

Applications of Ultrasound to Materials Chemistry

Kenneth S. Suslick

The following is an edited transcription of the address that Kenneth S. Suslick, recipient of an MRS Medal Award, gave at the 1994 MRS Fall Meeting. Suslick received this honor for "incisive studies of the chemical effects of ultrasound on solids and surfaces and the use of sonochemistry as a new synthetic approach to unusual, inorganic compounds or materials."

This article will begin with an introduction to acoustic cavitation, the physical phenomenon responsible for the chemical effects of ultrasound. Some recent applications of sonochemistry to the synthesis of nanophase and amorphous metals, as well as to heterogenous catalysis, will then be highlighted. Finally, we will examine the effects of ultrasound on metal powders in liquid-solid slurries.

Cavitation

The chemical effects of ultrasound do not come from a direct interaction of sound with molecular species. Ultrasound has frequencies from around 15 kilohertz to tens of megahertz. In liquids, this means wavelengths from centimeters down to microns, which are not molecular dimensions. Instead, when sound passes through a liquid, the formation, growth, and implosive collapse of bubbles can occur, as depicted in Figure 1. This process is called acoustic cavitation.

More specifically, sound passing through a liquid consists of expansion waves and compression waves. As sound passes through a liquid, if the expansion wave is intense enough (that is, if the sound is loud enough), it can pull the liquid apart and form a bubble (a cavity). The compression wave comes along and

compresses this cavity, then another expansion wave re-expands it. So we have an oscillating bubble going back and forth, say, 20,000 times a second.

As this bubble oscillates, it grows through several mechanisms, one of which is rectified diffusion. In rectified diffusion, the surface area on expansion is slightly larger than on recompression, so growing processes are kinetically slightly faster than shrinking processes. This oscillating, growing bubble reaches a resonant size determined by the frequency of the sound field. When the

bubble is in resonance, it is well-coupled to the sound field, it can absorb energy efficiently, and it can grow rapidly in a single cycle. Once it has grown, however, it is no longer well-coupled to the sound field. At this point, the surface tension of the liquid combined with the next compression wave implosively collapse the bubble on a submicrosecond time frame. A shock wave can be generated in the gas of the bubble in addition to the simple compressional heating of the gas. When gas is compressed, heating results. When gas is compressed this rapidly, the heating is nearly adiabatic. The heat has no time to flow out, so a very localized, transient hot spot forms, and that hot spot is responsible for the chemistry that is observed.

The conditions formed during that transient cavitation are extreme. We have been able to measure temperatures and pressures by comparative rate thermometry and by using sonoluminescence as a spectroscopic probe of the species formed during cavitation. Our current best estimates of the hot-spot conditions give temperatures above 5000 K, pressure of about 1700 atm, and time duration under 100 ns, and the time may be substantially less than that. We therefore have cooling rates associated with this process of more than 10^{10} degrees/s. For calibration purposes, if I thrust a poker of red-hot iron into ice water, I get a cooling rate of a few thou-

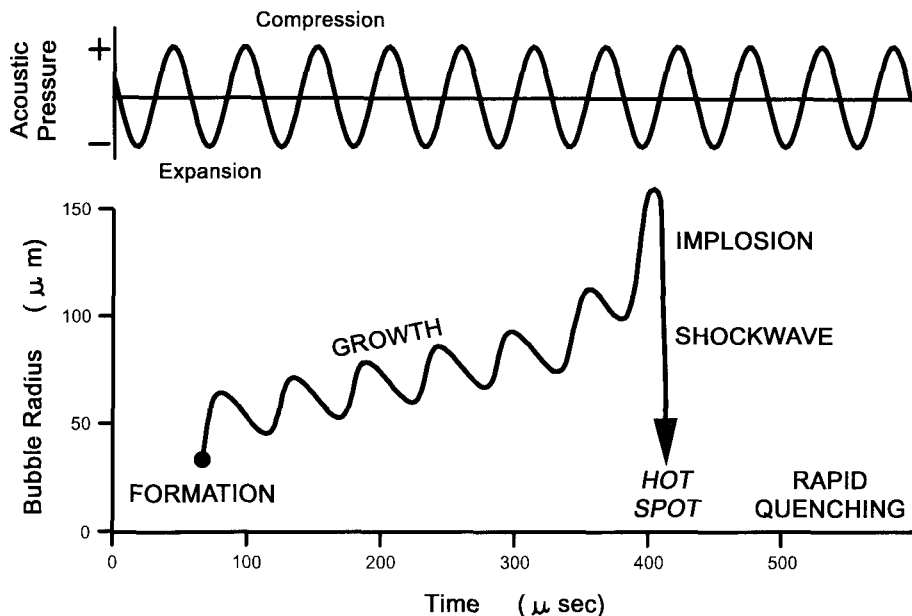


Figure 1. Transient cavitation.

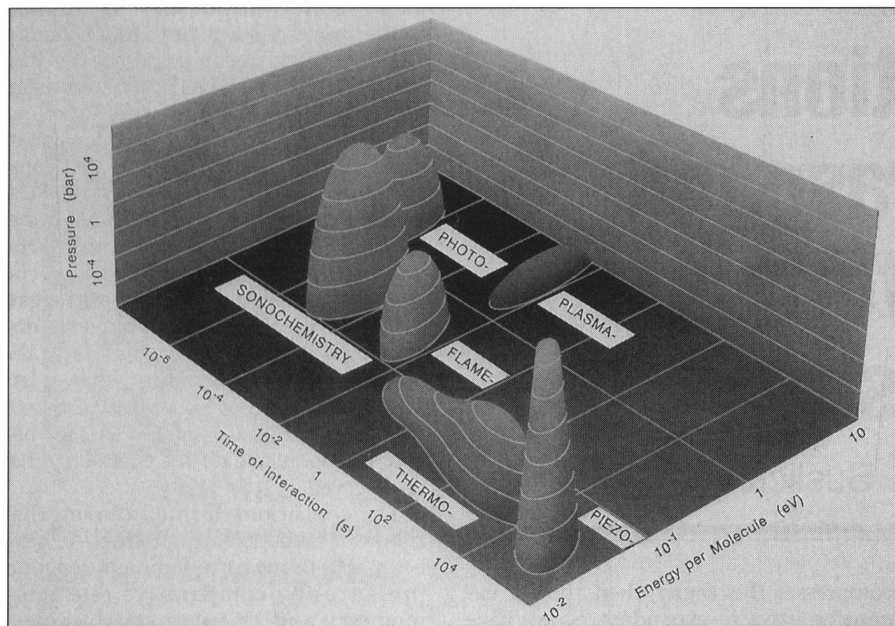


Figure 2. Islands of chemistry as a function of time, pressure, and energy. Adapted from "The Chemical Effects of Ultrasound," by Kenneth S. Suslick. Copyright © 1989 by Scientific American Inc. All rights reserved.

sand degrees per second. If I splatter molten metal onto a liquid-nitrogen-cooled surface, I get cooling rates of a few million degrees per second. We will return to the implications of these cooling rates later.

This understanding of cavitation allows us to compare sonochemistry with other forms of chemistry. Fundamentally, chemistry is the interaction of energy and matter. The parameters that control that interaction are the time of the interaction, the amount of energy in the interaction, and the pressure, which together describe the three-dimensional space depicted in Figure 2. This figure shows the heavily overpopulated island of thermal chemistry at medium pressure, time, and energy. For high-pressure, long-time scales such as occur under geological conditions, the graph shows the spiked island of piezochemistry. The island of sonochemistry is near photochemistry and flame chemistry. All of these are related because they are all forms of interacting energy and matter. However, each has its own specific characteristics because each occupies a different region of this three-dimensional space.

To introduce ultrasound into solutions in the laboratory, we use a high-intensity ultrasonic horn that consists of a solid titanium rod connected to a piezoelectric ceramic and a 20 kHz, 500 V power sup-

ply (Figure 3). This commercially available apparatus can be thermostated and the atmosphere above the solution can be controlled. It is useful for small-scale work, which is mostly what we do. Note that large-scale processing of liquids with ultrasound also exists. Large-scale cleaning baths are available, and are used, for example, by the military, to clean intact jet engines. Flow reactors also exist and are commercially available in stackable 20 kW units. The largest

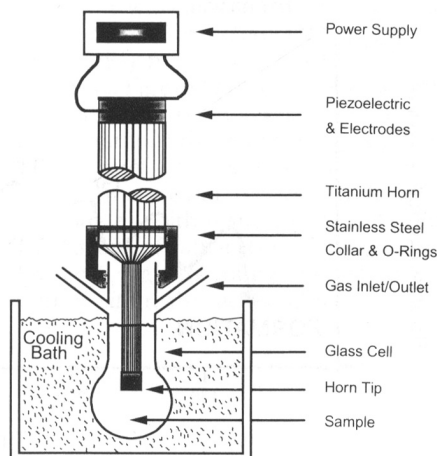


Figure 3. Sonochemical apparatus.

scale application of ultrasound that I know for the physical processing of a liquid was for coal beneficiation at 20 tons/h.

Applications

The Synthesis of Amorphous and Nanoscale Materials

Given the unusual conditions created during cavitation, we considered various potential applications, one of which was the possibility of using ultrasound as a way of generating amorphous and nanoscale materials. Amorphous metals have unusual magnetic, electronic, and catalytic properties. To form an amorphous metal we need high cooling rates (above a million degrees per second) so that the material can be frozen before it crystallizes. Thermal quenching of molten metal usually requires the addition of nonmetal alloying components; boron is common. Consequently, making pure amorphous iron has proven difficult.

We realized that given these cavitation hot spots, sonochemistry provides enormous cooling rates fast enough to cause solidification before crystallization can occur. However, the primary reaction site of cavitation is the gas phase inside the bubble, in which case, we need a way of producing metal inside the cavitation event. Drawing on the same ideas used in organometallic chemical vapor deposition (CVD), we need a volatile precursor. We initially considered metal carbonyls and metal nitrosyls. When they are irradiated with ultrasound, we are able to generate metals from iron and cobalt complexes. From the early transition metals we tend to form metal carbides.

We used sonoluminescence as a spectroscopic probe to see if, in fact, we can strip the ligands off of our precursors. If we start with iron pentacarbonyl, and irradiate with ultrasound in, say, a dodecane solution, the light coming out is emission from excited-state iron atoms. This shows that iron pentacarbonyl is being sonochemically decomposed to iron atoms, and that some of those iron atoms are in electronically excited states. Similar atomic emission is observed from other volatile organometallics.

Once we have these volatile precursors in the cavitation event and we strip off the ligands, we can form small clusters of metal atoms in that cavitation bubble and can work with them. As shown in Figure 4, we can let them agglomerate to form amorphous metals. We can trap them with a polymeric ligand, such as polyvinylpyrrolidone and form a

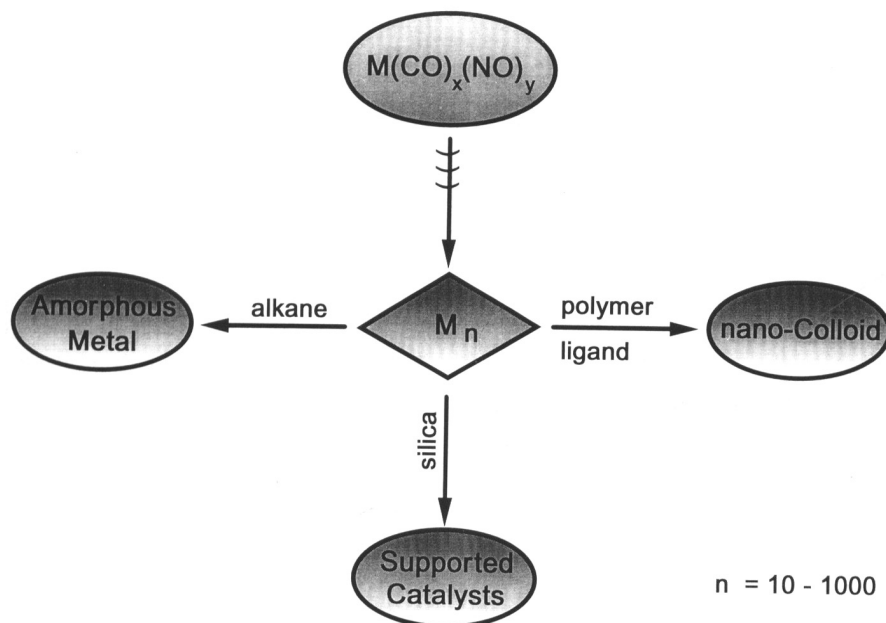


Figure 4. The sonochemical synthesis of amorphous metals, nanocolloids, and supported catalysts.

nanocolloid; or we can deposit these small clusters on an oxide support, such as silica, and form supported heterogeneous catalysts.

In fact we have been able to do all three of these. If we irradiate iron pentacarbonyl carbonyl with ultrasound, in a relatively unreactive alkane, a highly reactive, black powder is formed. It has a high surface area of about $150 \text{ m}^2/\text{g}$, and it burns spontaneously in the air because of that high surface area. Under modest magnification, the material is clearly not crystalline and shows conchoidal fractures. It is relatively pure iron by elemental analysis. On higher magnification, the material shows a porous, coral-like structure (see Figure 5). On still higher magnification, the individual particles that make up this agglomerate are apparent, and nanometer-sized clusters can be seen that form the building block of this coral-like material. Initially as prepared, the material is amorphous by x-ray diffraction, by neutron diffraction, and by e-beam microdiffraction. Furthermore, it shows a one-time irreversible crystallization exotherm in the differential scanning calorimetry (DSC) at about 350°C .

As an example, characterization by x-ray diffraction (XRD) pattern shows no peaks for the material as formed. As we heat the material to above 200°C , crystallization begins to set in, and by about 350°C , the material is fully crystallized into normal α -iron. We have no evidence from XRD or other techniques for the

formation of carbidic or oxide phases.

If we want to trap the material in the small nanometer-cluster size, we can use a weakly coordinating ligand, such as polyvinylpyrrolidone. To do that, we can

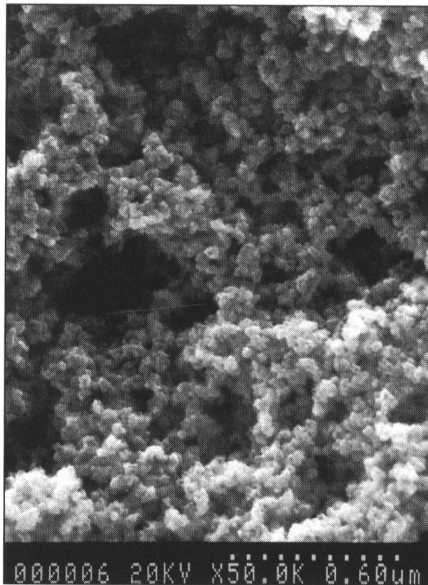


Figure 5. Porous, coral-like structure of sonochemically prepared amorphous iron. From K. Suslick, *Ultrasonics* 30 (1992) p. 171, by permission of the publishers, Butterworth-Heinemann Ltd. ©.

add the polymer to the iron pentacarbonyl solution and irradiate at room temperature with high-intensity ultrasound. If we want to make a supported catalyst, we can do the same thing, except we would replace the polymer with an oxide support. We have characterized these extensively. Initially, as formed, the colloids are also amorphous. Electron microdiffraction shows no crystallinity associated with them, and they undergo a one-time irreversible crystallization exotherm in the DSC.

These very soft magnetic materials show virtually no hysteresis in magnetization curves. In magnetic-property studies done in conjunction with Myron Salamon, a professor of physics at UIUC, the nanophase amorphous iron in bulk is a very soft ferromagnet. Its magnetic moment lies between crystalline iron and molten iron. We have agreement in magnetic measurement from SQUID and neutron-diffraction data. The effective exchange is relatively modest between the irons—about 30% of crystalline iron—and this has been modeled with a correlated spin-glass random packing model.

The nanocolloidal iron is superparamagnetic (that is, essentially a single domain ferromagnet that can be thermally oriented). The nanophase iron supported on silica is also superparamagnetic, with properties similar to those of the colloidal iron.

Catalytic Properties

Amorphous surfaces are interesting catalysts for many reasons. They have high concentrations of low coordination sites; that is, they are heavily defected. They are roughly single phase, so we need not be much concerned about whether {111} or {100} planes, for example, are exposed. In other words, they are relatively isotropic surfaces. The problem with amorphous metals as catalysts is they are very difficult to make and usually have low surface areas. In general, the surfaces are also heavily passivated during processing. The other disadvantage is that the materials are not in an equilibrium state and are likely to crystallize.

To examine the catalytic reactivity of our amorphous powders, we use an industrial-strength catalytic microreactor, which is basically a glorified digital gas mixer that flows appropriate gases through a catalyst bed, consisting of our powder, and into a gas chromatograph mass spectrometer (GCMS). The reactions we initially chose had a bifurcated pathway; that is, two products were pos-

sible. Thus, we could look at selectivity differences rather than argue about which catalyst was more active. For example, the reactions of cyclohexane over metals can lead to either formation of benzene—a highly desirable process—or the hydrogenolysis to methane—an undesirable process. My graduate stu-

dent, Taeghwan Hyeon, recently discovered that we could use our amorphous metals and a series of alloys to dramatically influence the selectivity (Figure 6). This came as a complete surprise. As is known in the literature, iron and cobalt are bad catalysts for the dehydrogenation of alkanes. They do not lead to the for-

mation of benzene, but rather to cracking to produce methane. Our amorphous iron and our amorphous cobalt both turn out to be poor catalysts for dehydrogenation. But the alloys are superb. We cannot yet account for the origin of this phenomenon.

We can make supported catalysts, as I mentioned earlier. For example, we have sonochemically prepared silica gel with deposits of iron nanometer clusters. The iron clusters cannot penetrate into the silica, so we get essentially an eggshell catalyst. This differs greatly from the result of normal methods where, for example, we deposit an iron nitrate solution onto silica. If we look at higher magnification on the TEM, we can see those few nanometer-sized clusters against the gray amorphous silica background. And again, the clusters are a few nanometers in size in these materials.

These supported catalysts are extremely active. In this case we are looking at Fischer Tropsch synthesis hydrogenation of CO, to form low molecular weight hydrocarbons. Both conventional and sonochemical methods were used to prepare catalysts. At low temperatures, the sonochemically prepared catalyst is much more active than the conventional catalyst with similar concentrations of iron and similar dispersions. As we heat the sonochemically prepared catalyst to the point of crystallization, we begin to lose much of the activity, leading us to suspect that this increase in activity corresponds to the high defect concentration in these nanometer-scale clusters.

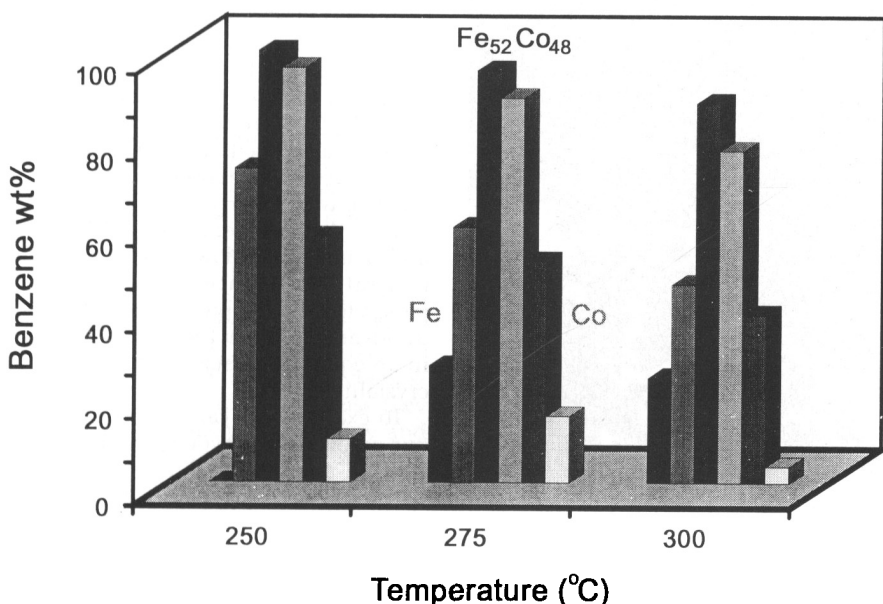
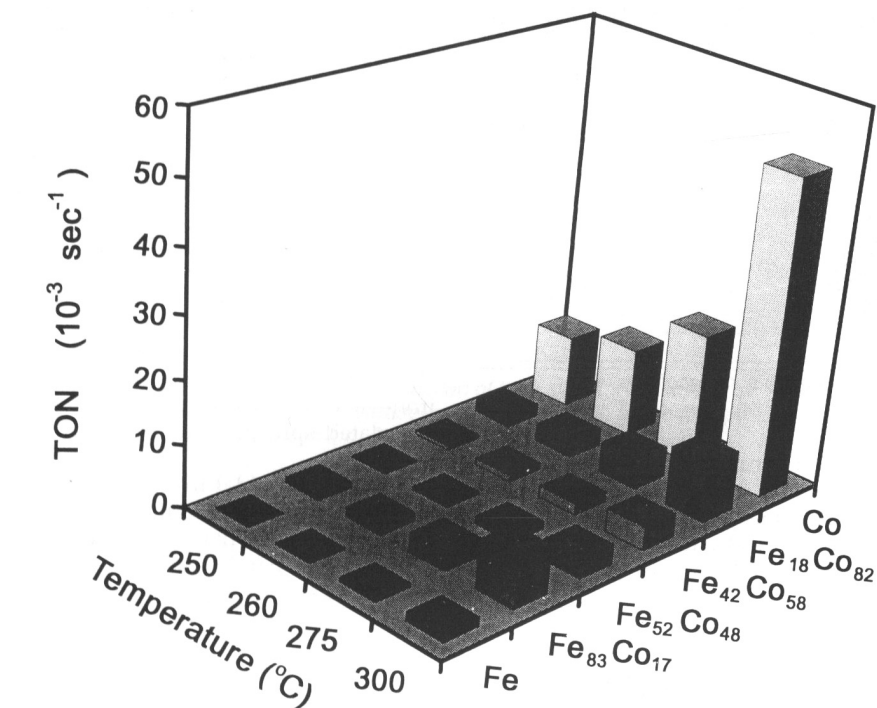


Figure 6. Catalytic activity and selectivity of nanophase Fe-Co.

Heterogenous Sonochemistry

I will now touch briefly on ultrasound applications that involve liquid-solid reactions. Because of space confinement I will simply mention that there are now hundreds of examples of the use of ultrasound to drive liquid-solid reactions, especially of highly reactive metals such as Li or Mg. When we began, we decided to follow the Zeroth Law of Engineering, which is "If it works, don't fix it." So we went looking for the world's worst heterogeneous catalyst.

We decided that near the bottom of the list is nickel powder right out of the bottle. Raney nickel (a porous form of the metal) is, of course, a very active hydrogenation catalyst but it is also expensive, pyrophoric, and environmentally problematic. The point is, though, that if we take ordinary nickel powder and irradiate it with ultrasound, we can increase its reactivity by more than 100,000-fold and regain Raney nickel-like activity.

When we study the morphology of the

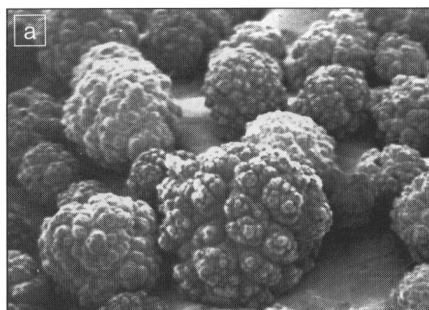
powder, we find that before sonication the nickel powder is crystalline on the surface. After ultrasonic irradiation, the crystallites are removed and the surface is smoothed on a macroscopic scale (which means that it is roughened on an atomic scale), as shown in Figure 7.

If we examine sonicated nickel powder at lower magnification, we see agglomeration occurring as well. It looks like ball milling on a microscopic scale. If the particles hit at a glancing angle, material is brushed off and smoothing occurs; if the particles hit directly, they stick. The consequence is that we remove passivating coatings on the surface. Auger depth profiling reveals that, before ultrasonic irradiation, a deep oxide coating is present. That is why these metals are unreactive. If we irradiate with ultrasound, that oxide coating is removed.

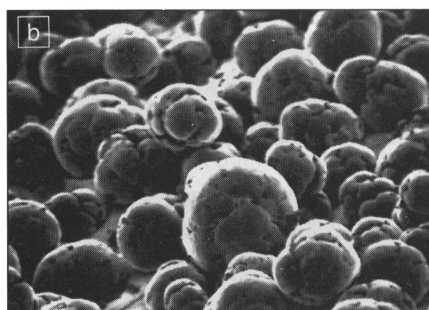
I would like to close by examining more closely the effects of ultrasound on slurries. Figure 8 shows where particles have collided and generated what appears to be a melted neck between them. If we do this with two different metals, we can actually do elemental Auger mapping and demonstrate that the neck is an alloy between the two different metals—tin and iron. For example let us assume that the spot welding on collision represents true melting (although we may debate whether it is fully melted or at least partly a plastic deformation). The melted neck size is about a cubic micron. About 90 KJ/mol is needed to melt a metal such as iron. That means 0.1 erg was needed to melt the neck. We can take that energy to be a lower limit for the kinetic energy of impact between the particles when they collided. This gives us a velocity on the order of hundreds of meters per second, a significant fraction of the speed of sound in these liquids. That is impressive: We have a flask of a cold liquid, an ultrasonic horn in it, and we generate interparticle collisions between particles at velocities that are half the speed of sound.

The origin of these high-velocity collisions comes from acoustic cavitation. The collapse of bubbles during cavitation is like setting off a microscopic depth-charge in the liquid, and it generates shock waves that travel through the liquid at or above the speed of sound. When such a shock wave comes across solid particles in close proximity, it can accelerate one particle and smash into the next. If the particles hit at a glancing blow, we get smoothing; if they hit directly, we get spot welding at the point of impact.

What kind of local conditions occur



Before U.S.
~160 microns



60 min. U.S.
~80 microns

Figure 7. Surface Morphology of Ni powder (a) before ultrasound showing crystallites on the surface and (b) after ultrasound, which removes material and smooths the macroscopic surface. From K. Suslick, Solid State Ionics 32-33 (1989) p. 447.

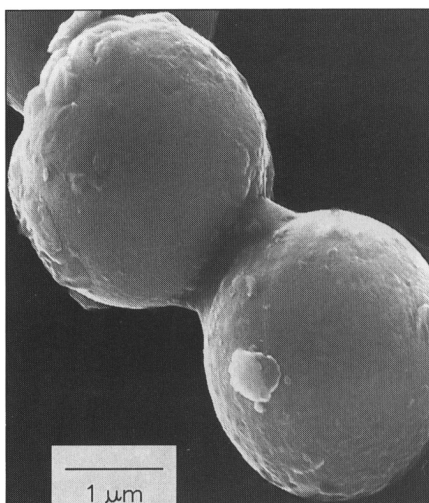


Figure 8. Neck formed by particles of zinc colliding in a slurry irradiated with ultrasound. Reprinted with permission from K. Suslick, Science 247 (1990) p. 1067. Copyright 1990 American Association for the Advancement of Science.

when these particles collide? We can probe these conditions by examining a series of metal-powder slurries. For example, we can look at chromium, molybdenum, and tungsten with the same particle size, concentration, inert solvents, and ultrasonic intensity. For chromium we see tremendous agglomeration before and after ultrasonic irradiation, and at higher magnification, we see substantial deformation of the individual particles in the scanning electron micrographs (Figure 9). Chromium melts at 1800 K. Molybdenum melts at 2600 K. Agglomeration still occurs, but it is not nearly as dense; and with higher magnification in the SEM, no smoothing or deformation of the individual particle is observed. Tungsten melts at 3400 K, and the micrographs show that ultrasonic irradiation has no effect.

If we make a chart of different metals, with their corresponding melting points, occurrence of agglomeration, or changes in surface morphology, we discover a breaking point around 3000 K. That temperature is unrelated to the temperature of the hot spot, but it is another indication of the extreme conditions that can be formed in liquids irradiated with ultrasound.

Conclusion

Through the process of cavitation, ultrasound performs high-energy chemistry. There are applications of this to the synthesis of inorganic materials, amorphous metals, alloys, nanophase colloids, and supported catalysts. There are other biomaterial applications through the synthesis of protein microspheres. These protein microspheres have applications for medical imaging, drug delivery, and blood substitutes, but are beyond the scope of this discussion. The applications of high-intensity ultrasound to materials science are diverse and the range of possibilities is only now beginning to emerge.

Acknowledgments

I would like to thank all of my students and co-workers who have been involved in this project over the years: for the work discussed in this article, especially Dom Casadonte, Seok-Burm Choe, Andrzej Cichowlas, Steve Doktycz, Ming Fang, Mark Grinstaff, and Taeghwan Hyeon. I thank Prof. Myron Salamon for collaboration on magnetic properties, and Profs. Galli and Bellissent for collaboration on neutron diffraction. This research has been funded by the National Science Foundation and the Exxon Foundation, and has been further supported

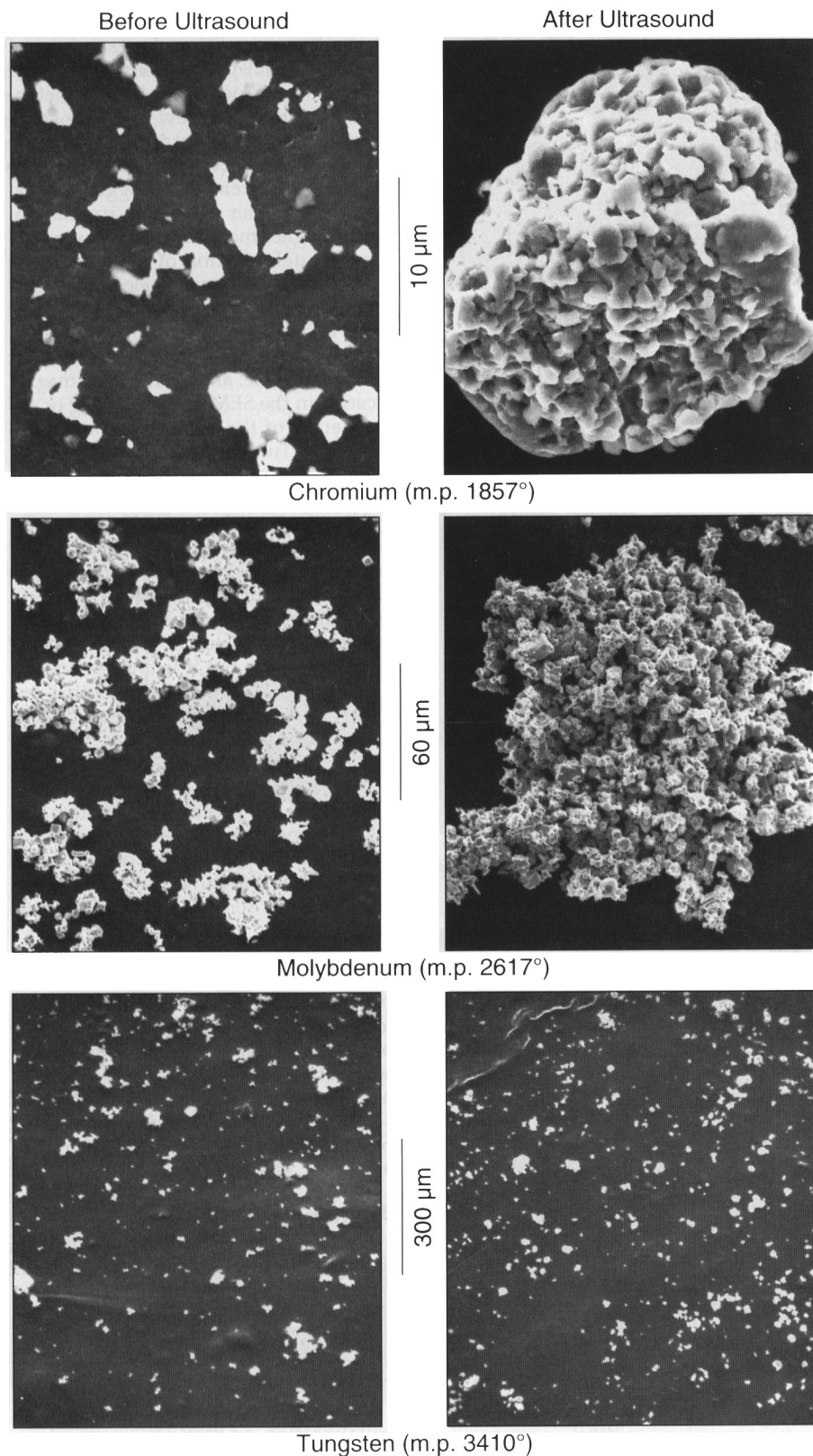


Figure 9. Agglomeration of metal powders after ultrasonic irradiation of decane slurries. Reprinted with permission from K. Suslick, *Science* **247** (1990) p. 1068. Copyright 1990 American Association for the Advancement of Science.

by UIUC Materials Research Laboratory and the Center for Microanalysis of Materials, which is funded by the Department of Energy.

Some Leading References to Materials Science Applications of Sonochemistry

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