt)^{1/2} \tag{1}$$

where t is the time at temperature. The value of X is 50 μm for t of 25 sec. The average distance between whiskers is only 50 to 100 μm as determined by optical metallography (see fig. 1 for example). Thus, diffusion of Ni would have occurred throughout the matrix in something less than a minute during liquid phase hot-pressing. The molten aluminum-silicon matrix would have been saturated with nickel and, upon cooling, $NiAl_3$ would have precipitated. This is precisely what Castleman and Seigle observed in aluminum melted in the presence of nickel which was examined metallographically after cooling [10]. Complete loss of Ni from sapphire whiskers in a molten aluminum matrix was observed by Mehan et al. [11]. In their study the presence of $NiAl_3$ in the resulting solid samples was confirmed by x-ray diffraction methods.

Reference to the Ni-Al constitution diagram shows that the solubility of Ni in solid Al is very low (much lower than in liquid aluminum) [12]. Furthermore, formation of the phase Ni_2Al_3 is inhibited by the application of pressure and the pressure induced decrease in the diffusion coefficient is the rate controlling factor in the growth kinetics of Ni_2Al_3 [6]. Therefore, we conclude that the "blue dots" are $NiAl_3$ and that the matrix alloy contains some Ni in solid solution. No great amount of Ni_2Al_3 or other phases richer in nickel would be expected.

2.2. Electron Probe Microanalysis

Electron probe microanalysis was performed to determine the actual nickel distribution within the coated whisker composite. In addition, specimens of composites containing uncoated whiskers and a control specimen of Al-10 percent Si without whiskers were examined. Composites containing uncoated whiskers contained no nickel; a search was made with the microprobe to make certain of this. However, the silicon was found to be inhomogeneously distributed within the specimen; the same was true for the matrix alloy containing no whiskers. Such an inhomogeneous silicon distribution in the matrix would not have helped to improve whisker bonding and may have had an injurious effect.

Scanning photographs of a specimen of a composite containing nickel coated whiskers were prepared [13]. The presence of clumps of nickel concentrates near the edges of whiskers as well as the presence of nickel dispersed within the matrix was noted. The presence of nickel away from the blue dots was confirmed by step scanning the spectrometer through the Ni-Kα x-ray peak with a finely focused static

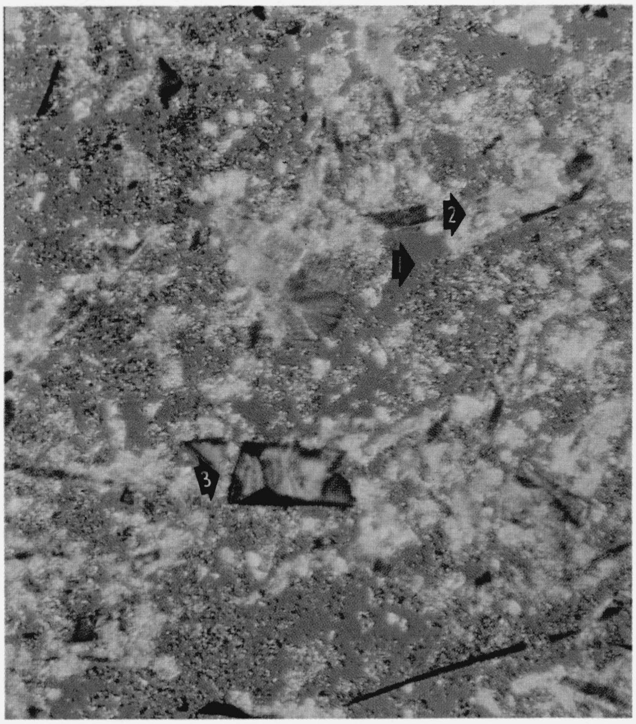

FIGURE 1. *Photomicrograph taken in polarized light of composite containing 15 v/o Ni–coated sapphire whiskers in the as–pressed condition.*

Note the blue dots which are probably $NiAl_3$ (A–1). Note also the broken whiskers which appear yellow to white (A–2). Larger whiskers are blue and orange (A–3). ×1000.

FIGURE 2. *Photomicrograph taken in polarized light of composite containing 15 v/o uncoated sapphire whiskers in the as–pressed condition.*

Note the complete absence of the blue dots. Again many broken whiskers are present. ×1000.

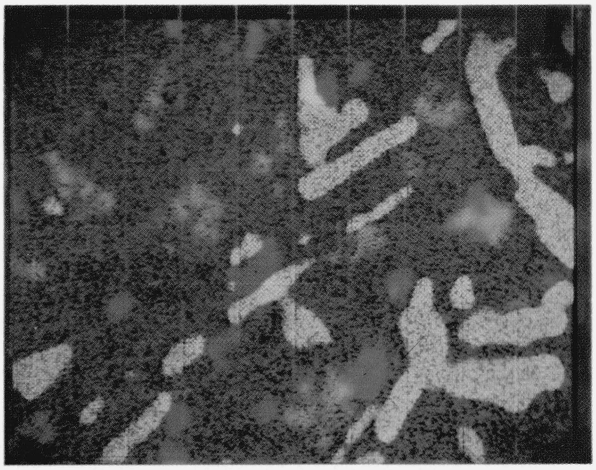

FIGURE 3. *Composite map of scanning microprobe photographs of composite containing 15 vol. percent Ni coated sapphire whiskers in the as–pressed condition.*

The yellow–green areas are the whiskers as photographed by means of cathodoluminescence. The red represents the Ni distribution. The pale blue represents the Si distribution. Note the nickel clumps (solid red blobs) at or very near whisker edges. The remainder of the Ni is distributed throughout the matrix without regard for the presence of Si clumps. Color–addition methods were used to combine separate cathodoluminescence (whiskers), Ni-K x–ray distribution, and Si-K x–ray distribution photographs of the same area. ×1125.

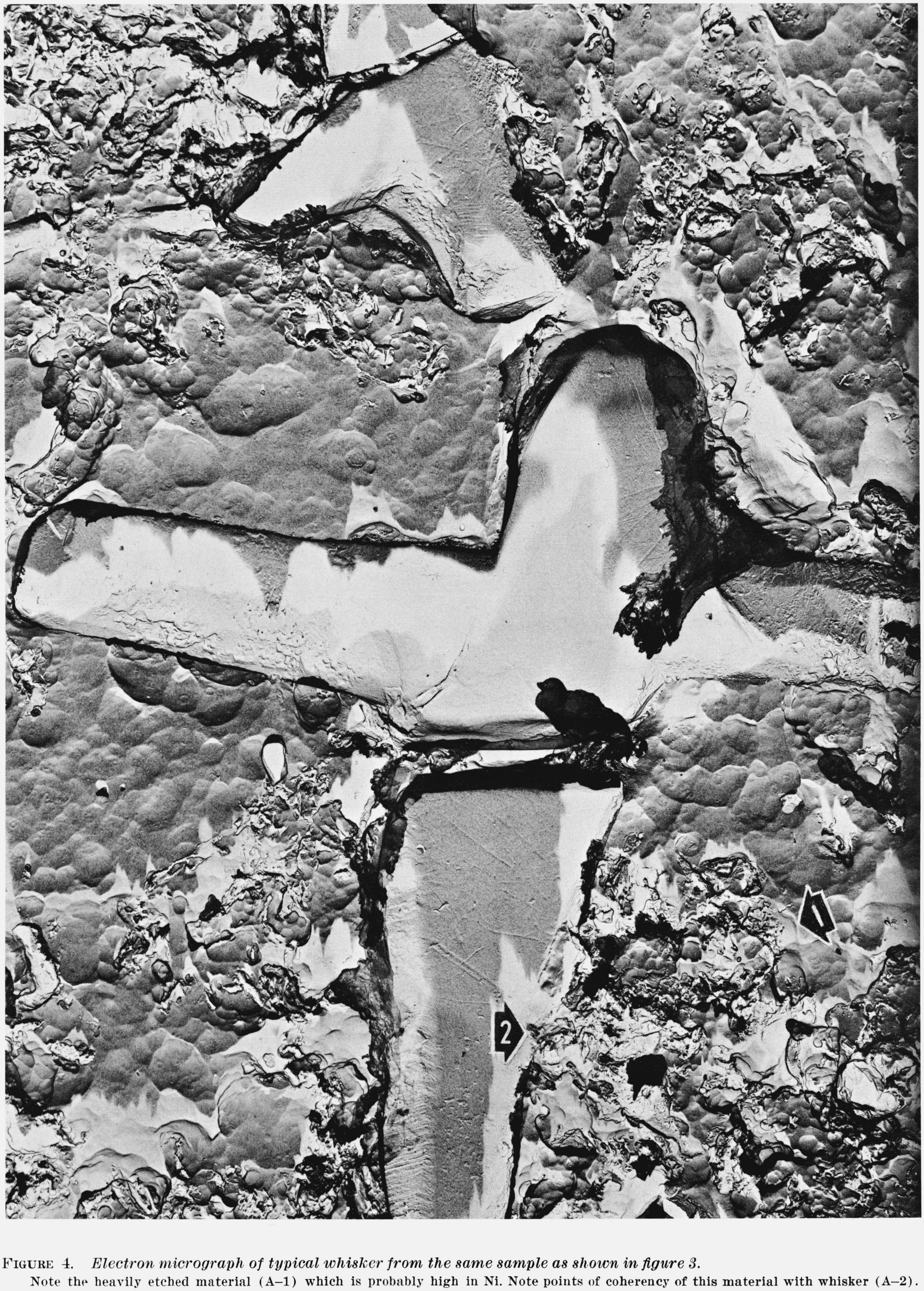

FIGURE 4. *Electron micrograph of typical whisker from the same sample as shown in figure 3.*
Note the heavily etched material (A–1) which is probably high in Ni. Note points of coherency of this material with whisker (A–2).

probe placed in the matrix as far away as possible from the blue dots. Nickel count rates were 15 percent above background in these regions.

In order to show the distributions observed, a composite map in color was prepared using the data from the scanning photographs. The result is shown in figure 3. Most of the Ni coating has been lost from the whisker and is dispersed in the matrix. The regions of Ni concentration at or near whisker surfaces were investigated further in an effort to determine what role, if any, such regions play in the bonding of the sapphire to the nickel. It has been postulated that the wetting of sapphire by nickel is caused by the formation of $NiO \cdot Al_2O_3$ spinel although the complete mechanism is not yet fully apparent [2, 3]. Therefore, a microprobe search of the Ni concentrate regions for Ni and oxygen in combination was performed using x-ray scans at magnifications of 2350 × and 4700 ×. The oxygen distribution indicates that the high nickel regions are not spinel but that there are portions of these regions which appear to contain oxygen. In addition, the high nickel regions also contain aluminum but virtually no silicon. Hence, the results of the search for spinel were inconclusive.

2.3. Electron Metallography

The electron microscope was used to search for evidence of spinel formation at the whisker-matrix interface. Several replicas were taken from metallographically polished and etched surfaces of specimens containing Ni-coated whiskers. A typical electron micrograph is shown as figure 4. We believe the heavily etched region to be the material richer in Ni since similar roughening occurs between Ni-base alloys and sapphire where definite reactions have indeed been confirmed [5, 14]. This roughened material tends to blend into the whisker at several spots. There is no evidence for the formation of a discrete phase at the whisker-matrix interface at magnifications up to 20,000 ×. As control samples, replicas were taken from specimens containing no whiskers and from specimens containing uncoated sapphire whiskers respectively. In the case of no whiskers the electron microscope revealed an almost textureless surface punctuated by large masses of high Si material. For the uncoated whisker case, the surface between whiskers was also free of texture.

It seems reasonable that the areas where the Ni rich material blends directly with the whisker would be the areas where the matrix and whisker are most adherent to one another. Nevertheless, like Ritter and Burton [3], we were unable to find evidence of the presence of a region which might be $NiO \cdot Al_2O_3$ even in these areas. If any spinel is present it is contained in a band which is not visible at 20,000 ×. If the spots where Ni and whiskers blend are responsible for improvement in bonding then the whiskers are bound into the matrix at more or less random points along the interface. Such randomness would aid in explaining why an unacceptably large percentage of composites were still not strengthened even after the change to Ni-coated whiskers was made.

2.4. Hardness Testing Results

If the blue dots are indeed dispersed $NiAl_3$, the average hardness of specimens containing such a hard, brittle intermetallic phase would be expected to be greater than that of specimens prepared without nickel coated whiskers.

Hardness measurements were made in typical specimens containing both Ni coated fibers and uncoated fibers. The Knoop indenter with a 20 × objective and 200 g load was used; the results were converted to Rockwell *B* values. While there was considerable scatter of the data, the average hardness was greater for composites containing Ni-coated fibers than for composites containing uncoated fibers. Typical values were R_B of 65 for the Ni-coated fiber composites and R_B of 40 for uncoated fiber composites. The Al-Si base alloy without fibers was too soft to give a meaningful Rockwell *B* value. Thus, these results are certainly not at variance with the conclusion that the blue dots are dispersed $NiAl_3$.

3. Conclusions

Considerable diffusion of nickel occurred in the composites containing nickel-coated whiskers during the liquid phase hot-pressing step. This resulted in the formation of a blue dot phase dispersed within the alloy; evidence indicates strongly that this phase is $NiAl_3$. Electron probe microanalysis and hardness tests are not at variance with this conclusion.

Concerning the bonding of the nickel to the sapphire whiskers, the evidence is not conclusive. However, the electron probe microanalyzer results indicate that nickel-rich clumps often appear at whisker surfaces. It is not unreasonable to conclude that whatever the mechanism of bonding the whisker to the nickel, it occurs in these regions.

Tensile tests of strengthened coated and uncoated fiber composites gave approximately the same results since the fibers are the same and they are equivalently combined into the matrix with or without the aid of nickel. The $NiAl_3$ formed in the coated fiber composites increased the hardness of the material but the (brittle nature of) $NiAl_3$ was apparently ineffective in improving the tensile strength when the $NiAl_3$ is in the randomly dispersed small spherules.

The results indicate that better bonding of the nickel to the sapphire might further improve the percentage of strengthened samples. There is definite evidence that nickel will bond to sapphire by diffusion in the presence of oxygen [2]. Possibly heating the nickel-whisker matte at 1350 to 1400 °C for an appropriate time in vacuum of about 0.1 to 1 torr (prior to liquid-hot-pressing) would offer improvement.

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