Mechanical Alloying

Many useful combinations of metals cannot be achieved by melting or by conventional powder metallurgy. Such materials can be made by cold-welding metal powders in a special high-energy ball mill

by J. S. Benjamin

One of the serious limitations of modern technology is the reluctance of some metals to form alloys. For example, it is quite difficult to alloy by conventional techniques a metal with a high melting point and one with a low melting point. Even though two such metals may form a solution in the liquid state, the metal with the lower melting point tends to separate out in the course of cooling and solidification. Over the past few years a new technique of combining metals has been developed that circumvents many of the limitations of conventional alloying. Called mechanical alloying, it creates true alloys of metals and metal oxides that are very difficult or impossible to combine by other means. Mechanical alloying has produced high-strength superalloys for jet engines, and there is good reason to believe the technique will find a rich diversity of other applications.

It was discovered early in human history that the use of certain copper ores in smelting resulted in a metal with properties superior to those of metal produced from other copper ores. This was owing to the unrecognized presence of traces of arsenic and antimony. Hence some "copper" was in fact an alloy rather than a pure metal. In particular the melting point of the alloy was lowered, making it easier to cast, and the strength of the alloy was increased, making it more useful for weapons and tools. Somewhat later tin was deliberately alloyed with copper to produce bronze.

Today the large majority of alloys are still made by heating different metals together to temperatures above their melting points so that they form a solution with each other. For combinations of metals that resist such alloying metallurgists have resorted to the mechanical blending of powders, for example mixing powdered tungsten carbide, which has a high melting point, with powdered cobalt, which has a low melting point. The mixed powders are formed into solid metal by the application of high pressure and heat. These two operations can be performed in sequence (cold-pressing and sintering) or simultaneously (hot-pressing). The result is an alloy consisting of discrete particles of tungsten carbide embedded in a matrix of cobalt.

When solid articles are made from blends of different metal powders, the degree of homogeneity attained in the final product is limited by the size of the particles in the powders. If the particles are too coarse, the different ingredients will not interdiffuse during consolidation or prolonged heating. This problem can be overcome to some extent by starting with very fine powders.

One way to make a fine metal powder is to grind a coarse powder in a ball mill. There is, however, a practical limit to the fineness of the powder that can be obtained in this way: the particles begin to weld together as the milling continues. Sometimes lubricants such as kerosene or fatty acids are added to prevent the particles from coming in contact. Although lubricants make finer grinding possible, they may severely contaminate the powders and degrade the alloy made from them. Another serious limitation on fine grinding is the tendency for fine metal powders to burn spontaneously.

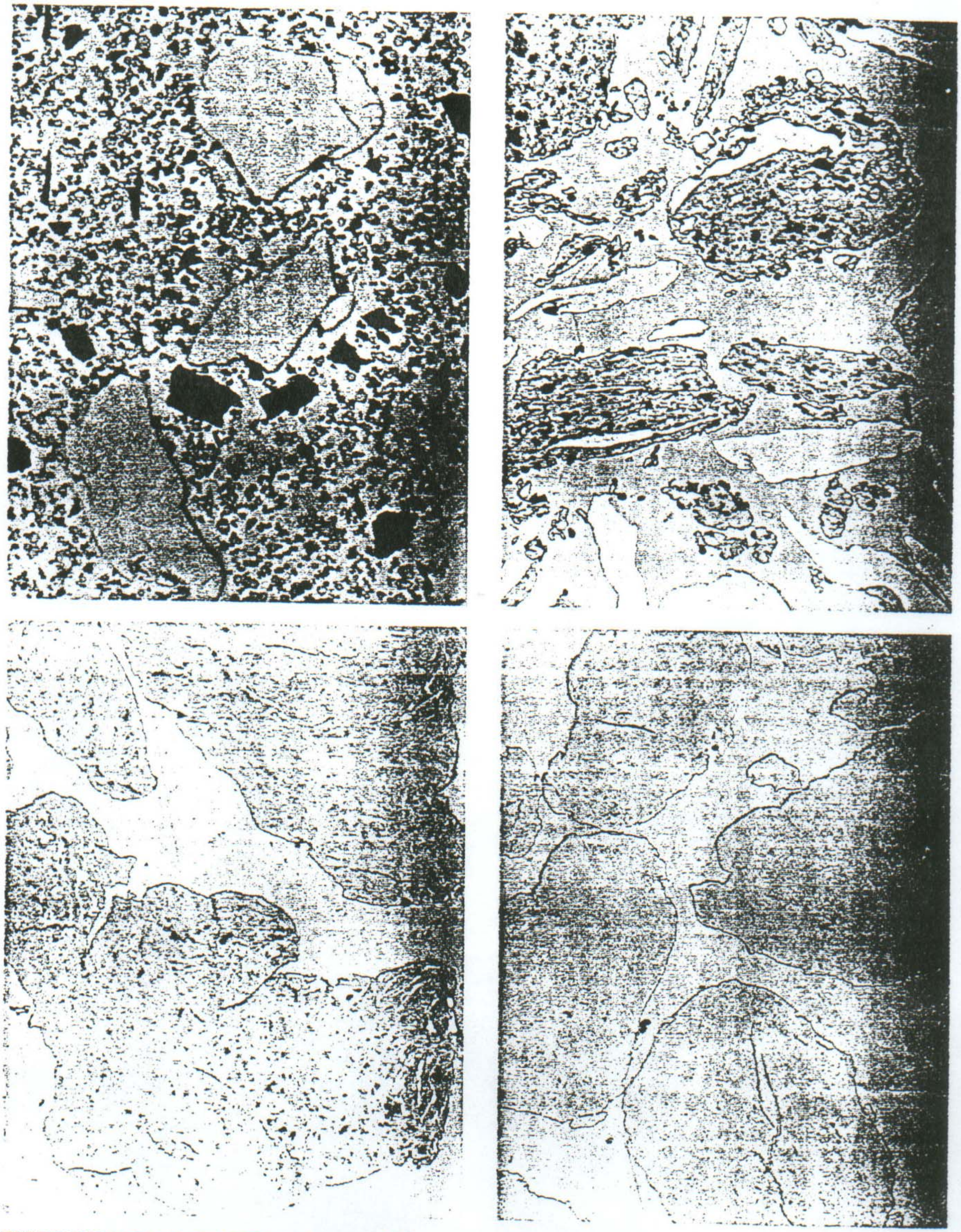
Mechanical alloying was developed as a means of overcoming the disadvantages of powder-blending without encountering the difficulties associated with ultrafine powders. It was found that when certain combinations of metals were milled together in the absence of a lubricant, they tended to form metal composites. Hard powders such as tungsten carbide, which normally do not form composites, can be made to form a solid with a soft powder such as cobalt by tumbling a mixture of the powders in a ball mill. Because the rolling and falling balls in a conventional ball mill have a limited energy, however, the formation of composites in this way took an exceptionally long time. For example, to produce a fine dispersion of tungsten carbide in cobalt by conventional milling one must first intensively mill the carbide so that it is broken down into fine particles before the cobalt is added.

In order to accelerate the formation of metal composites, to eliminate the dependency of final powder homogeneity on initial powder size and to avoid the hazards of fine powders, my colleagues and I at the Paul D. Merica Research Laboratory of the International Nickel Company turned to ball mills that would generate higher energies than conventional ball mills. A conventional ball mill consists of a rotating horizontal drum half-filled with small steel balls. As the drum rotates, the balls drop on the metal powder that is being ground; the rate of grinding increases with the speed of rotation. At high speeds, however, the centrifugal force acting on the steel balls exceeds the force of gravity, and the balls are pinned to the wall of the drum. At this point the grinding action stops. A ball mill capable of generating higher energies consists of a vertical drum with a series of impellers inside it. A powerful motor rotates the impellers, which in turn agitate the steel balls in the drum. Such a machine can achieve grinding rates more than 10 times higher than those typical of a conventional mill. Still higher grinding rates can be achieved on a small scale with a high-speed shaker ball mill. Such a mill produces only a few grams of powder, but it is a useful tool for testing new processes.

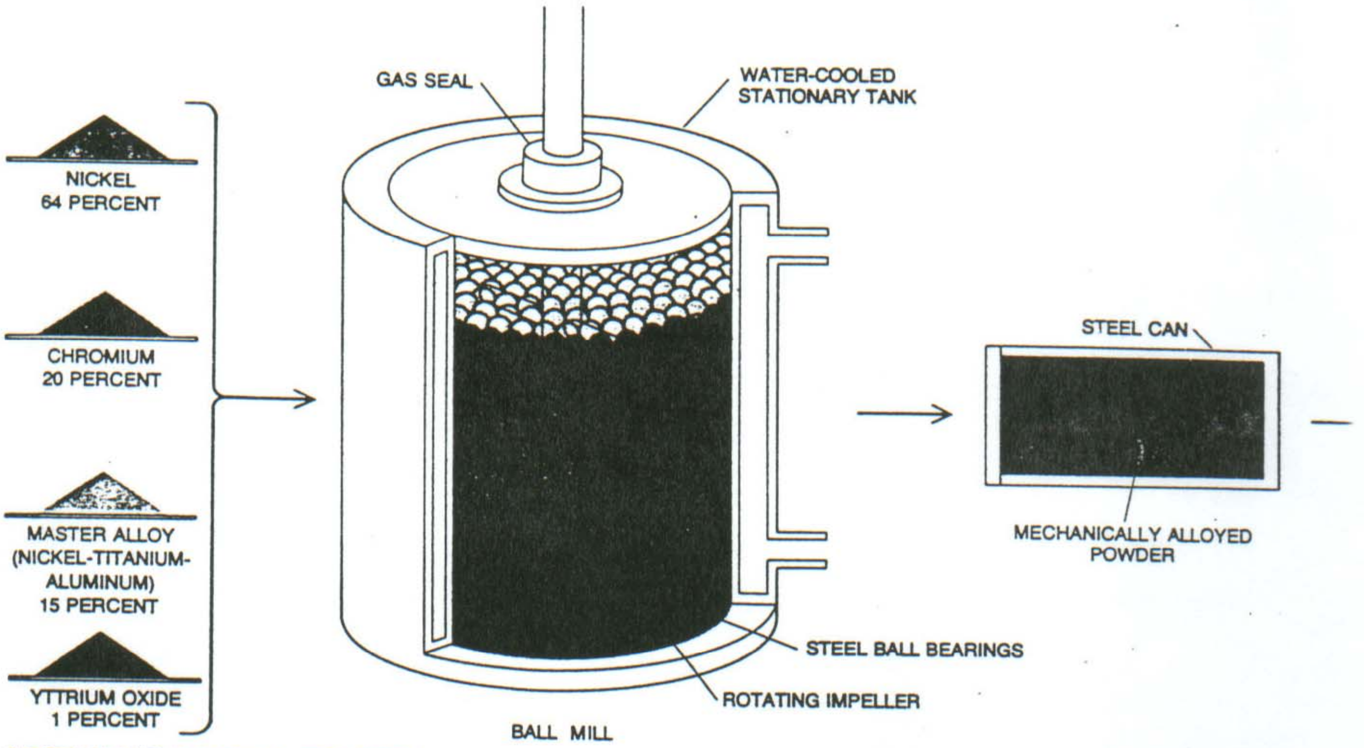
In a high-energy mill the particles of the metal powder are repeatedly flattened, fractured and rewelded. Every time two steel balls collide they trap powder particles between them. The force of the impact deforms the particles and creates atomically clean new surfaces. When the clean surfaces come in contact, they weld together. Since such surfaces readily oxidize, the milling operation is conducted in an atmosphere of nitrogen or an inert gas.

At early stages in the process the metal powders are still rather soft, and the tendency for them to weld together into larger particles predominates. A broad range of particle sizes develops, with some particles being two to three times larger in diameter (10 times larger in volume) than the original ones. As the process continues the particles get harder, and their ability to withstand deformation without fracturing decreases. The larger particles are more likely to incorporate flaws and to break apart when they are struck by the steel balls. In time the tendency to weld and the tendency to fracture come into balance, and the size of the particles becomes constant within a narrow range.

The composite particles that are formed by the welding of smaller particles have a



WELDING OF METAL PARTICLES and refinement of their structure during mechanical alloying are shown in this sequence of micrographs. (The metal particles were embedded in plastic and then polished and etched to bring out the different colors.) The particles in the raw powders (*upper left*) vary in size. The large gold particles are chromium, the purple and magenta particles are an alloy of nickel, aluminum and titanium and the small pink particles are nickel. After half an hour of processing in a high-energy ball mill most of the chromium and alloy particles are welded together in a matrix of nickel (*upper right*). After four hours of processing, all the ingredients have been welded together (*lower left*). After 10 hours the individual ingredients of the composite particles are nearly invisible (*lower right*). The uniform color of the particles indicates that a true alloy has been formed. The enlargement of the micrographs is about 250 diameters.

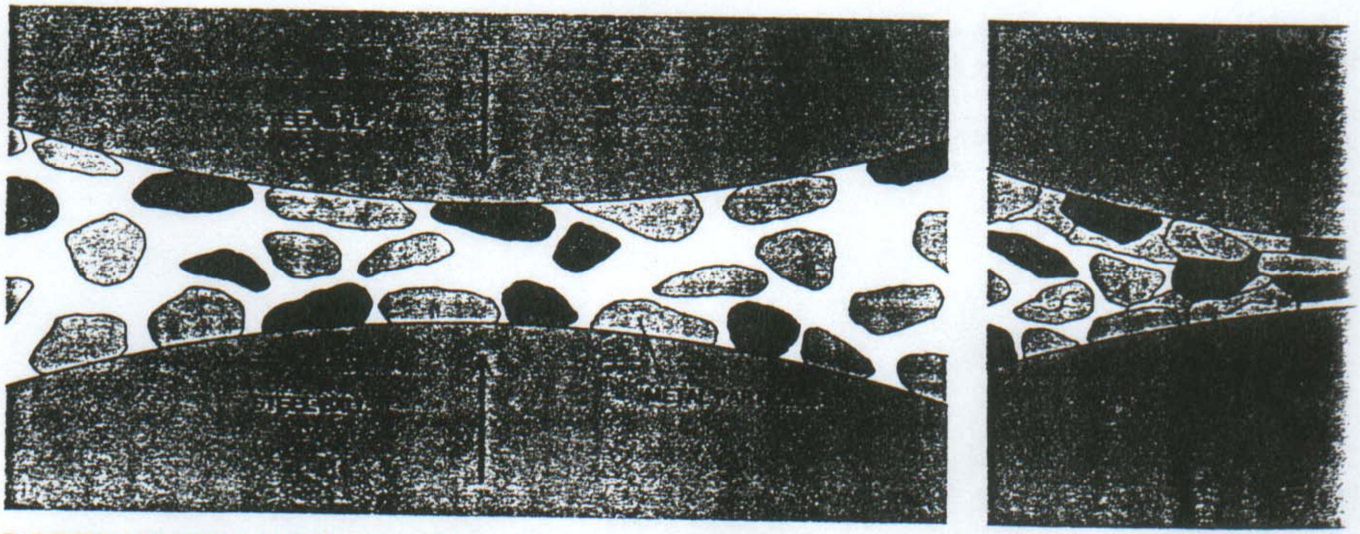


MECHANICAL-ALLOYING PROCESS for making a superalloy begins with grinding metal powders in a high-energy ball mill for about 20 hours. The mechanically alloyed powder is sealed in a steel can and formed into a metal bar by hot-extrusion. The extruded bar is

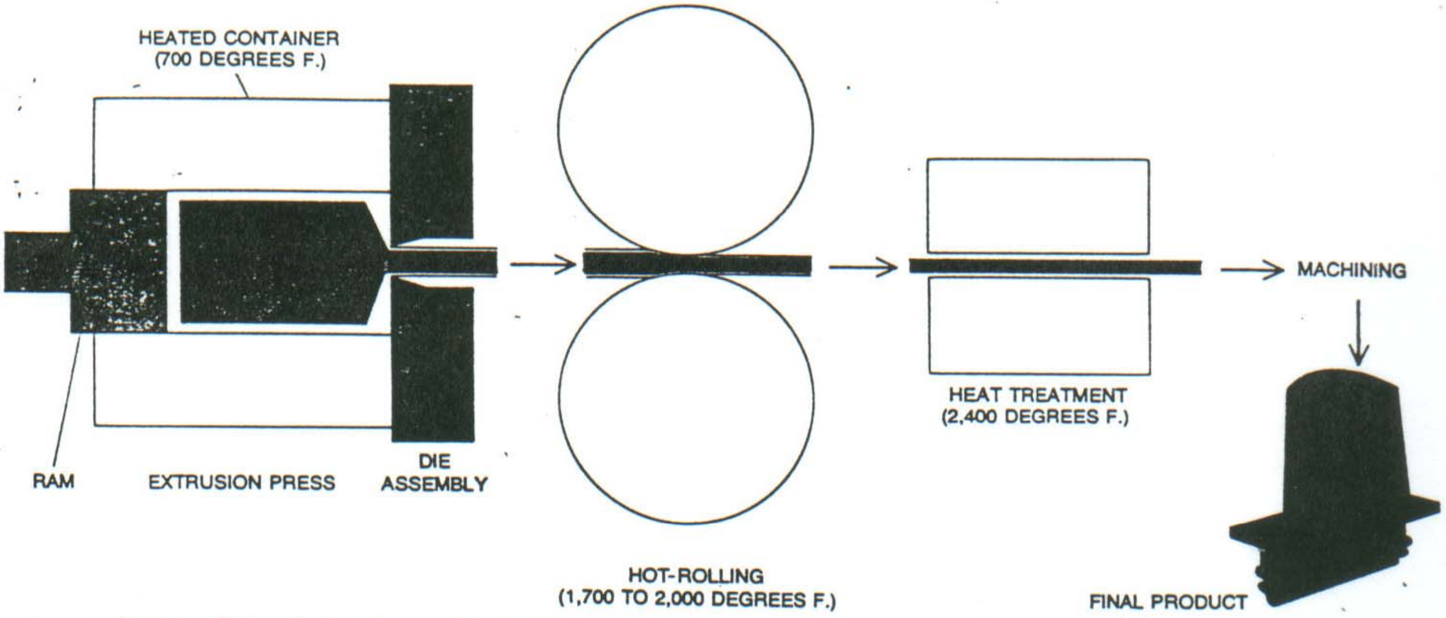
characteristic layered structure. Although there is little change in the size of the particles after the balance between welding and fracturing is attained, the structure of the particles is steadily refined. The thickness of each layer in the composite particles decreases because of the repeated impact of the steel balls, and at the same time the number of layers within each particle increases. The rate of refinement of the internal structure of the particles is roughly logarithmic with processing time. As a result the penalty for starting with coarser powders is not severe. For example, when the particles are initially some nine micrometers in diameter, it takes about 48 minutes to process them in a high-energy shaker mill, and increasing the size of the particles by a factor of 10 increases the processing time by only 22 minutes.

There is a slight tendency for the rate of refinement of the internal structure to decrease after a long period of processing because the particles get exceedingly hard. The hardness is the result of the accumulation of strain energy. Eventually a constant value called the saturation hardness is attained.

My colleagues and I have followed the refinement of the structure in mechanical alloying to the point where the layers in the particles cannot be resolved by light microscopy. It could be assumed that with further processing the powders still consist of discrete fragments of ever decreasing size, but that is not the case. John H. Weber and E. Lee Huston of our laboratory have shown that true alloying has



PARTICLES OF METAL POWDER in a ball mill are trapped between colliding steel balls. The force of the impact flattens the particles. The deformation spreads out the surface of the particles, creating gaps in the layer of adsorbed gases and exposing atomically clean metal. Where the clean surfaces come together cold pressure welds are formed. The force of the impact also causes some particles to frac-



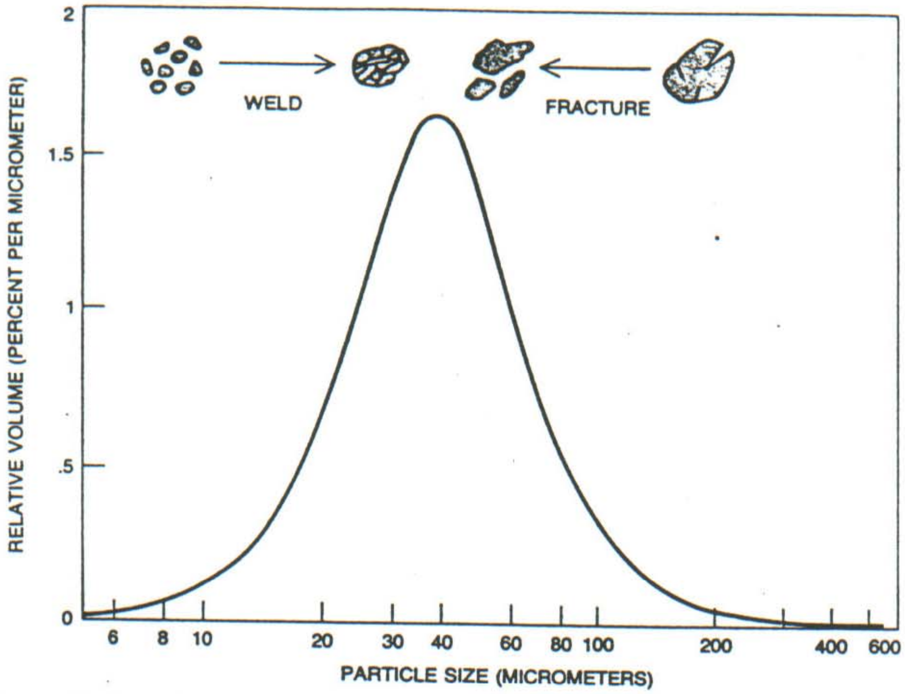
reduced in thickness by hot-rolling. The steel jacket of the bar is removed before the bar is annealed. During annealing the superalloy develops coarse grains that improve its strength at high temperatures. The product, a jet-engine blade, is machined from a section of the bar.

reached a significant point when the layers of a particle can no longer be optically resolved. In their experiment they worked with a mixture of nickel, which is magnetic, and chromium, which is nonmagnetic and destroys the magnetic response of nickel when alloyed with it. Weber and Huston processed the metals in a high-energy ball mill that produced a homogeneous powder in 10 to 15 hours. The magnetic response of the nickel decreased rapidly in the early stages of the processing. As the layers of nickel and chromium in the composite particles were brought into more intimate contact, more of the nickel was demagnetized. When the layers could no longer be resolved optically, the magnetic response had reached a value as low as that of a completely homogeneous nickel-chromium alloy produced by melting and working. This showed that the two metals were now intimately mixed on an atomic level. They had formed a true solid solution rather than a mixture of fine fragments.

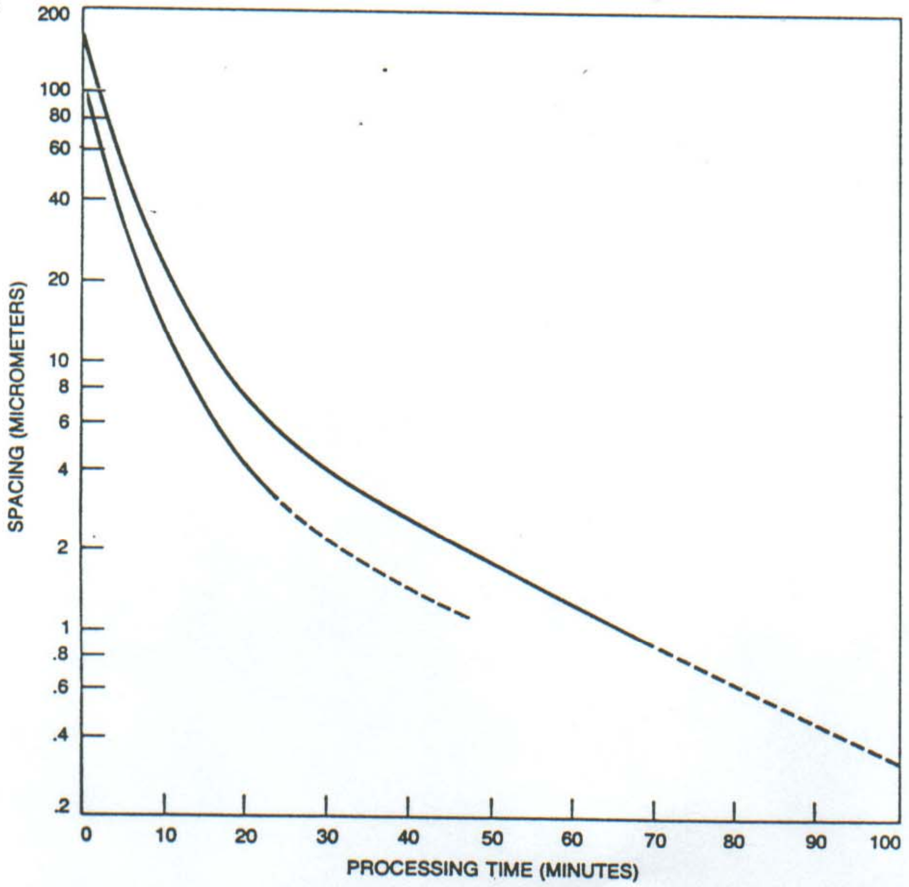
There is surprisingly little contamination of the powder by the iron in the steel grinding balls. In the course of the grinding process the balls become coated with a layer of the metals in the mixture. This layer and the free powder that is trapped in each collision absorb most of the energy when the balls collide.

Although mechanical alloying can produce composite metal particles with a homogeneous internal structure, there is no particular advantage in applying the technique to many combinations of metals, including the combination of nickel and chromium. The same results can be obtained by

ture. The repeated flattening and rewelding of the particles build up composite particles with a characteristic layered structure. The micrograph at the right shows the result of processing iron powder (*dark particles*) and chromium powder (*light particles*) in a high-energy shaker ball mill for a few minutes. Even in this early stage of processing, cold welds between particles of iron and chromium are evident.



BALANCE BETWEEN WELDING AND FRACTURING is achieved during mechanical alloying, which leads to a relatively constant particle size. Smaller particles are more likely to be able to withstand deformation without fracturing when they are struck by the steel balls, and they tend to be welded into larger pieces. Larger particles, on the other hand, are more likely to have flaws and to fracture when they are struck. The overall tendency is therefore to drive the very fine particles and the very large particles toward the middle of the size distribution.



REDUCTION IN THICKNESS of the layers within a composite iron-chromium particle during mechanical alloying is approximately logarithmic with time (*black curve*). The average spacing of the layers is about twice the average spacing of the welds (*colored curve*) because of the formation of chromium-chromium and iron-iron welds that do not decrease layer spacing.

conventional means. The value of mechanical alloying becomes apparent when one attempts to make an alloy that cannot be made any other way.

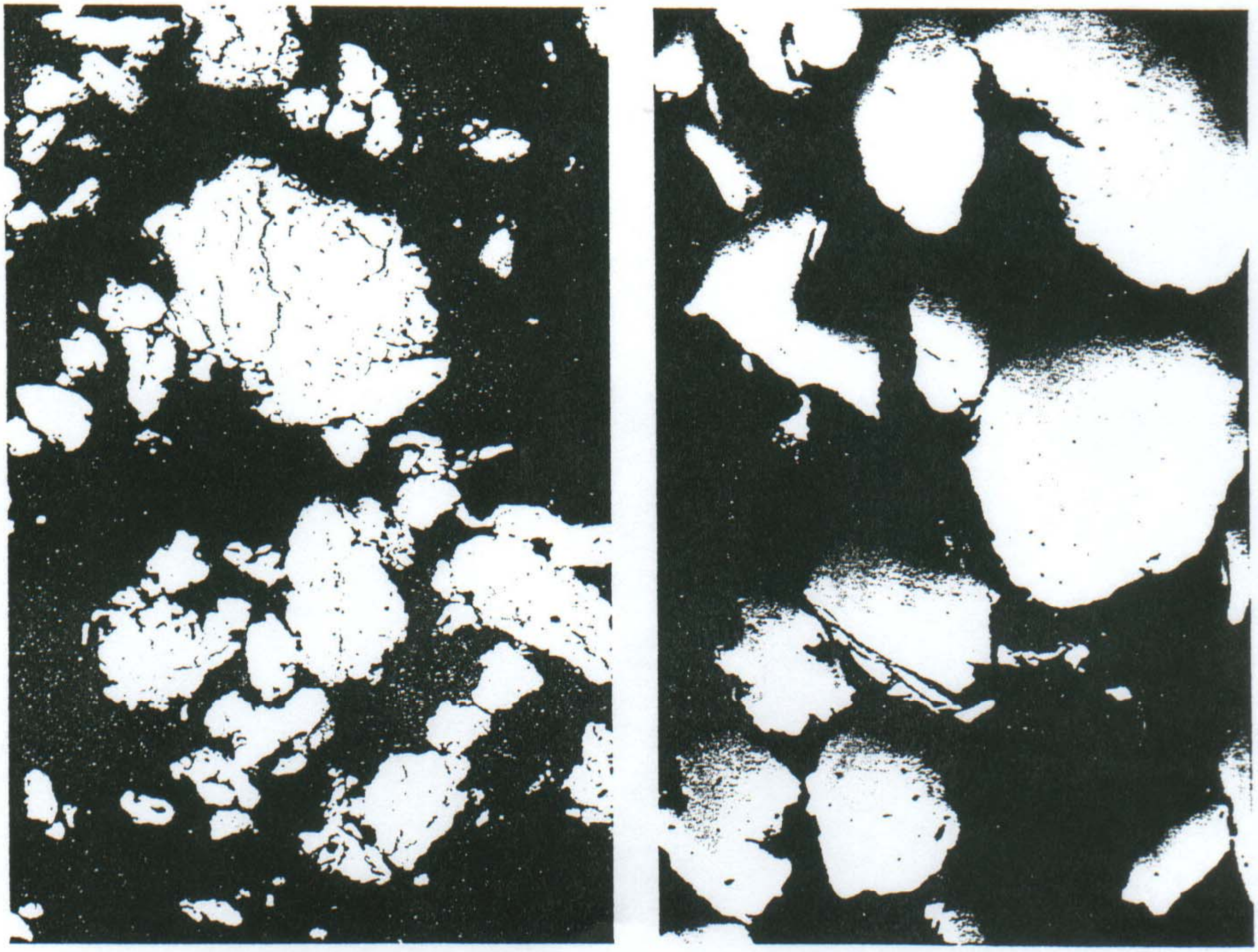
There are some applications where high strength at temperatures approaching the melting point of a metal can be of great value. For example, the propulsive thrust and fuel economy of a jet engine can be greatly improved if the engine can be operated at higher internal temperatures. One component of a jet engine that limits its internal operating temperature is the turbine blades. These blades are small airfoils that extract energy from the stream of hot gas passing through the engine. They are located at the periphery of the spinning turbine rotor, where they are subjected to a rigorous combination of stress, temperature and hot, corrosive exhaust gases. Under these conditions turbine blades tend to creep, that is, to gradually extend with time, and they can be seriously damaged by attack from the oxygen and sulfur in the hot exhaust gas.

Most jet-engine turbine blades are currently made out of nickel-base alloys containing small but critically important amounts of chromium, aluminum and titanium. These alloys are strong enough at moderate temperatures and resist corrosion by the hot gases, but they lack strength at higher temperatures. It has long been known that the high-temperature strength of metals can be greatly improved by dispersing a very fine stable oxide in them. Dispersion-strengthened nickel containing thorium oxide or yttrium oxide has good strength at high temperatures, but its ability to withstand stress at lower temperatures is poor. In addition dispersion-strengthened nickel does not possess adequate resistance to corrosion by hot exhaust gases.

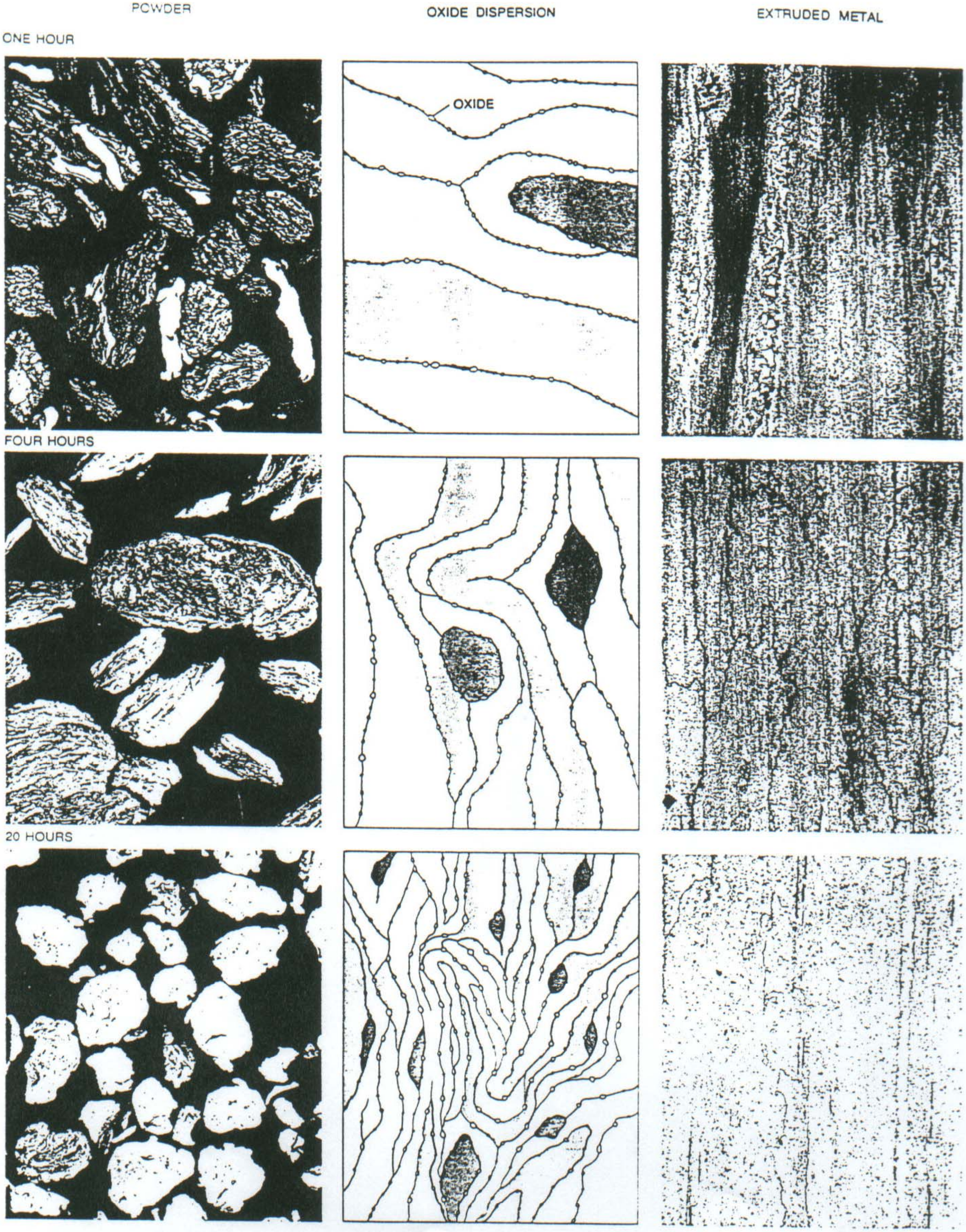
An alloy that combines the properties of nickel-base alloys and those of dispersion-strengthened nickel has been a goal of metallurgy for many years. Such an alloy, however, cannot be made by conventional means. Simple mixing techniques do not disperse the oxide well enough, or they require a powder so fine that it burns spontaneously, or they introduce so much contamination that reactive metals such as aluminum and titanium are also converted into oxides. Aluminum and titanium oxides are so stable that they cannot be reduced to the metallic state required in an alloy without reducing the deliberately dispersed oxide as well.

We attempted to produce a dispersion-strengthened nickel-base superalloy by simply blending a very fine high-purity nickel powder, a fairly coarse chromium powder, a master-alloy powder of nickel, aluminum and titanium and a very fine powder of yttrium oxide. The powders were hot-extruded into a bar, which was then heat-treated in an attempt to force the chromium, aluminum and titanium to diffuse into the nickel. The result was an inhomogeneous product

REFINEMENT OF INTERNAL STRUCTURE of composite iron-chromium particles at various stages of mechanical alloying is shown enlarged about 160 diameters. After five minutes of processing (*left*) the structure of the welded particles is still coarse. After about 20 minutes the particles have developed a striated structure (*middle*). The thickness of the layers continues to be reduced, and after 100 minutes of processing, the composite particles have been refined to the point where individual layers of iron and chromium are barely visible.



POWDERS FOR A HIGH-TEMPERATURE SUPERALLOY are shown at an early stage of mechanical alloying (*left*). The initial ingredients can be seen within the composite particles. Some fragments are still unprocessed. When alloying is completed, the powders have been processed to visual homogeneity, and individual layers within the composite particles cannot be resolved with a light microscope.



DISPERSION OF A REFRACTORY OXIDE at various stages of mechanical alloying is depicted. The oxide particles become trapped in the welds of the composite particles. After an hour of processing, the welds are far apart and the concentration of the oxide particles at the welds is fairly dense. A metal bar made from this powder consists of fine crystals and large fragments and is unsuitable for high-temperature applications. After four hours of processing, the welds have moved closer together and the spacing of the oxide particles has increased. Consolidation of the powder and heat treatment yield a metal bar that has a coarser crystalline structure but still shows some striations where certain constituents have not been adequately dispersed within the crystals. Finally, after 20 hours of processing, the oxide is evenly distributed along the welds. A metal bar made from this powder has a fine, uniform structure with coarse, elongated crystals.

with none of the desired high-temperature properties.

We now processed the same blend of powders in a high-energy ball mill. When such a mixture is mechanically alloyed, the degree to which its various constituents maintain their form depends on their relative hardness and their ability to withstand deformation. Nickel, which is the softest constituent of the mixture, is the cement that binds the other constituents together. Chromium is somewhat harder and less ductile than nickel, so that it tends to form platelike fragments that are embedded in the nickel. The master alloy of aluminum, titanium and nickel is the most brittle constituent; it tends to break up into small rectangular fragments that also become embedded in the nickel.

The yttrium oxide disperses along the welds in the composite particle. At first the welds are far apart, and the concentration of the oxide particles at each weld is rather dense. With further processing the spacing between the welds decreases, but the spacing of the oxide particles along each weld increases. Finally, when the powder has been processed to the point where the welds cannot be detected with a light microscope, the spacing between the welds is less than half a micrometer, a distance about equal to the spacing of the oxide particles along the welds. This nearly random dispersion of oxide particles in the metal matrix cannot be enhanced by further processing. At this point the powder is considered to be adequately processed for a dispersion-strengthened superalloy.

The effective dispersion of an oxide within a nickel-base alloy is only the first step in obtaining the full benefits of the material. When the mechanically alloyed powder is converted into a metal bar by hot-extrusion, the grain structure of the extruded bar is very fine. In order to gain the maximum high-temperature strength the grains must be induced to recrystallize to make them coarser. That can be achieved by reducing the thickness of the metal bar by hot-rolling and then annealing it at about 2,400 degrees Fahrenheit for about 30 minutes. The bar develops quite coarse grains that are elongated in the direction of extrusion.

More complex dispersion-strengthened nickel-base alloys can be made by mechanical alloying. In addition to nickel, chromium, aluminum, titanium and yttrium oxide, other elements such as tantalum, molybdenum and tungsten, which give added strength at lower temperatures, can be incorporated. We made such a complex alloy and found that it combined the high strength of nickel-base alloys at moderate temperatures and the strength characteristics of dispersion-strengthened nickel at high temperatures. In addition the mechanically alloyed material had superior corrosion resistance. These results demonstrate that the long-sought combination of high- and low-temperature strength in alloys can be achieved by the mechanical-alloying process.

The mechanical-alloying process is not limited to the production of nickel-base superalloys. Indeed, the process should be viewed as a new means of assembling many metal composites with controlled microstructures. The ways in which mechanical alloying can overcome problems inherent in forming metals by conventional casting, working and heat-treating can best be shown by considering some simple alloy systems. For example, a mixture of equal amounts of copper and lead forms a complete liquid solution at a sufficiently high temperature. Lead, however, has a lower melting point than copper, and a casting made of a copper-lead alloy tends to separate into large blobs of copper and lead even if it is stirred while it is cooling. Mechanical alloying of equal volumes of copper and lead, on the other hand, will give rise to a highly uniform dispersion of fine copper particles in the softer lead matrix. With a much smaller proportion of lead the copper forms the matrix, and the resulting material is similar to the leaded brasses that are used in bearings.

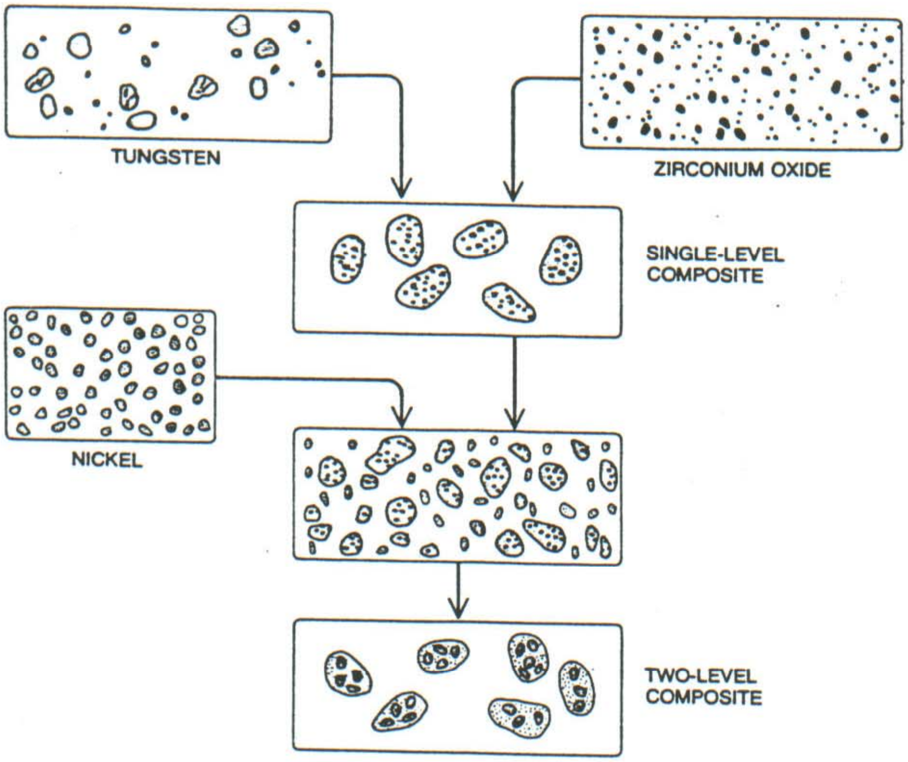
Fine dispersions of one metal in another have been produced by a technique known as solution treatment and aging. The technique takes advantage of the fact that a solid metal will dissolve more of another solid metal at a higher temperature than it will at a lower one. For example, if a mixture consisting of 97 percent copper and 3 percent iron is heated to 1,900 degrees F. and cooled rapidly, the iron will remain dissolved in the copper. If the alloy is later heated to 1,400 degrees F., the iron will be precipitated as fine particles. Unfortunately the technique is limited by the relatively low solubility of solid metals. For example, the maximum amount of iron that will dissolve in copper is about 4 percent. The addition of more iron results in the formation of large, coarse iron particles.

The limitations of the iron-copper system can be overcome by mechanical alloying. Almost any ratio of iron in copper can be achieved in this way. After the iron and copper have been processed in the high-energy ball mill the resulting alloy powder is heated to about 1,200 degrees F. The heat causes the thin plates of iron in the copper matrix to break up into small spheres. The end result is a dispersion of fine iron particles in copper.

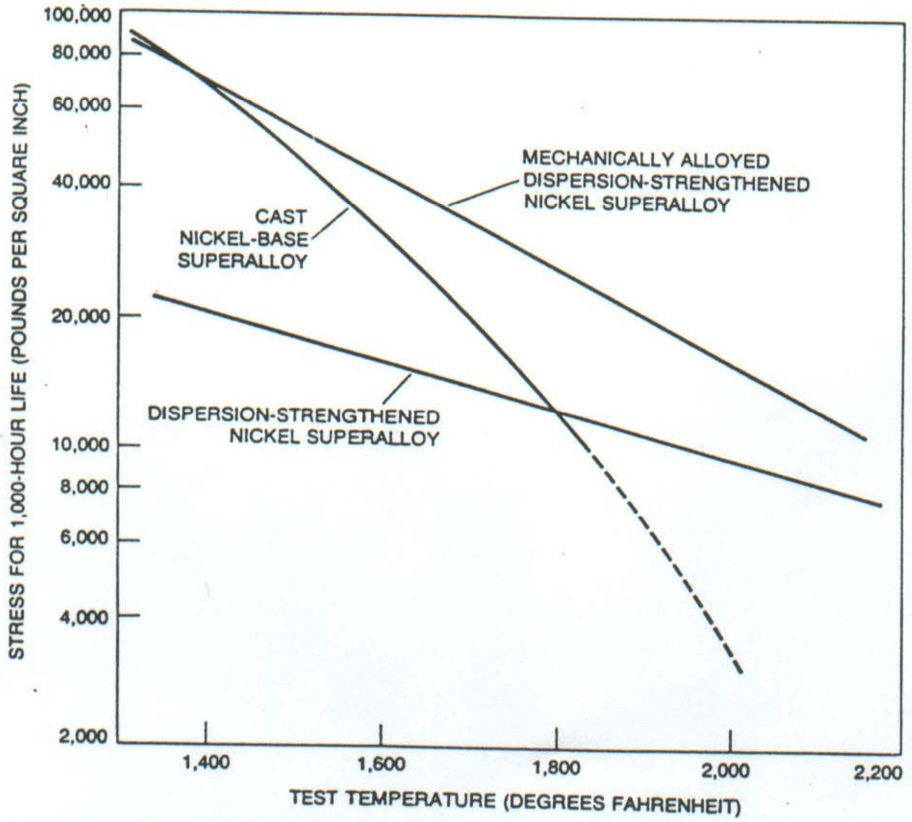
In mechanical alloying soft, ductile metals have a tendency to coat and surround hard, brittle materials. In general softer materials tend to form the matrix and the harder materials disperse within it. This tendency, together with the tendency of mechanically alloyed materials to become harder with increased processing, can be utilized to make complex, multilevel metal composites. For example, if tungsten, a relatively ductile metal, is mechanically alloyed with a very fine zirconium oxide powder, the result is a dispersion of zirconium oxide in tungsten. If nickel powder is now added and is processed with the zirconium oxide–tungsten composite, a two-level composite is formed: the hard, brittle zirconium oxide–tungsten is broken up and dispersed in a continuous matrix of the more ductile nickel. Contact between the zirconium oxide and the nickel is minimal because the zirconium oxide remains coated with tungsten. With a little imagination one can see that the number of levels within such a composite and the relative degree of dispersion of different ingredients that can be obtained by this technique are almost limitless. One potential application for such hierarchical composites might be the production of superconducting materials.

We have produced an austenitic stainless steel by mechanical alloying that is much stronger than conventional Type 304 stainless steel both at room temperature and at elevated temperatures. A potential application for this material might be a skin for

UNPROCESSED POWDERS for a high-temperature superalloy are shown enlarged 160 diameters in the micrograph at left. The fine particles are nickel, the large white particles are chromium and the medium-sized gray particles are a master alloy of nickel, aluminum and titanium. A fine powder of yttrium oxide is also added. Consolidation of a blend of these powders by hot-extrusion results in an inhomogeneous product with no useful properties (*right*).



MULTILEVEL METAL COMPOSITES can be created by mechanical alloying. For example, when tungsten and zirconium oxide are mechanically alloyed, a single-level composite of zirconium oxide in tungsten is produced. During the processing the composite becomes hard and brittle. Following the addition of nickel powder further processing yields an unusual two-level composite: zirconium oxide dispersed in tungsten, which in turn is dispersed in nickel. There is very little contact between the zirconium oxide and the nickel because the zirconium oxide is coated by the tungsten. It is possible to make even more complicated structures in this way.



SUPERALLOY FOR JET-ENGINE BLADES produced by mechanical alloying combines the very high strength of cast nickel-base superalloys at moderate temperatures and the stability and creep resistance of dispersion-strengthened nickel at high temperatures. In addition the mechanically alloyed material exhibits superior resistance to corrosion by exhaust gases.

supersonic aircraft. The superior strength of the material is due in part to an even dispersion of chromium oxide throughout the alloy.

If one considers the mechanical-alloying process from a more general standpoint, its potential uses become even more apparent. Mechanical alloying was first developed in order to add to alloys phases (oxides) that are insoluble in liquids. The tendency of extremely stable compounds not to form solutions with liquid metals is common and is true not only of oxides but also of nitrides and carbides. Mechanical alloying can be regarded as a way of forming a dispersion of any liquid-insoluble phase in a metal or an alloy provided that enough ductile metal powder can be introduced.

The mechanical-alloying process was extended to making alloys of metals with quite different melting points, such as copper and lead. The process might also be applied in more extreme cases where the metal with a low melting point would actually vaporize at temperatures above the melting point of the second metal. Exotic metals with a very low melting point, such as lithium and cesium, could be added to metals with a high melting point, such as nickel and iron, in quantities that could not be achieved by other methods. Such additions could have unanticipated effects on strength and corrosion resistance.

We have shown that the degree of dispersion of one metal or nonmetal within another can be closely controlled by the mechanical-alloying process. If the two metals will form a solid solution, the mechanical-alloying process can in fact be used to accomplish this end without resorting to very high temperatures. On the other hand, if the two metals are insoluble in the solid state (as is the case with iron and copper), an extremely fine dispersion of one of the metals in the other can be achieved.

Certain combinations of metals form structures, known as intermetallic compounds, that have definite formulas. Some of these compounds, which are of great importance for their superconducting properties, are extremely difficult to produce. There is a very real possibility that the atomically intimate mixture of different metals produced by mechanical alloying could represent a new procedure for making these superconductors.

So far the major application of mechanical alloying has been the production of dispersion-strengthened superalloys for jet-engine parts. It is clear that there are many other potential applications for the technique. Metal composites of a type and complexity that cannot be achieved by other methods can be assembled by mechanical alloying. In addition the process can produce relatively large quantities of alloyed powder, which indicates that it can be applied on a substantial scale. The most exciting application of mechanical alloying, however, may be the creation of entirely new metallic materials that have unique properties.