Sonochemical Formation of Intermetallic Coatings

J. D. Sweet and D. J. Casadonte, Jr.*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Received May 26, 1994. Revised Manuscript Received August 22, 1994®

An energy-dispersive X-ray (EDX) study of the agglomerates produced during the sonication of a series of mixed-metal powders in decane indicates that metal particles are both fused by the action of ultrasound and develop coatings which are intermetallic in nature. The principal mechanism of these effects is believed to be interparticle collision caused by the rapid movement of particles of less than 50 μm diameter which are propelled by shockwaves generated at cavitation sites. By examination of mixed-metal systems including Ni/Co, Al/Ni, Al/Co, Ni/Mg, and Cu/Mo with substantially different tribological characteristics, it has been determined that the coatings are generated by both adhesive wear and direct impact. The fusion of Cu and Mo is particularly intriguing, as these two metals are immiscible below 1000 °C. This indicates the enormous impact temperatures produced in sonically induced collisions. The mechanisms of intermetallic coatings produced via ultrasound are discussed.

Introduction

In pure liquids or homogeneous solutions the principal cause of the chemical effects of high-intensity ultrasound is acoustic cavitation, viz., the generation, growth, and collapse of gas-filled bubbles as a result of applied oscillating pressure waves.[1] Kinetic[2] and sonoluminescence[3,4] measurements indicate that enormous local temperatures (>5000 K) and pressures (>100 atm) are generated during the nearly adiabatic and short-lived (<1 μs[5]) implosions which occur at the cavitation sites. Reactive gases trapped in a collapsing bubble are subjected to these physical extremes; consequently, much of single-phase high-intensity sonochemical reactivity is reminescent of pyrolytic chemistry.[6]

As in the case of homogeneous solutions, cavitation is responsible for the chemical effects observed in heterogeneous (solid/liquid) environments. This is achieved by (1) the fracture of easily cleaved solids to increase active surface area,[7] (2) enhanced mixing or transport of solid particles in solution,[8] and (3) the removal of passivating coatings (usually oxide in nature).[9-12] The precise morphological changes which occur in the solid particles during sonication is dependent upon the size of the particles and nature of the solid/bubble interface.[10] Bubble collapse near a surface which is larger than the diameter of the gas-filled vacuole immediately prior to collapse (i.e., ~150 μm at 20 kHz[1,13]) can generate high-speed microjets directed toward the solid surface which can lead to particle fracture or erosion.[14] If the particle surface is substantially smaller than the bubble diameter, microjet formation will not occur, but the usual cavitation collapse mechanism is still operant.

Metal powders with average particle diameters of 5–50 μm are propelled at high speeds when subjected to 20 kHz ultrasound in solution due to the shockwaves produced upon cavitation collapse. It has been estimated[9,13] that 5–10 μm size particles can travel at rates approaching 150 m/s. Interparticle collisions under these conditions can lead to surface erosion though glancing impacts, or to fusion of malleable materials when the collisions are more direct.[9-12] The wear which occurs between particles often generates extremely clean surfaces which can increase chemical reactivity. Rate enhancements of $>10^5$ have been observed for the hydrogenation of olefins in the presence of an ultrasonically activated Ni powder catalyst,[10] and a mixed-metal system containing Ru and Cu has been used as a dehydrogenation agent.[9]

Although substantial effort has been spent in characterizing the surface properties of single-component metal powders in solutions exposed to ultrasound, there has been relatively little investigation of the sonochemistry of mixed-metal heterogeneous systems.[9,11,13] We wish to report here a study of the sonication of several sets of mixed-metal powders in solution with substan-

---

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) (a) Flynn, H. G. In *Physical Acoustics*; Mason, W. P., Ed.; Academic Press: New York, 1964; Vol IB, p 67. (b) Atchley, A. A.; Crum, L. A. In *Ultrasound: Its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988, p 1.

(2) Suslick, K. S.; Cline, Jr., R. E.; Hammerton, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

(3) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397.

(4) Gaitan, D. F.; Crum, L. A.; Church, C. C.; Roy, R. A. *J. Acoust. Soc. Am.* **1992**, *91*, 3166.

(5) Barber, B. P.; Putterman, S. *Nature* **1991**, *352*, 318.

(6) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73.

(7) Suslick, K. S.; Casadonte, D. J., Green, M.; Thompson, M. E. *Ultrasonics* **1987**, *25*, 56.

(8) Boudjouk, P. In *Ultrasound: Its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988; p 165.

(9) Suslick, K. S.; Casadonte, D. J.; Choe, S. B.; Cichowlas, A. A.; Doktycz, S. J.; Ghosh, C. K.; Grinstaff, M. W. *Mater. Res. Soc. Proc.* **1990**, 209.

(10) Suslick, K. S.; Casadonte, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 3459.

(11) (a) Vedamuthu, M.; Casadonte, D. J. *Abstract of Papers*, Southwest Regional Meeting of the American Chemical Society, San Antonio, TX; American Chemical Society: Washington, D. C., 1991; Abstract INOR 208. (b) Vedamuthu, M. Sweet, J. D.; Casadonte, D. J. *Abstract of Papers*, National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, D.C., 1992, Abstract INOR 134.

(12) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. *Chem. Mater.* **1989**, *1*, 6.

(13) Doktycz, S. J.; Suslick, K. S. *Science* **1990**, *247*, 1067.

(14) Prosperetti, A. *Ultrasonics* **1984**, *22*, 115.

0897-4756/94/2806-2113$04.50/0

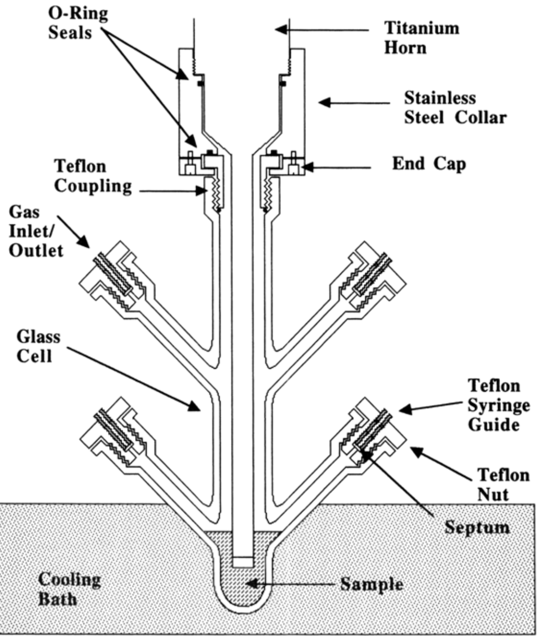

Figure 1. Sonochemical reactor schematic.

tially varying tribochemical (i.e., involving the chemistry between sliding or rolling surfaces) and metallurgical compatibilities. The results indicate that surface erosion and the formation of fused bimetal species occur even for incompatible metals. Most significant, however, is the observation that sonically induced collisions produce intermetallic coatings on the particle surfaces. These results point to the potential for using ultrasound in the selective coverage of substrates with layers of metals for the formation of catalytic or electronically useful materials.

Experimental Section

A schematic of the sonochemical reactor configuration is illustrated in Figure 1.[15] A Cole Parmer 4710 series 600 W ultrasonic homogenizer operating at 20 kHz provided the high-intensity ultrasound. The power setting of the sonicator was optimized to provide maximum acoustic power into the solution by monitoring the sonochemically induced transformation of I^- to I_3^- spectrophotometrically at different input power settings. Above the optimum power level a layer of bubbles builds up between the sonicator tip and the solution, leading to attenuation of the acoustic power in the air–liquid interface.[16] All reactions were carried out at 0 °C cell temperature (monitored with an Omega T type thermocouple and Phillips PM2525 multimeter). The metals were purchased from EM Scientific (Ni, Co, Mo), Aldrich Chemical, Inc. (Al, Mg), and Baker Scientific (Cu). All metals were greater than 99% purity. In a typical experiment, 0.500 g of each metal with an initial average particle size as determined by electron microscopic analysis of ≤ 15 μm (except for Mg, where the average particle size was ~ 250 μm) was added to a sonication flask containing 20 mL of decane which had been previously degassed by sparging with Ar. After sonication for 100 min the horn/cell assembly was transferred to a glovebag, and the mixture was vacuum filtered. The powders were stored under nitrogen and analyzed via electron microscopy and energy-dispersive X-ray (EDX) analysis[17] using a Hitachi Model H600 scanning transmission electron microscope fitted with a Noran light element (thin window) detector. The vacuum chamber of the microscope was covered by a glovebag before the sample was introduced to prevent contamination by oxygen.

Results and Discussion

An electron micrograph of a typical species produced when Ni and Co powders are sonicated together in decane is illustrated in Figure 2a.[15] It is evident that particle fusion has occurred, as has been demonstrated in previous studies.[9–12] The aggregates are often seen to be dumbell-shaped with an average particle size of slightly less than 5 μm, consistent with previous work involving sonicated Ni particles[10] and theoretical studies of agglomeration/dispersion in heterogeneous media exposed to ultrasound.[18]

An energy-dispersive X-ray (EDX) element map for Co in the agglomerate is given in Figure 2b. The map indicates that the larger particles are composed entirely of cobalt. The dark areas are cobalt-deficient regions. It is anticipated that these are due to the presence of Ni particles which are fused to the catenated Co particles.

The element map for Ni in the aggregate system is shown in Figure 2c. The areas which were dark in the cobalt analysis are indeed found to be due to Ni particles. Of special interest, however, is the observation that the *entire* surface of the agglomerate is coated with Ni. This coating behavior has not been previously reported, presumably because most metal particle slurries studied have involved single metal components.[9–12] Some studies have been performed on mixed-metal systems,[9,11,13] but the analysis has been largely directed toward an understanding of the composition of the zone of melt for fused particles.

Given that high-speed interparticle collisions occur when metal particles of 15 μm or less are sonicated in solution, it is tempting to ascribe the coverage of Co particles by Ni in Figure 2 to an ultrasound-induced wear coating mechanism. During glancing impacts solid-phase welds are formed at asperity junctions (i.e., the point at which a surface irregularity on each particle comes in contact) as particles of Co and Ni begin to slide past each other. These welds must be sheared in order for sliding to continue. If shearing occurs at some distance from the particle interface, a fragment of the softer material will be transferred to the harder surface. Since Ni is approximately 10% softer than Cu based on indentation measurements[19] (2.06×10^3 vs 2.25×10^3 N mm^{-2}), it is reasonable that Ni will coat Cu by adhesive wear.

To explore further the mechanism of sonochemical coating in mixed-metal media, we have examined the characteristics of three additional binary systems with varying degrees of disposition toward the formation of intermetallic phases. Figure 3 shows the electron micrographs and EDX element maps for mixtures of Al/Ni, Al/Co, and Cu/Mo sonicated in decane. In each of the cases examined at least partial coverage is achieved on particles of less than 15 μm in diameter. According to the tribochemical classification of Rabinowicz,[20] these metal mixtures are considered to be compatible, of

---

(15) Casadonte, D. J.; Sweet, J. D.; Vedamuthu, M. S. *Ultrasonics*, in press.

(16) Suslick, K. S. *Mod. Synth. Methods* **1986**, *4*, 1.

(17) Newbery, D. E.; Joy, D. C.; Echlin, P.; Fiori, C. E.; Goldstein, J. I. *Advanced Scanning Electron Microscopy and X-Ray Microanalysis*; Plenum: New York, 1986.

(18) Fridman, V. K. *Ultrasonics* **1972**, *10*, 162.

(19) Bushan, B.; Gupta, B. K., *Handbook of Tribology*; McGraw-Hill: New York, 1991; Chapter 3, p 26.

(20) Rabinowicz, E. *ASLE Trans.* **1971**, *14*, 198.

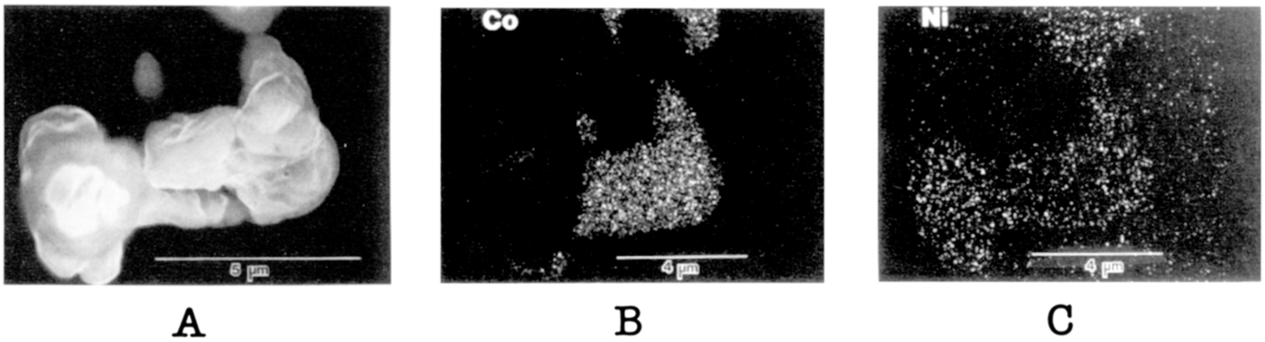

Figure 2. (a) Electron micrograph of an agglomerate produced by the simultaneous sonication of Ni and Co powder in decane. (b) Energy-dispersive X-ray (EDX) Co map of the fused particles shown in (a). The dark areas indicate Co-deficient regions. (c) Ni map of the agglomerate shown in (a), indicating total coverage of the Co surface by Ni metal.

limited compatibility, and incompatible, respectively. Adhesive wear theory suggests that in order for contact between two metallic components to produce a coating, the two metals must either be miscible or capable of forming surface bonds.[21] This process is enhanced if the crystal packing of the individual metals is similar.

In Figure 3i, coating of both Al by Ni and Ni by Al occurs. Al coverage of the Ni particle in Figure 3i is greater than the corresponding Ni coating of the Al particles, consistent with the fact that Ni is almost 8 times harder than Al.[19] A fundamental question which must be addressed in light of the evidence for intermetallic layering is whether or not the shockwaves produced during cavitation, and the resulting interparticle collisions are capable of producing the coating behavior observed during the time frame of the experiment.

The extent of wear coating between metals in heterogeneous media depends on a number of properties, including (1) the compatibility (i.e., mutual solubility) of the metals involved, (2) the degree of lubrication (i.e., liquid/solid interaction), (3) the normal loading or impact force, and (4) the relative hardness of the metals. To evaluate whether a sonochemical wear coating mechanism would be capable of providing universal particle coverage, it is necessary to develop an estimate for the efficiency of coating per interparticle collision. A semiquantitative measure of the maximum wear (and, consequently, coating) volume per sliding distance in a collision, Q, is given by the Archard equation:[22]

$$Q = kWd/H \qquad (1)$$

where k is the wear coefficient, W is the normal loading force, d is the sliding distance, and H is the hardness of the softer material. As an example, using the Al/Ni system the maximum coating volume for a single ultrasonically induced collision can be evaluated. From SEM data[23] the average asperity size for crystalline Al particles used in this study (with an average particle diameter of 3.5 μm) is approximately 0.4 μm. It is assumed that during a collision this corresponds to the sliding distance, i.e., that the Ni particle will slide across the entire asperity. The maximum normal force can be calculated assuming conservation of momentum with an average particle speed of 100 m/s and an interparticle impact time of 5 ns[13] to be 0.2 N. The hardness for Al is taken to be the indentation hardness,[19] 270 N mm^{-2}. The value of the wear coefficient depends on the degree of lubrication of the solid surfaces. Hydrocarbons such as decane are considered poor lubricants,[22] and as such the value of k is taken to be approximately 100×10^{-6} for two metals which are considered soluble. Insertion of these values into eq 1 yields a value for Q of approximately 3×10^{-11} mm^3 (3×10^{-2} μm^3). Assuming a hemispherical coating geometry,[24] the coated surface area is approximately 2×10^{-1} μm^2. For a 3.5 μm Ni particle (an average size as determined by SEM) this corresponds to 0.01% surface coating in a single collision. If half-redundant coverage (i.e., half of a coated surface is again coated during a subsequent impact) is assumed, then approximately 2000 impacts by Al would be required to fully cover an average Ni particle. Since some collisions will result in fusion rather than coating and since the amount of redundant coverage may be substantially larger than approximated, the number of necessary collisions is probably higher and the calculated value should be taken as a rough estimate only.

To assess whether an ultrasound-induced wear coating mechanism is feasible, the number of cavitation collapses which should occur over the course of the experiment must also be determined. During the course of a 100 min sonication with a 20 kHz input frequency approximately 6×10^7 oscillations will occur. If only 0.003% of these oscillations are capable of producing transcient cavitation events in close proximity to metal particles leading to high-speed impacts of the type described above the coating scenario described would be feasible.

For the case of two metals with limited compatibilities such as Al and Co, Figure 3ii shows that Co is capable of coating the Al particle. This is somewhat surprising, given that Co is 8.5 times harder than Al.[19] At room temperature Al packs in an fcc arrangement and Co displays hexagonal closest packing. Limited solubility is thus anticipated on the basis of dissimilar crystal structures. However, above 390 °C α-Co (hcp) undergoes a transition to the β form, which has an fcc structure.[25] Given the enormous impact speeds during glancing interparticle collisions, local temperatures well

---

(21) Zum Gahr, K. H. *Microstructure and Wear of Materials*; Elsevier; Amsterdam, 1987; p 84.

(22) Rabinowicz, E. In *CRC Handbook of Lubrication Theory and Practice of Tribology*, Booser, E. R., Ed.; CRC Press: Boca Raton, FL, 1984, Vol. 2, *Theory and Design*, p 201.

(23) Sweet, J. D.; Casadonte, D. J. Unpublished results.

(24) Arnell, R. D.; Davies, P. B.; Halling, J.; Whomes, T. L. *Tribology: Principles and Design Applications*; Springer-Verlag: New York, 1991; p 69.

(25) *Smithells Metals Reference Book*; Brandes, E. A., Ed.; Butterworth: London, 1983; Chapter 6, p 5.

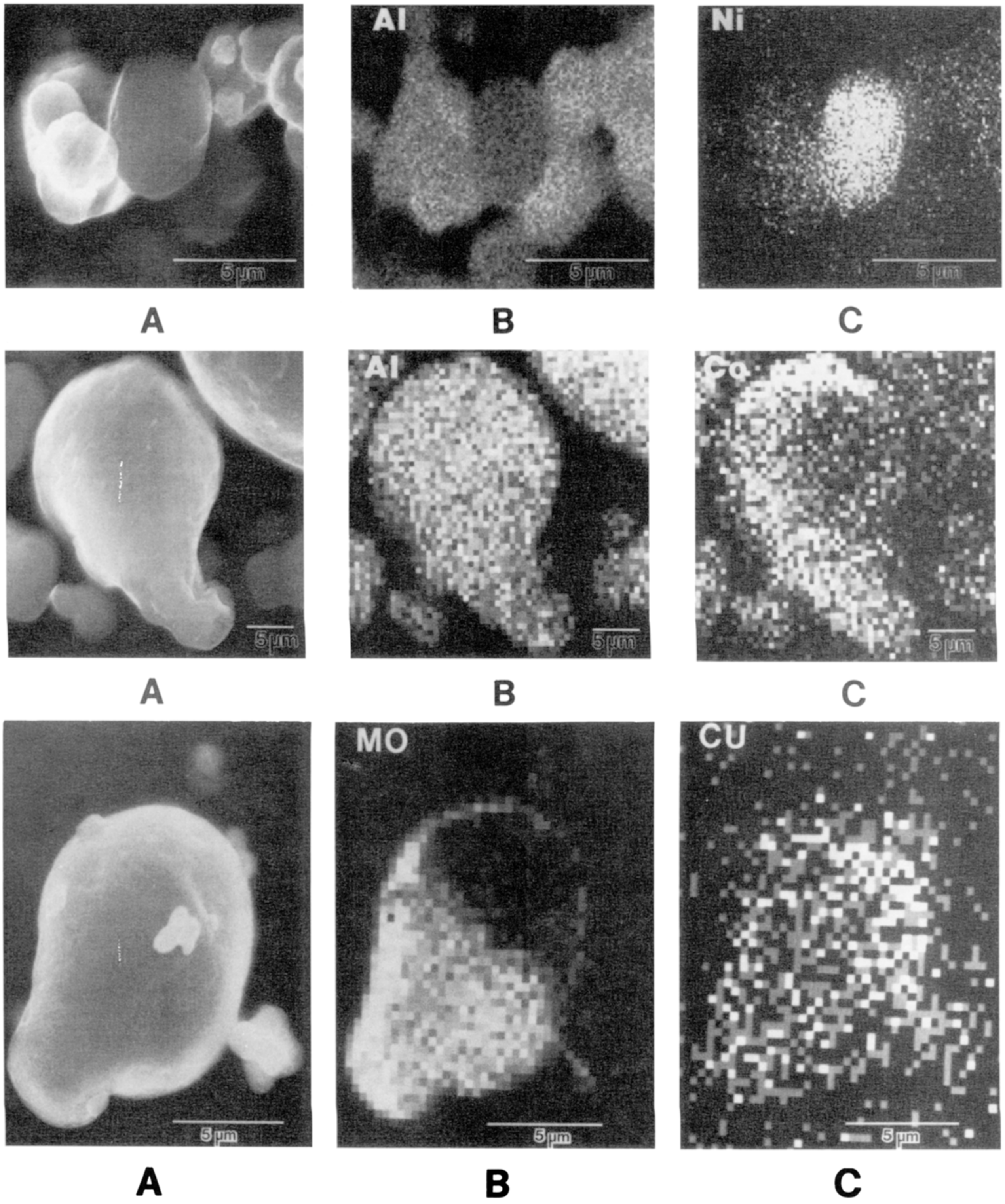

Figure 3. Electron micrographs and element maps for the sonication in decane of binary metal mixtures of varying metallurgical compatibilities. Shown from most compatible to least compatible are (i, top) Al and Ni, (ii, middle) Al and Co, and (iii, bottom) Cu and Mo powder. Note the direct impact fusion of Cu and Mo, two immiscible metals.

above this value are anticipated (vide infra). According to the Al/Co phase diagram, a solid solution between the two metals will form above 300 °C, and this may provide the source of the solid-phase welds.

The bright crescent-shaped portion of the Co map in Figure 3ii suggest the possibility of ultrasound-induced *impact* coating as well as adhesive wear coating between metal particles. This interparticle melting would require both plastic deformation and rapid cooling. A striking illustration of plastic flow leading to overcoating is seen in the Cu/Mo system of Figure 3iii. Cu and Mo are considered incompatible in a tribological sense. Since Mo is approximately 4 times harder than Cu[19] (2900 vs 800 N mm^{-2}), it might be anticipated that if any coating were to form, it would be due to Cu coating the Mo surface. However, Cu is immiscible with Mo at all concentrations of Mo,[26] and this should preclude

---

(26) Hansen, M. *Constitution of Binary Alloys*, 2nd ed.; McGraw-Hill: New York, 1958; p 600.

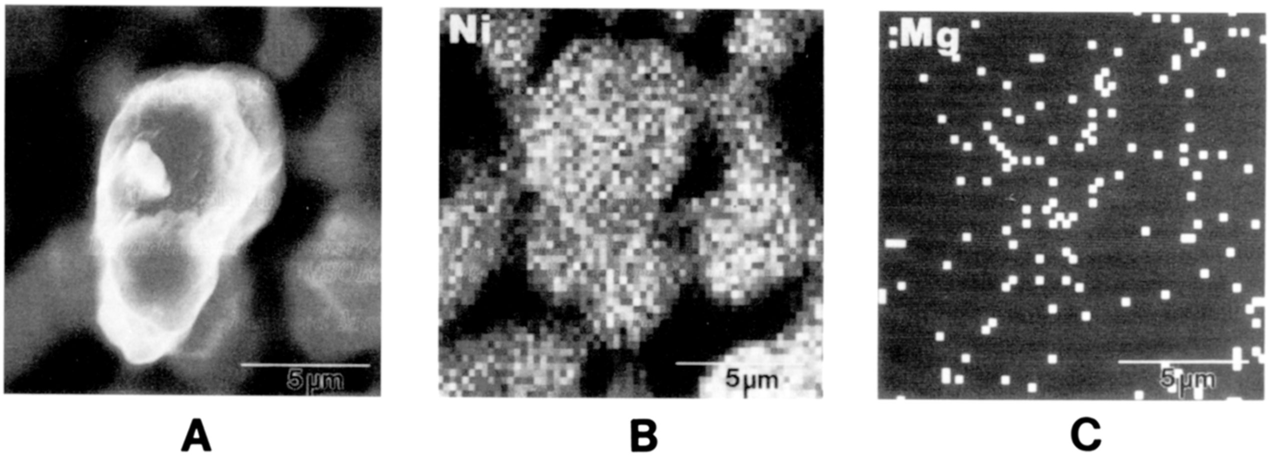

Figure 4. Electron micrograph and element maps for the sonication of 5 μm Ni and 250 μm Mg powder in decane. No evidence for Mg coating of Ni is observed.

welding at the points of frictional contact from an adhesive coating perspective. Close examination of Figure 3iii indicates fusion of two particles, with the lower particle being strongly deformed and essentially melting over the spherical surface of the upper particle. The EDX map for Cu shows that there is Cu present throughout the entire agglomerate and that the back spherical domain is essentially pure Cu. Of special interest is that the Mo map for the agglomerate shows that the smaller Mo particle (lower left) has deformed and melted over the surface of the Cu particle to form a kind of coating similar to what one might observe when hot solder impacts a cool surface. This is the first evidence for *direct impact* coating between two metal particles in a sonicated heterogeneous environment. It is clear from Figure 3iii that the much harder Mo has not covered the surface of the Cu particle except by impact coating and has undergone substantial plastic deformation. The intermetallic coatings generated between immiscible metals in this study indicate that typical tribological coating mechanisms may not hold at the high speeds and impact forces generated as a result of cavitation. A rough estimate[13] of the temperature produced during direct impact between two sonicated metal particles is 2600−3400 °C. The possibility thus exists that intermetallic coating in a heterogeneous environment exposed to ultrasound occurs via two mechanisms. Adhesive wear is the principal means of particle coverage when the impacts are glancing. If the impact is direct, sufficient energy transfer occurs to cause localized melting and flow.

The ability of high-intensity ultrasound to produce a coating is dependent on the size of the particles sonicated. The results of sonicating Ni particles with an average size of ~5 μm in the presence of 250 μm Mg in decane are shown in Figure 4. Upon examination of a variety of particles no evidence of Mg-coated Ni nor Ni-coated Mg was observed. The reason for this is unclear, although (i) Ni and Mg are only very slightly miscible[19] and (ii) presumably when the size of the collapsing bubble is similar to that of the particle the resulting shockwaves lack sufficient energy to propel the larger particle with the force needed for adhesive wear. We are currently examining the tribological aspects of these ultrasound-induced coatings through a much wider range of metals. Of particular interest is the depth of coverage, the phase nature (amorphous or crystalline) of the coatings, and the ability of the liquid into which the metal particles are immersed to wet or lubricate the metal surfaces and consequently to affect the frictional melting processes.

Acknowledgment. We wish to thank Charles Butterick and the Texas Tech University Health Sciences Center Electron Microscopy Center for help in obtaining the electron micrographs and X-ray microanalyses. This research was supported by the Robert A. Welch Foundation under Grant D-1183.