Letter

Observations on Whisker Stability in Metal Matrices

Although a major consideration in the production of whisker-reinforced composites is the risk of incompatibility between the whisker and the matrix, little effort has so far been directed towards the relevant physical and chemical factors. As far as ceramic whiskers are concerned, it seems to have been assumed that, as long as the ceramic was chemically more stable than any known matrix compound, compatibility was assured. However, experience with silicon nitride whiskers in nickel, iron, and silver has shown that chemical stability is no guide to whisker/matrix compatibility; for, although the whisker material does not dissolve in or appear to react with the matrix metal, each whisker tends to lose its characteristic shape and is transformed into a useless series of roughly spherical inclusions in the matrix. This letter presents a discussion of a possible mechanism to explain this incompatibility, based upon experimental observations.

Nichols and Mullins [1, 2] have carried out work on the effect of surface and volume diffusion on the stability of various geometric configurations. For example, it is shown that cylindrical bodies are inherently unstable if the frequency of surface undulations is greater than the cylinder's circumference.

The present work shows the extreme importance of the surface geometry of whiskers or fibres in controlling their stability in metal matrices at high temperatures. In particular, the degeneration of whiskers to small, useless, discontinuous fragments has been considered in terms of the undulations occurring on the surface of some "as-grown" whiskers (SiC), and in other cases (Si_3N_4) generated on the whisker surface during composite preparation.

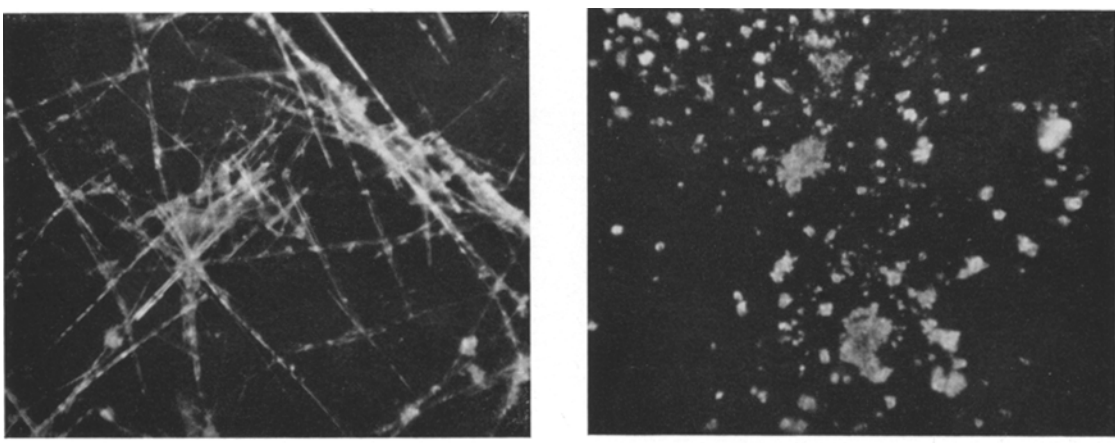
Silicon nitride whiskers have been introduced, by a hot-pressing technique, into matrices of silver (at 900° C), nickel (at 1200° C), and iron (at 1200° C), under a vacuum of 1 μtorr, a pressure of 1.57 kg/mm^2, and a pressing time of 2 h.

These three metal/ceramic systems showed contrasting behaviour during thermal treatment.

(*a*) The silver/silicon nitride system remained stable after 50 h at 900° C in air, provided the vacuum (1 μtorr) was maintained during the initial densification of the compact. However, hot-pressing under identical thermal conditions, but in 1 atm of fast-flowing air, caused intense spheroidisation of the whiskers in 2 h.

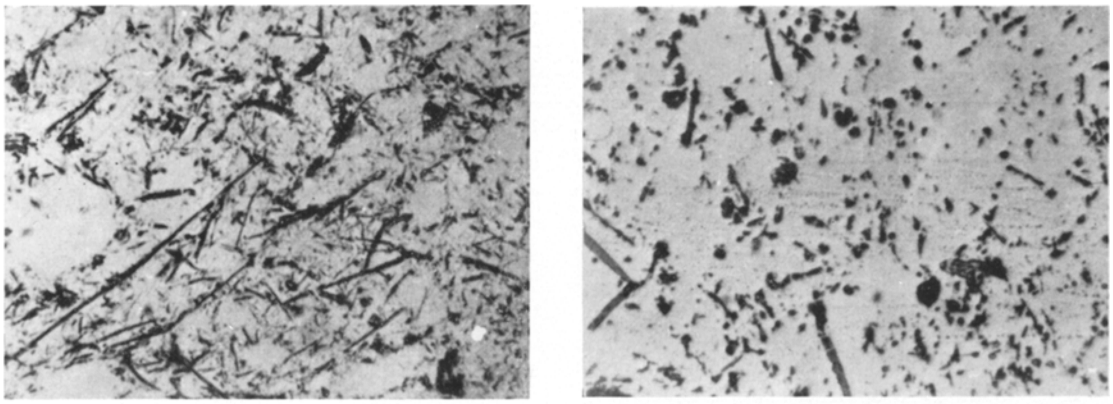
(*b*) The nickel/silicon nitride and iron/silicon nitride systems showed whisker spheroidisation during the initial hot-pressing procedure of 2 h at 1200° C and under a vacuum of 1 μtorr.

Following the marked effect of air on the



(a) (b)

Figure 1 Whisker debris reclaimed from silver/silicon nitride whisker mixes: (a) after treatment in hydrogen; (b) after treatment in air (×367).



(a) (b)

Figure 2 Nickel/silicon nitride whisker composites prepared (a) from silicon nitride whiskers heated in air at 950° C and (b) from silicon nitride whiskers heated in hydrogen at 950° C (×135). The composites had been heat-treated at 1100° C for 5 h.

stability of a whisker in silver, further experiments were carried out.

(*a*) Intimate mixtures (10% theoretical density) of 15 vol % silicon nitride whiskers and silver powder (2 μm particle size) were exposed to either hydrogen or oxygen atmospheres at 950° C for 2 h, and the changes of the whiskers after the heat-treatments were compared. Whisker instability was noted only where the silicon nitride had been exposed to oxygen (fig. 1). Visual inspection of the whisker debris suggested that each whisker had degenerated into a number of particles.

(*b*) Prior to their incorporation by hot-pressing into nickel, silicon nitride whiskers were heated in either air or hydrogen at 950° C for 2 h. Compacts were hot-pressed at 1200° C under 1.57 kg/mm^2 for 2 h in vacuum (1 μtorr) and subsequently heat-treated at 1100° C for 5 h. Fig. 2 contrasts the stability of those whiskers pre-exposed to the oxidising atmosphere with the instability of those pre-exposed to hydrogen. Unfortunately, oxidised whiskers also become unstable after 5 h at 1200° C in air.

Two general observations can be drawn from the foregoing experimental work: (i) when a whisker becomes unstable in a matrix, it breaks down into a series of egg-shaped particles (i.e. "ovulation" occurs), and the particles agglomerate; (ii) the stability of silicon nitride is dependent on the matrix material and on the atmosphere with which it is in contact.

Fig. 3 shows a whisker in the course of ovulation, and undulations can be clearly seen along its length. Undulations may originate from: (i) dissolution of some whisker material in the matrix; (ii) plastic deformation of the whisker surface during hot-pressing; (iii) phase changes in the whisker material leading to changes in volume; and (iv) periodic variations of whisker radius with length developed during growth.

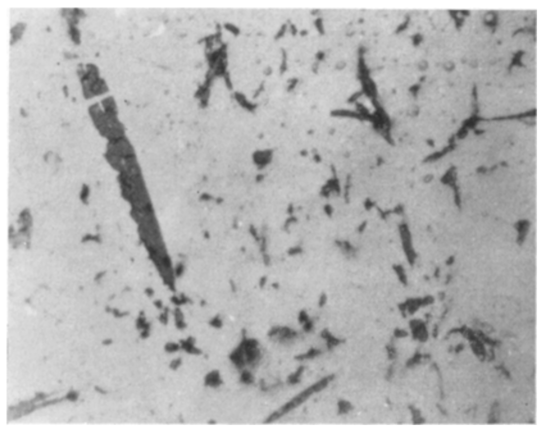


Figure 3 Silicon nitride whisker in the course of breakdown (×367).

Silicon nitride whiskers have a higher elastic modulus than the matrix materials in this series of experiments, phase changes do not occur below 1550° C, and as-grown whiskers rarely have undulating surfaces. It follows, therefore, that the undulation sources (ii), (iii), and (iv) are unlikely. The most likely mechanism is one based on (i) above.

The mechanism is very similar to the one usually given for the formation of a "neck" between a ball and a plate during sintering [3]. In the case of a metal particle resting against a whisker, interaction occurs at the point of contact and, owing to the vacancy gradient set up, whisker material migrates from the surface regions adjacent to the point of contact to form a neck at the point of contact and a surface undulation results.

In the present study, the interaction at the zone of contact is likely to be caused by dissolution and diffusion of the whisker anion in the metal, since the replacement of the anion in silicon nitride by oxidation causes the stability of the whisker to be markedly affected. For example, oxygen is less soluble than nitrogen in iron and nickel matrices at 1100° C; and this explains the improved stability of oxidised silicon nitride compared with pure silicon nitride. In silver, however, it would be expected that silicon nitride in both the oxidised and pure forms would be equally stable, since the solubilities of oxygen and nitrogen in silver at 930° C are very similar. In this case, the observed instability of the oxidised whisker arises from the increased diffusion rate of oxygen in silver compared with the diffusion rate of nitrogen.

Once undulations have been established on the whisker surface, the rate of breakdown is directly proportional to the controlling diffusivity, whether it be surface, internal, or external diffusion [1, 2]. The time to complete breakdown is, however, dependent on the fourth power of the whisker radius [1], and thus the high stability shown by continuous filaments is simply caused by their larger radius and consequently slower rate of degradation.

Conclusions

(*a*) Silicon nitride whiskers are stable in silver over prolonged periods at 900° C if incorporated in non-oxidising conditions, but not when oxidation of the whiskers is allowed to occur.

(*b*) Silicon nitride whiskers are unstable in nickel and iron matrices after short periods at 1200° C; however, at 1100° C, oxidised silicon nitride whiskers are more stable in a nickel matrix than unoxidised whiskers.

(*c*) Chemical incompatibility between whisker and matrix can lead to surface undulations on the whisker, resulting in a very unstable system. In this respect, both solubility and diffusivity of the whisker components in the matrix are important.

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