Fiber Composite Alloys: Preparation by Controlled Dissociation of Metallic Solid Solutions

Abstract. *Fiber-reinforced alloys have been prepared by the controlled dissociation of gold-nickel and aluminum-zinc solid solutions. To cause the dissociation, the alloys were taken from a one-phase field to a two-phase field by lowering the temperature. The new two-phase structure was in each case formed by diffusion controlled processes, and under certain conditions one of the new equilibrium phases appeared in the form of fibers, a few tenths of a micron in diameter, embedded in a matrix of the other. The precipitated phase first appeared in the form of spherical particles, but these aligned and then coalesced to form the fibers.*

We have reported that fiber-reinforced Au-Ni alloys, containing from 50 to 70 atom percent Ni, had been prepared by the controlled dissociation of Au-Ni solid solutions (*1*). The technique was based on the miscibility gap in the Au-Ni phase diagram (Fig. 1). To obtain the fiber-reinforced structure we brought the alloy to equilibrium at temperature T_1 where the two metals are completely miscible in the solid state, quenched it to room temperature, and then annealed it at temperature T_2 just inside the miscibility gap. At this temperature the equilibrium form of the alloy consists of two phases of compositions, C_1 and C_2. These two phases are formed by diffusional processes from the unstable solid solution. The Ni-rich phase of composition C_2 appears in the form of fibers a few tenths of a micron in diameter in a matrix of the Au-rich phase of composition C_1. The intermediate step at room temperature is a matter of convenience and, as far as we know, not an essential part of the process.

When this initial work on Au-Ni alloys was first presented (*1*), we had no understanding of the details of the diffusional processes which led to the formation of the fibers. Neither did we know whether fiber-reinforced alloys could be prepared in other binary systems in the same way. Now, however, we present two new sets of results. The first clarifies the fiber formation mechanism in Au-Ni alloys, and the second shows that our technique can be used to prepare a fiber-reinforced Al-Zn alloy.

The evidence relating to fiber formation in Au-Ni alloys was obtained when we extended our original study to an alloy containing 40 atom percent Ni. Specimens were solution treated at 1000°C, quenched to room temperature, and aged for 1 hour at various temperatures within the miscibility gap. They were then polished, etched, and examined by replica electron microscopy with a Philips EM 200B microscope. In some specimens the kinetics were such that the reaction was complete in 1 hour, but in others it was not. Where the reaction was incomplete, a sharp reaction interface was created (*1, 2*), since the reaction nucleates at grain boundaries and then spreads inward into the grains. Special attention was paid to these reaction interfaces because in them the sequence of events leading to the formation of the fibers could be seen most clearly.

From this study of the reaction interface and of the specimens which had reacted completely, the following picture of fiber formation emerged. First, small spherical particles precipitated at the interface. They then formed into

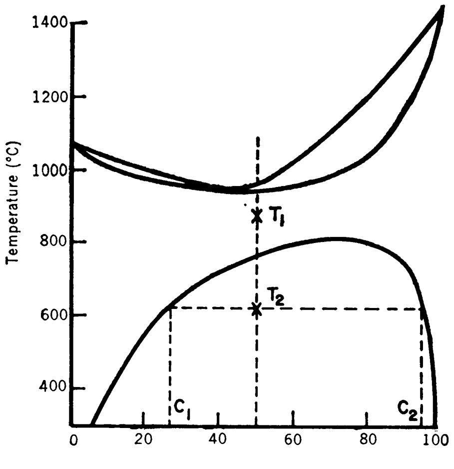

Fig. 1. Phase diagram for the Au-Ni system.

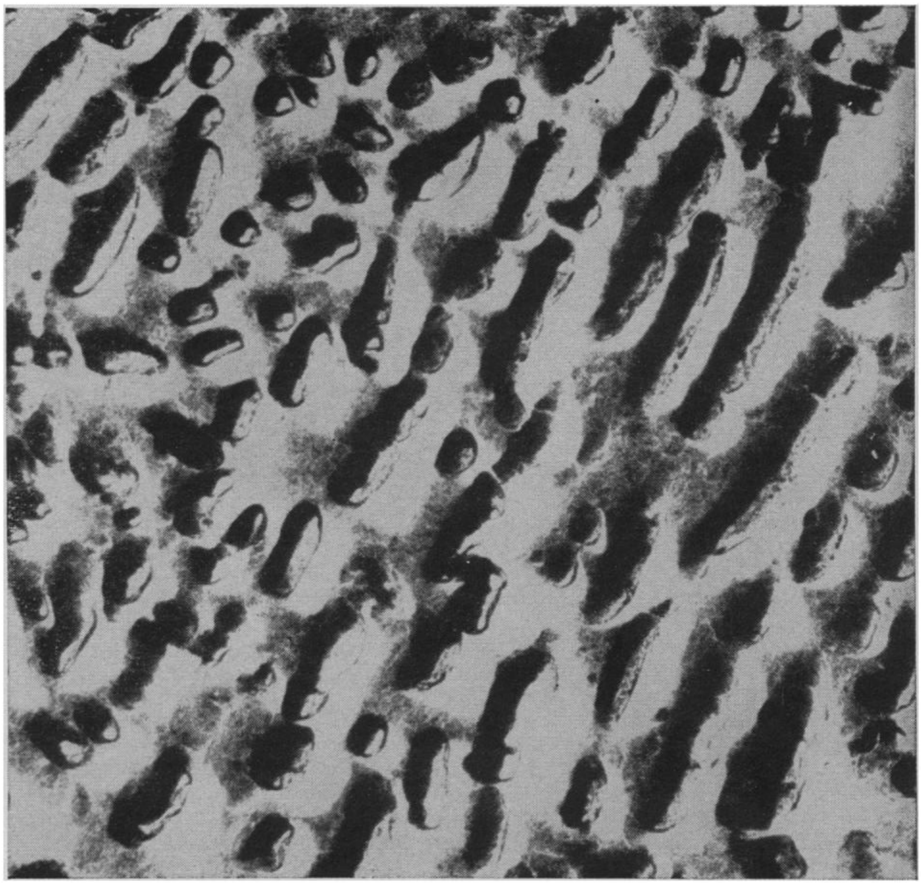

Fig. 2 (right). Replica electron micrograph of a Au-Ni alloy containing 40 atom percent Ni and showing the partial alignment and coalescence of spherical Ni-rich precipitate particles during the formation of Ni-rich fibers (magnification, × 30,000).

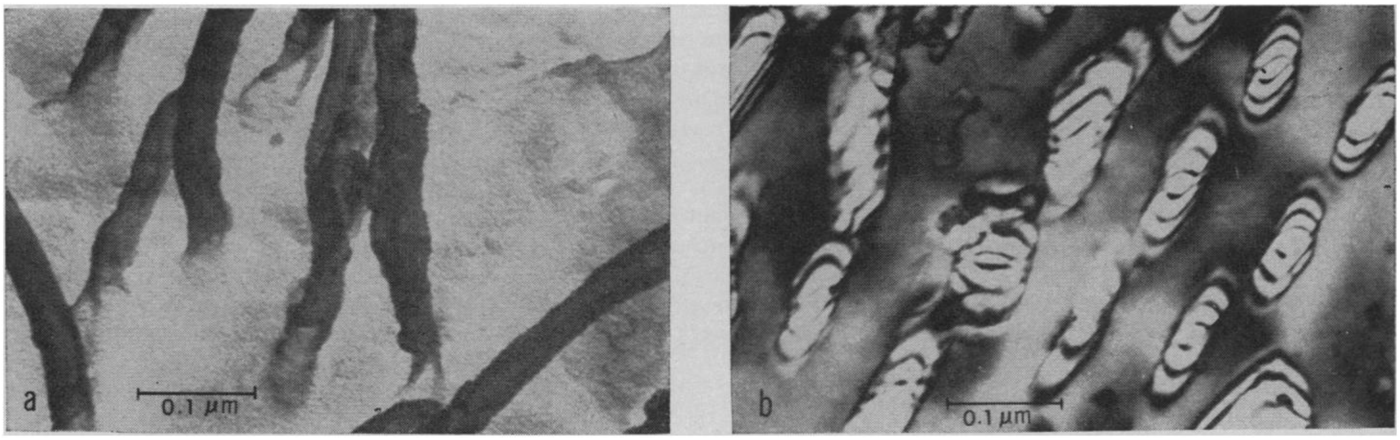

Fig. 3. The structure of a fiber composite Al-Zn alloy containing 22.5 atom percent Zn. (a) A replica electron micrograph and (b) a transmission electron micrograph showing the structure of a thin foil specimen after the fibers have been etched away.

parallel linear arrays and began to coalesce. Finally, the coalescence (Fig. 2) was completed, and irregularities in the fiber surfaces became smoothed out.

At first sight it is surprising that parallel fibers should be formed as one of the equilibrium products of a solid state reaction in an alloy. If this morphology represents a thermodynamic equilibrium state of the alloy at the reaction temperature, the only reasonable interpretation is that the precipitate-matrix interfacial energy is highly anisotropic. In discussing the earlier set of results on Au-Ni alloys, we tentatively adopted this point of view (*1*) and pointed out that our results implied that any other alloy system exhibiting fibrous precipitates would also have to have strongly anisotropic precipitate-matrix interfacial energy. In the light of our new results on the formation mechanism of the fibers we offer a rather different interpretation of both sets of results.

That the formation of the fibers proceeds in several reasonably well defined steps implies, according to thermodynamic theory, that each step results in a reduction in the free energy of the alloy. It is therefore pertinent to examine each step and to consider how the reduction in free energy comes about. Initially the thermodynamic driving force for the reaction is the difference in chemical free energy between the solid solution and the two reaction products. When the spherical precipitate particles appear, much of this free energy is released, but some is taken up in creating the new precipitate-matrix interfaces and some more appears as elastic strain energy in the strain fields that develop around each particle. At this point the alloy is probably quite close to chemical equilibrium but by no means in thermodynamic equilibrium.

A further reduction in free energy accompanies the alignment of the spherical particles. This effect has been observed in an Al-Ni alloy by Ardell and Nicholson (*3*), and a theoretical treatment has been worked out by Eshelby (*4*). The energy liberated is part of the elastic strain energy surrounding the particles. The origin of the thermodynamic driving force for the coalescence of the particles is less obvious. Intuitively one might suppose that there is a further reduction in energy because part of the strain field of each particle is relieved on coalescence (*5*), but this could be largely offset by the energy required to form the larger interfacial areas of the fibers. The exact mechanism by which the coalescence occurs is also obscure at present. One possibility is that each particle elongates until it touches its neighbor. Another is that the matrix at this point is still slightly supersaturated with Ni, providing the extra Ni needed for each particle to grow sufficiently to impinge upon its neighbor. When impingement has occurred, the "bumpy" fibers that have been formed develop into smooth fibers, presumably by an interfacial and a volume diffusion mechanism. The thermodynamic driving force for this mechanism is obviously the reduction in interfacial energy resulting from the reduced surface area of each fiber.

This line of thought necessarily leads one to question whether the fiber composite structures obtained in these experiments are themselves truly equilibrium structures. Is it possible, for example, that, if the specimens had been held at the reaction temperature for longer periods, some other variations in morphology would have developed? If the interfacial energy, as well as the strain energy, is isotropic, it might be quite reasonable to assume that in time each fiber would develop into a large spherical particle.

Our second set of results was obtained with an Al-Zn alloy containing 22.5 atom percent Zn (*6*). The phase diagram for this system is more complex than that for the Au-Ni system, but it is such that at moderately high temperatures solid solutions containing up to about 50 atom percent Zn can be prepared. The dissociation of one of these solid solutions at lower temperatures can occur in a variety of ways, depending on the temperature. The best known involves the formation of small spherical Zn-rich Guinier-Preston zones. However, our alloy was solution treated at 400°C and then held at 200°C for 1 hour or less. Under these conditions the chemical equilibrium phases appear to form directly without intermediate metastable phases such as the Guinier-Preston zones. These equilibrium phases are almost pure Zn and a dilute solution of Zn in Al. The Zn is precipitated in a matrix of the Al-rich solid solution, the reaction being nucleated at grain boundaries just as in the Au-Ni alloys.

Figure 3a shows the Zn-rich fibers in one of the specimens examined by replica electron microscopy. Thin foils prepared from similar specimens by electropolishing were examined by transmission electron microscopy. During the electropolishing process the fibers were dissolved away, and roughly cylindrical channels through each specimen were left (Fig. 3b). The cylindrical shape of the channels is clearly demonstrated by their associated extinction contours. Their shape was further confirmed by taking stereoscopic pairs and examining them in a stereo viewer. Conclusive evidence as to the fiber formation mechanism in this alloy has not yet been obtained, but some of the replica electron micrographs obtained suggest that it may be the same as in the Au-Ni system.

Eventually fiber-reinforced alloys in a wide range of other alloys may be prepared with our technique. The straightforward approach is to prepare the fibers first, often by growth from the vapor phase, and then to permit an appropriate matrix material to solidify around them. This is a difficult and costly process, and it is therefore desirable to devise methods of growing the fibers *in situ*. During the past few years some progress in this direction has been made with unidirectional solidification of eutectic alloys (*7*), but this approach is of limited value because the volume fraction of fibers obtainable is fixed by the necessity of using alloys at or near eutectic compositions. Our technique involves only heat treatment in the solid state, and the volume fraction of fibers can be varied over a wide range with variation of the alloy composition.

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Lead Effects on Corn Mitochondrial Respiration

Abstract. *Oxidation of exogenous nicotinamide-adenine dinucleotide and succinate by corn mitochondria was measured as a function of lead chloride concentration. Lead chloride (50 to 62 micromoles per liter) stimulated oxidation of exogenous reduced nicotinamide-adenine dinucleotide by 174 to 640 percent depending on the reaction mediums, whereas lead chloride (12.5 micromoles per liter) inhibited succinate oxidation by more than 80 percent. When inorganic phosphate was included in reaction mediums the subsequent addition of lead was without effect due to the low solubility of lead phosphate. If addition of lead was followed by addition of phosphate the inhibition of succinate oxidation by lead was released, but there was no reduction in the stimulation of oxidation of reduced nicotinamide-adenine dinucleotide by lead. The effects of lead on plant growth might be accentuated under conditions of phosphate deficiency.*

Each year motor vehicles in the United States liberate approximately 225×10^6 kg of particulate lead into the atmosphere. About 50 percent of this lead is deposited within 30 m of the roadways (*1*), and the remainder is scattered over large areas. Lead accumulation in soils near roads varies with traffic volume and decreases rapidly with distance from the road. Lead has been found at concentrations of 128 to 700 ppm in soil adjacent to 12 highways in the Minneapolis-St. Paul area (*1*). Grass collected near an intersection of two heavily traveled highways near Denver, Colorado, contained as much as 3000 ppm lead, and at Canandaigua, New York, 16 vegetable samples from gardens less than 50 feet (15.2 m) from roads averaged 115 ppm lead and ranged from < 10 ppm to 700 ppm (*2*).

Vegetation near roads might be in danger if the present trend continues. Inhibitions of various animal enzyme systems is attributable to lead (*3*), but little is known of the effect of lead on plant enzyme systems. Hammett (*4*) showed a decrease in root tip mitosis at very low concentrations of lead. This study was therefore initiated to test the effect of lead on substrate oxidation in mitochondria of corn.

Mitochondria were isolated from 3-day-old etiolated corn shoots (*Zea mays* L., WF9 × M14) (*5*). Experiments were performed with the addition of mitochondrial suspensions (approximately 1 mg of protein) and $PbCl_2$ in known concentrations to a completely filled 4-ml glass reaction cell that was temperature controlled ($27° \pm 0.2°C$) and equipped with a Clark oxygen electrode (Yellow Springs). The reaction mediums contained 200 m*M* KCl or 300 m*M* sucrose, 20 m*M* tris (*p*H 7.5), and 1 mg bovine serum albumin (BSA) per milliliter under most conditions. Reduced nicotinamide-adenine dinucleotide (NADH) or succinate was added 4 minutes after addition of mitochondria to the medium, and rates of respiration were determined as a function of concentration of $PbCl_2$.

Micromolar concentrations of $PbCl_2$ influenced oxidation of both exogenous NADH and succinate in either KCl- or sucrose-containing mediums. The effect of lead was not the same on the two substrates tested, even though both are donors in electron transport. In a KCl medium, succinate oxidation was inhibited 37 percent by 6 μM $PbCl_2$, and 100 percent by concentrations of 25 μM or greater (Table 1). Oxidation of exogenous NADH by mitochondria in a KCl medium was stimulated 174 percent by 62 μM $PbCl_2$, with some stimulation (28 percent) at $PbCl_2$ concentrations as low as 6 μM (Table 2). Even greater stimulations of oxidation of exogenous NADH were found with mitochondria suspended in a sucrose medium (Table 2). Oxidation of succinate was inhibited in sucrose as it had been in KCl and was independent of the presence of BSA (Table 1).

Studies measuring oxidation of exogenous NADH and succinate in a diaphorase reaction with 2,6-dichlorophenolindophenol as the electron acceptor, and 1m*M* KCN as the regular blocker of electron transport, gave results similar to those obtained by measuring oxygen uptake. In whole mitochondria oxidation of exogenous NADH was stimulated, but oxidation of succinate was inhibited. Even when mitochondria were disrupted by high-frequency sound for 2 minutes and centrifuged at 46,000*g* for 30 minutes, the supernatant maintained activity of NADH diaphorase that was stimulated 12 to 25 percent by 62 μM $PbCl_2$.

The diaphorase reaction is a general reaction that is catalyzed by flavoprotein and involves, among others, flavoproteins from the first part of the electron-transport chain. Since these flavoproteins are utilized solely in the diaphorase reaction, and are a part of the