

# Transformation Behavior in Nano-Scale Binary Aluminum Alloys

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V. K. Vasudevan and J. A. Sekhar, "Transformation Behavior in Nanoscale Binary Aluminum Alloys," in: *Advances in the Metallurgy of Aluminum Alloys*, TMS, Warrendale, PA, pp. 398-405 (2001). **Abstract**

A study was made of the microstructure and transformation behavior of nanometer scale Al-Cu and Al-Zn particles. The alloy particles were made by rapid plasma ablation followed by rapid quenching. The particles were found to be in the supersaturated state in both the Al-4.4wt% Cu and Al-(15-40) wt% Zn alloys studied. The particles all displayed a variation in the individual particle composition when compared to the precursor bulk alloys. The particles were exposed to air and were found to contain a 3nm thick adherent aluminum oxide scale which prevented any further oxidation. Several of the particles were faceted and bound by (111) planes. The alloys were heat treated in order to examine the precipitation sequence in the Al-Cu alloys and to examine the spinodal decomposition in Al-Zn alloys. Differences in the transformation behavior of these alloys when compared to bulk alloys of the same composition were observed. In the Al-Cu alloys, precipitates, which were rich in copper, were noted at the beginning of the transformation. These then transformed to precipitates with lower copper content, as the heat treatment progressed. For the Al-Zn alloys, a spinodal structure was noted in the particles. A face centered cubic zinc precipitate was also observed in the Al-Zn alloys.

NANOMETER scale materials have the potential to enable the significant leaps required in the science, technology and application of new lightweight, high-strength, high conductivity, medium-temperature materials. Such new materials are expected to find use in the ever-demanding energy, transportation, propulsion, space, and structural systems. Nanoscale building blocks (particles) are of interest, as in this size range, the phenomena associated with atomic and molecular interactions strongly affect the macroscopic properties of materials very differently than do building blocks at, say, the micrometer scale. The microstructure, processing and properties of these types of nanoscale materials are unique and represent the next frontier in alloy development of new materials, specially for the scientific study of phenomena where the length scales of diffusion, precipitation and spinodals are all very similar. Additionally, these materials possess design possibilities that make them of intrinsic technological interest. The infinite variety of materials that may now be combined in several forms also

allows for the construction of new nanoscale hybrid materials or composites with unique combinations of mechanical, optical, electrical, and chemical properties with functionalities that may far surpass those of the individual components/constituents. A variety of products are foreseen in structural components, high-performance coatings, electronics, aeronautics, space, energy and biomedical engineering systems. New industries are already rapidly being spawned from the fundamental discoveries in nanoscale materials science & engineering which are rapidly being made. In this article, some of the developments specific to conventional aluminum alloys in the nano scale regime are presented. In particular, the precipitation phenomena and spinodal decomposition in nanometer scale particles of important aluminum binaries and their potential effects on properties are shown for the first time.

The two binary systems studied are the Al-Cu and Al-Zn alloys. Copper is a common alloying element added to aluminum to increase strength. Copper may be retained in solid solution at room temperature by quenching the alloy from a higher temperature (548°C) where up to 5.7 wt% may be taken into solid solution. In addition, rapid quenching of liquid aluminum copper alloys is known to display solid solubility up to 35wt%Cu. When super saturated solutions are further age hardened, four structures are recognized, namely, (a) GP1 zones which are very fine (1-3nm) independent of the matrix copper concentration and consist of coherent atomic copper layers in the (100) plane of the matrix, (b) GP2 zones also called T'' are about 1-4nm thick with a plate size of 10-100nm (the GP2 zones have a tetragonal lattice with the 'a' parameter same as the matrix), (c) the T' phase which has the CuAl<sub>2</sub> lattice, with a thickness 10-15nm and disk diameter 10-600nm and (d) the equilibrium CuAl<sub>2</sub> phase. The T' is noted always with a ring of dislocations so that no coherency strains exist. The equilibrium CuAl<sub>2</sub> is generally thought to replace the T', although it is recognized that the equilibrium structure may form directly from the matrix also. Although, all the four phases have been reported to have independent nucleation and growth tendencies, the GP2 zones are also often thought to be a product of the GP1 zones and are known to grow much slower than the GP1 zones. The formation of the T' phase as a product of T'' has also been considered. A comprehensive review is given in Reference 1.

Zinc is often added to aluminum alloys for imparting superplastic behavior or for causing zinc-magnesium precipitates to form in the matrix. The Al-Zn system contains a miscibility gap with a critical composition of 40 at%Zn (61.3 wt%Zn). The coherent spinodal and the chemical spinodal are very close in this system. (separated by about 35°C). Aluminum zinc alloys may be age hardened by the formation of mostly spherical GP zones, 1-6 nm in

diameter. When larger than 3nm, the precipitates become elliptical. These zones are eventually replaced by a face centered rhombohedral phase which is coherent with the matrix. The intermediate phase forms as platelets on the (111) plane. Dislocations cause a loss of coherency and the intermediate phase becomes fcc with a lattice parameter of 0.399nm. Eventually the intermediate phase changes to the hexagonal lattice. At higher aging temperatures, the GP zones do not form and a spinodal is noted. A fcc precipitate with a lattice parameter of 0.377nm has also been reported (1) which transforms to the equilibrium hexagonal phase. The suppression of the spinodal during the quench process is difficult. The data of the subsequent shift in wave number (an increase in the wavelength) with aging time is attributed variously to spinodal amplification (2) or coarsening (3). Aging at 1 hr at 65°C or 150°C for a Al-40 wt%Zn alloy produces wavelengths of approximately 5nm and 10nm respectively (2).

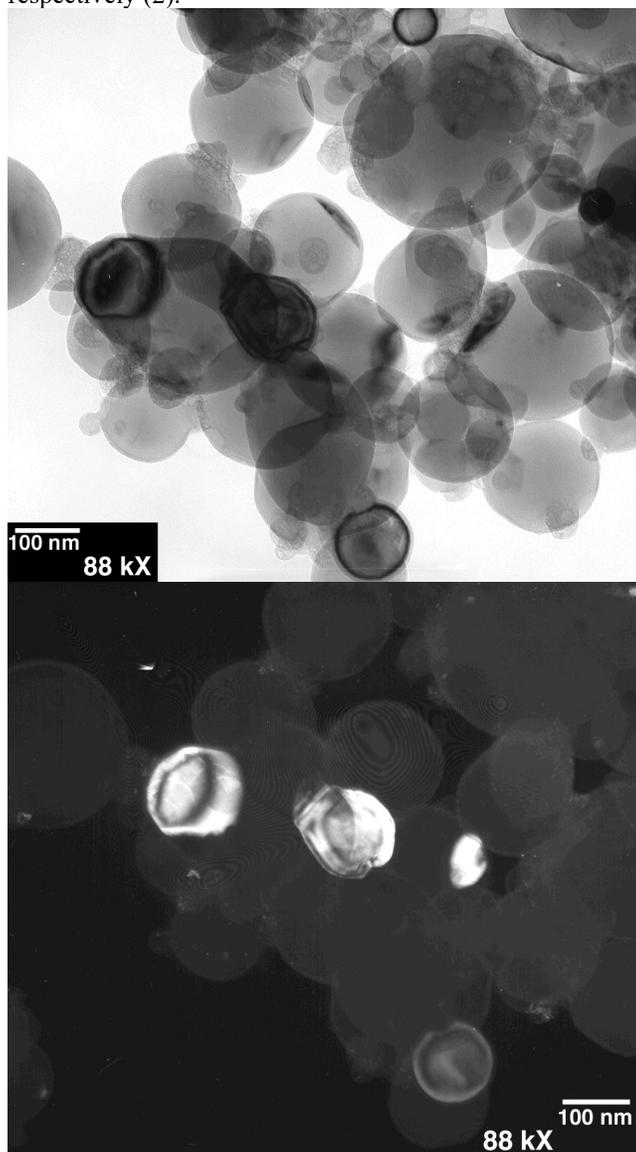


Figure 1(a) (top). A bright field TEM image of Aluminum-Copper nano particles. Figure 1(b) (bottom). The corresponding dark field (111) image.

## Processing

Two compositions (alloys) were initially made, namely, Al-4.4 wt%Cu alloy and Al-15 wt%Zn. As discussed below, the composition of the particles were found to be modified (after converting to the nanocrystalline state) when compared with the original bulk compositions.

Ultra high purity (5-9's) raw materials were melted under a clean nitrogen PlasmaAirtorch\* atmosphere in a graphite crucible. The alloys were cast into 2" diameter and 2" height ingots. The aluminum copper ingots were solution heat treated to 545°C for 48 hrs and the aluminum zinc ingots were solution heat treated to 450°C for 50 hrs. The alloys were next sent for making the nano particles\*. Although, most of the conditions under which the particles were made, were proprietary, the company released the following details.

The process relies upon a "plasma gun" by creating an arc between two electrodes, to produce a metal vapor plasma which is rapidly quenched to form a gas phase suspension of nano-scale metal particles. The power discharge typically is 30 to 100 MW per shot. The material is then collected in an ESP. There is some residue in the main tank also. The company normally manufactures oxide and other non metallic powders. For those powders, typically, the material in the ESP is very small, e.g. 10 to 50nm while the residue in the tank is somewhat larger, typically 100 to 200nm. For the metallic aluminum materials collected for this study, the tank particle size is 1 to 2 microns mean particle size, whereas, that collected in the ESP is much smaller in size. For example, for shot 1 (row 1 in Table 1) about 5 grams of 2 micron material is collected in the tank. For the aluminum copper alloy the mean particle size from the BET measurements and the corresponding amount of material collected in the ESP is given in Table 1 below. A similar collection is obtained for the aluminum zinc particles.

## Experimental Technique

The particles were examined in the as received (called as synthesized in the rest of this article) condition and in the aged condition. Ageing was conducted by heating in evacuated and Argon back filled capsules, which also had a thin titanium strip placed in them for oxygen getting. For the Al-Cu particles, aging was conducted at 130°C and 190°C for times ranging from 1 to 10 hours. The Al-Zn were aged at 130°C only, again for durations ranging from 1 to 10 hours. Longer time heat treatment studies are presently on going.

The nano particles were characterized by X-ray diffraction, scanning (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS) in theTEM.

\* The PlasmaAirtorch is a trade mark of MHI Inc. Cincinnati, OH, 45208

\* The particles were made by Nanotechnologies Inc., Austin Texas, 78758

Prior to TEM observations, the nano particles were dispersed in methanol in an ultrasonic unit and then deposited onto carbon-coated nickel grids using a pipette. TEM observations were performed using a Philips CM200 (LaB6 and FEG sources) microscope operated at 200kV under bright field (BF) dark field (DF) conditions and selected area diffraction (SAD) modes. For determining the chemical compositions of the particles, x-ray spectra were recorded using a Voyager ultra-thin window EDS systems fitted to the TEM; standardless analysis only was utilized to ascertain the compositions of the particles.

**Table 1: The typical collection of nanometer size particles per run.**

Average Particle Size in nm.	Collection in the ESP per run, mg
136	656
130	587
86	80
93	482

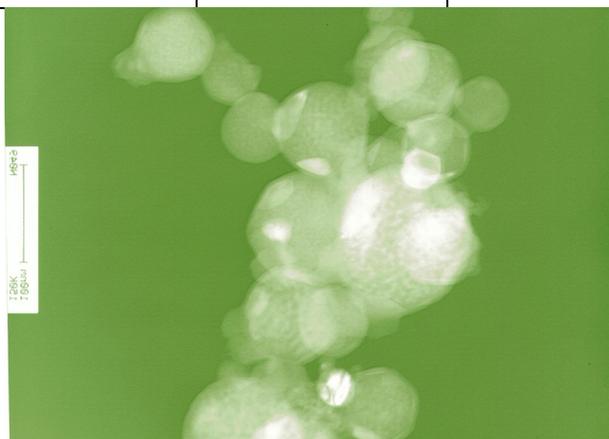


Figure 1 (c). A bright field TEM image of the as synthesized Al-Zn nano particles. Note the mottled structure in the particles. The bar is 100nm.

## Results

The particles were electron transparent to a diameter of about 200nm. All particles in the as synthesized state were single phase, indicating that for all the Al-Cu and Al-Zn compositions studied, the as synthesized state, at room temperature, was one which was mostly supersaturated (the Al-Zn alloys however also exhibited some mottling and occasional precipitation, discussed below).

### As Synthesized Microstructures

Al-Cu alloys: Figure 1(a) is the bright field TEM image of a typical Al-Cu alloy batch. Figure 1(b) is the corresponding dark field image recorded for a (111) fcc reflection. Both x-ray and electron diffraction gave confirmation of the fcc structure with a lattice parameter of  $\sim 0.404$ nm. The particles ranged in size from 20-150nm with occasional particles in the 200nm range as shown in Figure 2. A adherent oxide scale 3-4nm in thickness was noted to envelop the particles. No dislocations were noted in any of the particles. EDS analysis revealed considerable variation in the amount of Cu which ranged from 0.5 wt% to 4.5 wt%Cu. All measurements were obtained without standards. All the particles were single phase (supersaturated).

Al-Zn alloys: The particle size range was observed to be between 20-150nm (see Figure 1 (c)). No large particles were observed, unlike the Al-Cu alloy case. The particles were again faceted and bound by (111) planes. An oxide envelop of about 3nm was again noted. EDS analysis again indicated a considerable variation from 24-62 wt%Zn in the particles. This was surprising, as the starting composition was only 15 wt%Zn. Occasionally, pure Zn faceted particles were also noted. Although the particles were all single phase (supersaturated), the microstructure in the Al-Zn particles was noted to be mottled inside the particles with the mottling becoming more apparent at the higher concentrations of Zn.

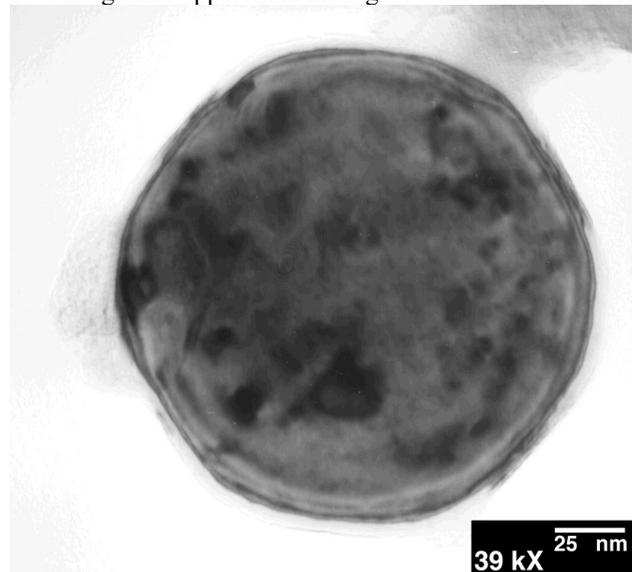


Figure 2. A large particle (much larger than the average size of the nano particles normally obtained from the processing) which clearly shows the aluminum oxide envelop and facets. All the nano-scale particles studied had a 3 to 4 nm oxide envelop. The large particle shown above displayed an average oxide envelop thickness of about 5nm, except at a location on the left side of the particle where the oxide had grown to about 15nm thickness. Such large thickness anomalous oxide growth was not seen in particles below 150nm(diameter) size.

### Aged Microstructures

Al-Cu alloys:

Aged at 130°C for 1 hour: Figure 3 shows a TEM bright field image of the particles. Note the appearance of the second phase in some of the particles. The average particle composition was noted to range from about 2.35 wt%Cu to 4.89 wt%Cu. The second phase precipitate appears plate-like with a plate length (diameter) of about 20nm and a thickness of about 10nm.

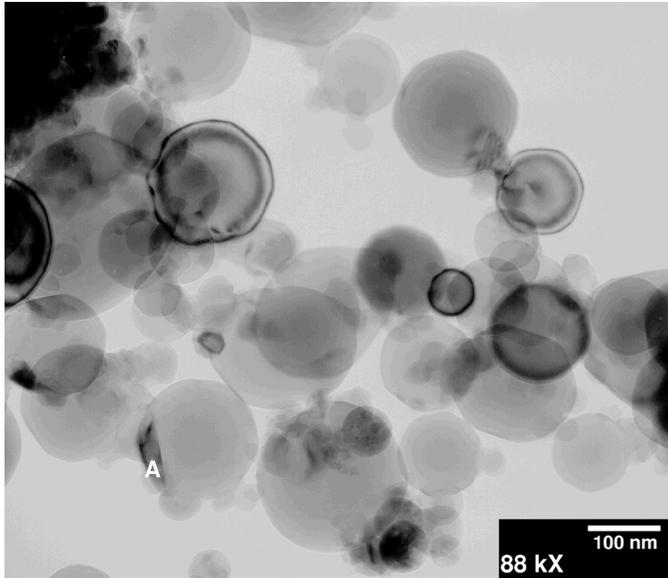


Figure 3: TEM bright field image of the Al-Cu particles aged at 130°C for 1 hr. Note the appearance of the second phase particle (e.g. at position labeled A)

Aged at 130°C for 10 hours: Figure 4 shows the TEM bright field image of the particles for this condition. Note the appearance of a larger number of precipitates of a second phase. In most cases the precipitates appeared at the aluminum oxide/particle interface. The second phase precipitate appears plate-like with a plate length (diameter) of about 20-50nm and a thickness of about 10-20nm. EDS analysis indicated a variation from 20-53 wt% Cu in the precipitate regions. The matrix region was largely depleted in Cu and indicated concentrations of in the range 0.2–0.4 wt%Cu. The beam size of the electron probe was about 10nm, so some sampling from the adjacent regions may be expected.

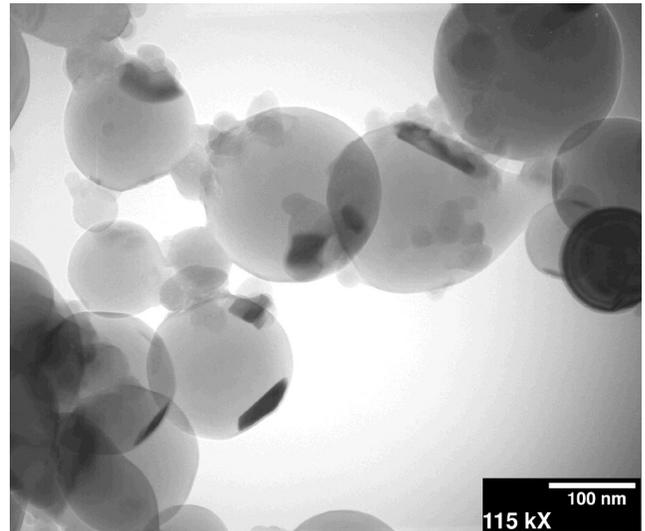
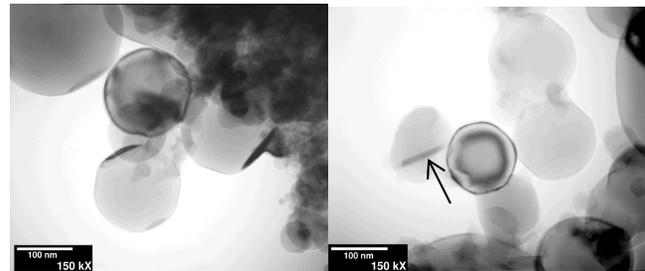


Figure 4: Bright Field TEM picture after aging at 130°C for 10 Hours. Note the emergence of more second phase precipitation compared to Figure 3 above.

Aged at 190°C and 1 hour: Figures 5 (a) and (b) show the particles with the precipitates. The copper concentration in the precipitates was noted to be between 75-95 wt% Cu. The matrix composition was between 0.5 and 1 wt% Cu.



Figures 5(a) (on the left) and (b) (on the right): TEM bright filed images of the precipitation observed in the Al-Cu particles when aged at 190°C for 1 hour. Note the distinct facets of the particles which are thought to be the (111) planes. The arrow points to a precipitate which appears to have nucleated either inside the particle or on the oxide/particle surface at a location on the top or bottom of the particle.

Aged at 190°C for 10 hours. Figure 6 shows a typical precipitate and particle photomicrograph for this condition. The precipitate composition was now found to be 35-45 wt%Cu and the matrix was noted to be substantially depleted in Cu, to a level less than 0.2 wt%Cu.

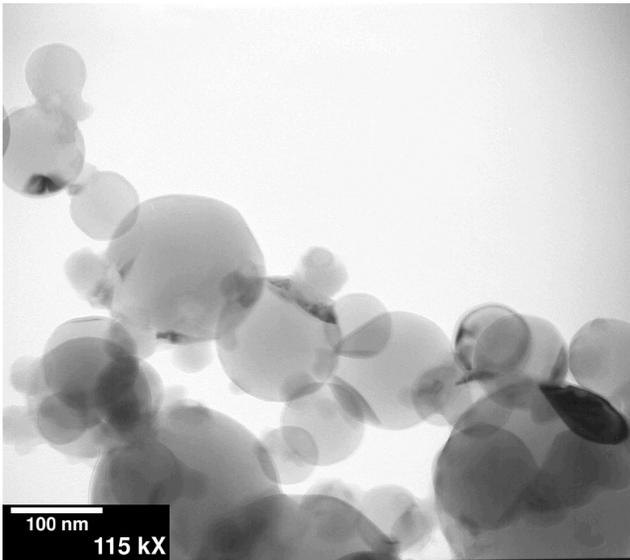


Figure 6: TEM bright field image of the precipitation observed in the Al-Cu particles when aged at 190°C for 10 hours.

Al-Zn alloys:

The Al-Zn alloys showed mottled structures which were noted in the higher Zn particles even in the as ablated and quenched (as synthesized) alloy particles (see figure 1(c)).

Aged at 130°C for 1 hour: Figures 7(a) and (b) show the wide variation in microstructures observed for this alloy. Most of the particles (Figure 7(a)) displayed two types of features. (a) a serrated structure in two orientations and (b) a much coarser precipitate or segregate which formed along the oxide/particle surface. The latter structure was found to be nearly pure Zn (85-95wt%). Preliminary diffraction analysis indicated this phase to be face centered cubic. EDS analysis performed along the serrations indicated that the serrations consisted of high and low zinc rich regions. A typical average Zn analysis indicated 35-45 wt%Zn. Occasionally, pure zinc particles as shown in Figure 7(b) were also noted. Such particles were also sometimes noted in the as synthesized samples of the Al-Zn alloys.

Aged at 130°C and 10 hours: Figure 8 shows a typical photomicrograph for this condition. The serrated structure was still apparent but seemed to have yielded to the pure Zn precipitates. The number of the Zn precipitates increased considerably over that observed in Figure 7(a).

The spacing of the mottled and serrated structures appears to have increased with the heat treatment exposure. However when analyzing such information, caution should be exercised because the starting composition of the particles varied considerably.

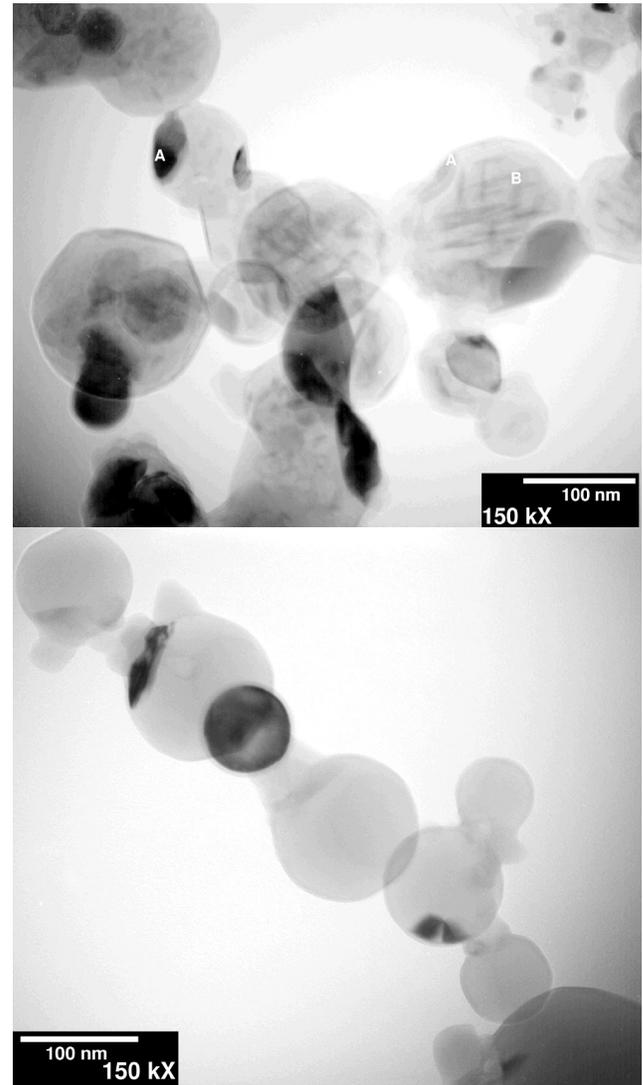


Figure 7, (a) (top): A TEM bright field image of the Al-Zn particles aged at 130C for 1 hour. Note the two types of transformations noted in the particle,s namely precipitates labeled A and the serrated structure labeled B. (b) (bottom): A TEM bright field image of the Al-Zn particles aged at 130C for 1 hour. The dark particle in the center of the photomicrograph is pure Zn. Note the facets in this particle.

## Discussion

The as synthesized alloys all were single phase and except for some mottling noted in the Al-Zn alloys no other features such as dislocations or boundaries were observed. After the heat treatment, a common feature which was noted for both alloys, was, that the precipitation in both alloys appeared to initiate at the aluminum oxide/particle interface. No dislocation were noted in either alloy particle at any condition, and when precipitates appeared, normally only one precipitate per particle was noted. On occasion, two precipitates per particle could be seen but this was very rare.

The as synthesized super saturated aluminum copper alloys appeared to follow a decomposition sequence normally noted in bulk alloys(1), however, some clear differences were noted from such a comparison. In bulk alloys, the precipitation (generally inferred from hardness measurements) begins at a temperature of about 130°C after a 1 hour soak and reaches a peak at 100 hours with a plateau region in the 10 hour range. During this processes, initially the GP1 zones nucleate on defects such as dislocations or collapsed vacancy clusters and then further possibly coarsen to T'', while metastable Al-Cu regions (called T') also begin to appear. The GP1 zones and T'' display coherency with the matrix and are associated with some lattice strain. In bulk alloys at the 100 hour time exposure, the volume fraction of such precipitates is high. Eventually at very high time or temperature exposures, the equilibrium Al<sub>2</sub>Cu precipitates appear, which are incoherent with the matrix. The appearance of the GP1 zone is associated with an increase in the hardness of the alloy and a decrease in ductility, peak hardness is normally seen when the GP2 and T' zones appear, the equilibrium phase is normally associated with a drop in hardness of the alloy.

In bulk Al-Cu alloys, the GP1 zones are about 1-3nm in thickness depending where the location of the boundary with the matrix is inferred. The distance between individual GP1 zones in bulk alloys is about 2-4nm and about 10<sup>14</sup>–10<sup>15</sup> zones are formed per mm<sup>3</sup> i.e. a cube with a 10nm edge, would be expected to contain roughly one GP1 zone. As the amount of copper remains nearly the same when GP2 zones form, the distance between GP2 zones is larger than between GP1 zones. Generally the GP2 zones are separated by 20- 100nm.

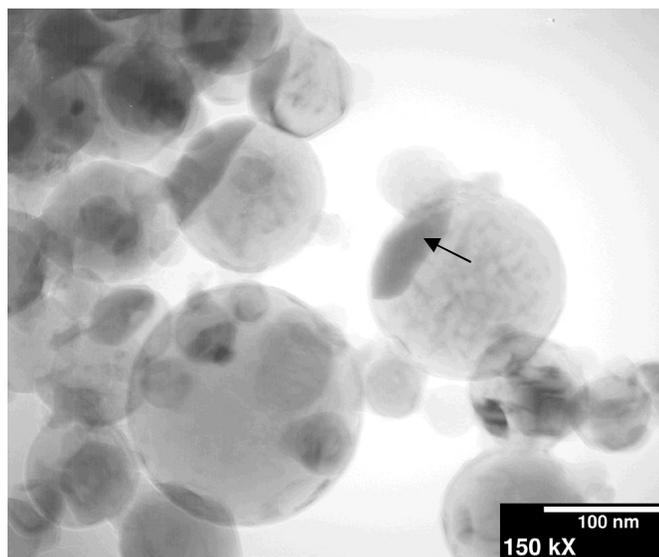


Figure 8: A TEM bright field image of the Al-Zn particles aged at 130°C for 10 hours. The arrow points to large zinc precipitate formed at the particle precipitate boundary.

For the nano particles aged at 130°C for one hour, the Cu rich regions were noted to form in sizes much larger than conventional GP zones (10-20nm vs.1-10nm in bulk

alloys). Only one precipitate per particle was normally noted. It was noted that for up to the 10 hour treatment at 190°C, no dislocations were present. Coherency was not disturbed by the heat treatment (this was inferred from the straight and sharp boundary between the matrix and the precipitates, with no dislocations). Such an observation is unusual for the alloys, in bulk form, when similar heat treatments are carried out and as mentioned earlier, the T' precipitates are always seen with a ring of surrounding dislocations

In the Al-Cu alloy particles, the sequence of precipitation was inferred to be: super saturated particles (ssp) to very high Cu concentration precipitates to compositions close to the equilibrium Al<sub>2</sub>Cu precipitates (T). The size of the Cu rich precipitate in the 190°C and 1 hour treatment was found to be about 10-20nm thick and again seemingly coherent with the Cu depleted matrix. This size i.e. 20nm, is nearly double that of the copper rich GP zones observed in bulk Al-Cu alloys. Once the precipitation began in the particles, the matrix was quickly depleted in Cu (in the order of time of one hour) and remained so for the entire subsequent precipitation sequence. Diffraction evidence is being gathered to identify the precise nature of the precipitates. The precipitates in the Al-Cu alloys were found to have a well defined, sharp and straight boundary with the matrix, suggesting that the interface was coherent. Such coherency was seemingly not disturbed by the changes in the heat treatment or precipitate composition.

In the Al-Zn alloy case, one key observation was that the nano particles were significantly enhanced in zinc content when compared to the parent ingot. It appears that the Zn may have vaporized in larger quantities during the ablation process and when the particles were cooled, the excess zinc was trapped in the nano particles. Conversely, the much larger particles or the ablated ingot surface should appear depleted in Zinc. We were unable to verify this issue on account of the fact that the ingots could not be recovered after the plasma ablation process.

A spinodal like microstructure was observed within the as synthesized nano particles. For compositions greater than 30 wt%Zn such a spinodal is expected to form by thermodynamic considerations (2). Again, differences in the rate of formation and decay of the spinodal were observed in the nano particles when compared with bulk alloys (this aspect will be discussed in detail elsewhere). It appears that the spinodal grows or coarsens, rapidly, and a zinc rich (nearly 100% Zn) phase simultaneously precipitates at the aluminum oxide/ particle interface. Often these precipitates indexed as face centered cubic. The mottled structure in the as synthesized particles displayed an average wavelength of about 7nm, and the treatment at 130°C (1 hr) and 130°C (10 hr) showed serrated structures with wavelengths in the 10-20nm range. As each particle had a zinc content which varied considerably when compared to the bulk, it was difficult to accurately compare these results from what could be inferred from early stage spinodal formation theory (4). A more

detailed analysis is on-going to follow the spinodal sequence for groups of particles which have the same composition.

The transition from the spinodal to the equilibrium structures is now being studied in more detail. Diffraction analysis of the precipitates is also on going to better understand the sequence of the transformation in both alloys.

## Summary and Concluding Remarks

Some key observations were:

- (1) The plasma ablated (as synthesized) nano particles show a variation in the composition when compared to the precursor ingots. In the case of the Al-Zn alloys, the nano particles displayed considerably more Zn than the parent ingot.
- (2) The particles were electron transparent to a diameter of about 200nm. All the particles in the as synthesized state were single phase, indicating that for all the Al-Cu and Al-Zn compositions studied, the as synthesized state at room temperature was one which was mostly supersaturated.
- (3) The particles, as synthesized and as heat treated, were completely devoid of dislocations.
- (4) Upon heat treatment, mostly, only one precipitate per particle could be observed. Very occasionally, two particles were seen but this was rare. All precipitates were located at the particle oxide interface. All the nano aluminum particles, for both alloys, were enveloped by a 3-4nm oxide envelop.
- (5) The Al-Zn alloy particle microstructures showed spinodal like decomposition which were noted in the higher Zn particles in the form of a mottled structure, even in the as synthesized alloy particles.
- (6) In the Al-Zn alloys, pure zinc precipitates were noted to appear along the particle oxide interface and additionally serrated (alternating zinc rich and zinc depleted regions, most likely a spinodal, which has grown or coarsened) were noted inside the particles.
- (7) There were no precipitates in the as quenched Al-Cu particles, but precipitation was apparent even for the heat treatment condition of 130°C for 1 hour.
- (8) In the Al-Cu alloys, the sequence of precipitation was super saturated particles (ssp) → very high Cu concentration precipitates to Al<sub>2</sub>Cu (T) precipitates. Once precipitation began, the matrix appeared quickly depleted in Cu and remained so for the entire precipitation sequence. Diffraction evidence is being collected to confirm the exact nature of the precipitates and the sequence of decomposition.
- (9) A heat treatment at a temperature of 130°C and soaking time of 10 hours appeared to be adequate for completing the transformation of the supersaturated particle to phases which compositionally appeared to

be the equilibrium precipitate/aluminum matrix phases in the Al-Cu alloys.

- (10) There was no evidence of any dislocations or dislocation activity, in any of the observed particles. (note HREM studies of the particle matrix interface are on-going).
- (11) The precipitates in the Al-Cu alloys were found to share a well defined, sharp and straight boundary with the matrix, suggesting that the interface was coherent. Such coherency was not disturbed by the changes in the heat treatment or precipitate composition. (Again further studies are on-going)
- (12) The size of the early Cu rich precipitates noted for all the 1 hour heat treatments, was found to be about 10-20nm thick. This size is nearly double in thickness of the copper rich GP zones observed in bulk Al-Cu alloys.

The type of microstructure and transformation behavior noted in these nano particles appear to be different than that noted in bulk alloys, and very different from that seen in rapidly solidified aluminum alloy particles and ribbons (5). The size of the particles appear to be small enough to relieve transformation strain, and this one aspect may significantly be influencing the transformation behavior for the precipitation and the spinodal. Further exploratory work is on-going at the time of writing this article.

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