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# The Electrodeposition of an Aluminum-Manganese Metallic Glass from Molten Salts

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## ABSTRACT

The electrodeposition of binary aluminum-manganese alloys from chloroaluminate molten salts is reported. The manganese content of the electrodeposit varies from 7 to 30 w/o and is dependent upon deposition potential and the relative concentrations of  $Al_2Cl_7^-$  and  $Mn^{++}$  in the melt. At small cathodic overpotentials the deposition process, with respect to alloy composition, is kinetically controlled. At larger cathodic overpotentials, it becomes mass transport limited in Mn<sup>+</sup> and then  $Al_2Cl_7$ . The most uniform and brightest deposits are obtained at a constant potential of -0.3V with respect to an aluminum wire in the same electrolyte. The potential dependence of alloy composition allows one to create homogeneous, graded and modulated structures from a single electrolyte. The structure of the as-deposited alloy appears to be that of a metallic glass above 27 w/o manganese and a mixture of glass and supersaturated aluminum below 27 w/o. Heating to 400°C converts the deposit containing less than 26 w/o Mn to a mixture of the orthorhombic Al<sub>6</sub>Mn intermetallic and aluminum. The ability to electrodeposit intermetallic compounds on a near atomic scale presents interesting possibilities for high temperature alloys.

Metallic glasses have received widespread attention because of their promising chemical, electrical, and mechanical properties. These single-phase alloys can be of the metal-metalloid type where late transition metals such as Fe, Co, Ni, Pd, or Au are combined with B, C, Si, P, or Ge. Binary metal-metal glasses such as Cu-Zr, Ni-Nb, Ti-Be, and Ca-Mg have also been demonstrated (1). Aluminum containing metallic glasses (Ca-Al, La-Al, and Y-Al) have been investigated recently for their electrical properties (2-5), but very little work has been reported on the properties of Al-rich metallic glasses.

Aluminum and some of its alloys can be electrodeposited from molten salt electrolytes. The chemical equilibria operative in AlCl<sub>3</sub>/NaCl melts under a wide range of AlCl<sub>3</sub> concentrations above the equimolar point are well known (6-9), and extensive work has been reported on the deposition of pure aluminum from these electrolytes (10-20). The electroactive species in 2:1 mole ratio AlCl<sub>3</sub>:NaCl melts is  $Al_2Cl_7$  and is present at concentrations approaching 3.5M. Its reduction occurs by the following

$$4\mathrm{Al}_{2}\mathrm{Cl}_{7}^{-} + 3e^{-} \longrightarrow \mathrm{Al} + 7\mathrm{Al}\mathrm{Cl}_{4}^{-}$$
[1]

The reduction of AlCl<sub>4</sub><sup>-</sup> occurs at potentials more negative than that required for  $Al_2Cl_7^-$  reduction and becomes prominent as the acidity (AlCl<sub>3</sub> content) of the melt is reduced. The kinetics for the aluminum deposition reaction are quite fast, and exchange current densities on the order of 20 A/cm<sup>2</sup> have been measured at 450°C using the galvanostatic double-pulse method (21). With exchange currents of this magnitude, the aluminum cathode is essentially at equilibrium even at deposition currents approaching 100 mA/cm<sup>2</sup>. Consequently, one has little electrochemical control over deposit morphology which is generally nodular and quite often dendritic (22)

Efforts to obtain bright aluminum deposits from chloroaluminate electrolytes have included studies of deposition onto various substrates, the use of ac superposition (19) and the addition of agents including water (14), organics and metal chlorides (23). The most remarkable improvement has been seen with the addition of small amounts of

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MnCl<sub>2</sub> (24, 25). Specular deposits containing 16-45 weight percent (w/o) Mn have been obtained from molten salt electrolytes containing 0.4 w/o MnCl<sub>2</sub> at current densities as high as 100 mA/cm<sup>2</sup>. The manganese content of the electrodeposit was reported to increase with increasing MnCl<sub>2</sub> and an empirical relationship was developed so that the manganese content of the electrodeposit could be predicted from melt composition. These investigators found alloy composition to be independent of current density. Hayashi reported a similar increase in Mn composition of the deposit as well as an increase in the activation overpotential with increasing  $MnCl_2$  (26).

The structures of these electrodeposited aluminummanganese alloys have been investigated (27). Low manganese deposits (arbitrarily chosen as less than 16 w/o Mn) consisted entirely of a supersaturated solid solution of manganese in aluminum. High manganese deposits were reported to contain the supersaturated solid solution and also exhibited electron diffraction patterns consistent with that of a glassy structure. The diffuse band could not be identified directly from electron diffraction, but other data (27) suggested that it was due to the Al<sub>6</sub>Mn intermetallic. A crystallite size for the intermetallic was not reported.

The purpose of this paper is to describe our work on aluminum-manganese alloy deposition from a eutectic AlCl<sub>3</sub>/ NaCl melt. Our efforts have concentrated on characterizing the aluminum-manganese deposition process and determining the parameters influencing alloy composition, deposit quality, and structure. Contrary to the previously cited literature, we find that the manganese content of the deposit is clearly potential dependent; consequently, the deposition of some very interesting structures is possible.

#### **Experimental Procedure**

The AlCl<sub>3</sub> was obtained from Aldrich<sup>1</sup> (99.99% pure) and was used as received. The NaCl (Mallinckrodt, Reagent) was dried for 4h at 500°C. The manganous chloride (Fisher, Reagent) was received in the hydrated form,  $MnCl_2 \cdot 4 H_2O$ , and was heated to 225°C for 4h to remove the water (dehy-

<sup>1</sup>Certain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

dration temperature is 198°C). The reagents were then transferred to an argon dry box. The composition of all melts was 2:1 mole ratio AlCl<sub>3</sub>:NaCl. The powders were thoroughly mixed in the dry box before being transferred to the cell, which has been described elsewhere (22). The temperature of the mixture was increased to 150°C and the resultant melt was pre-electrolyzed for 48h using a platinum screen working electrode held at a potential of +0.01V with respect to an aluminum wire in the same electrolyte. After pre-electrolysis, the background current density at a tungsten indicator electrode was 340  $\mu$ A/cm<sup>2</sup> at +0.1V vs. Al at a sweep rate of 0.1 V/s. The desired amount of MnCl<sub>2</sub> was then added. The melt temperature for all experiments was 150°C.

Potential control was maintained with a PAR Model 363 potentiostat/galvanostat and a PAR Model 175 universal programmer. The counter and reference electrodes were 2 mm aluminum wire (99.99%) while the substrate for the electrodeposits was copper (OFHC) either in the form of a 0.76 mm wire or 1 cm  $\times$  2.5 cm  $\times$  0.05 cm wafer. In all cases the copper was electropolished in 50% H<sub>3</sub>PO<sub>4</sub> and then thoroughly dried. After introduction into the melt, the working electrode was allowed to come to thermal equilibrium at a potential of +0.2V vs. Al to cathodically protect the copper. The deposition process was controlled galvanostatically at 40 mA/cm<sup>2</sup> until a charge of one C/cm<sup>2</sup> had passed to eliminate problems associated with nucleation overpotentials. At this time the PAR 363 was manually switched to the potentiostat mode (while the cell was disabled) and further deposition was controlled potentiostatically.

X-ray diffraction (Cu-K $\alpha$ ) patterns were measured for the deposited films after the copper wafer substrate was removed by concentrated HNO<sub>3</sub>. The manganese content of these free standing films was determined by atomic absorption. Deposits on copper wires were overplated with bright copper (after a room temperature zincate treatment and cyanide copper strike) and were then mounted in epoxy to expose the cross section. Alloy composition of these alloys was determined by energy dispersive spectroscopy (EDS) quantitative analysis using pure aluminum and manganese standards. Deposit hardness was measured on these polished cross sections using a Knoop indenter under a 10g load; the values reported are the average of four measurements.

#### Results

Steady-state current-potential measurements and linear sweep voltammetry at slow scan rates normally yield little kinetic information in molten salt systems since ohmic and mass transport contributions are significant when compared to the activation overpotential even at very low current densities. Figure 1 is a set of curves which qualitatively shows this effect and its dependence on MnCl<sub>2</sub>. In aqueous electrolytes, the reversible potential for manga-



Fig. 1. Linear sweep voltammetry in 2:1 mole ratio AlCl<sub>3</sub>:NaCl electrolyte with (a) 0.25 w/o MnCl<sub>2</sub>; (b) 0.50 w/o MnCl<sub>2</sub>; (c) 0.75 w/o MnCl<sub>2</sub>; (d) 1.0 w/o MnCl<sub>2</sub>. One C/cm<sup>2</sup> was first deposited onto a copper substrate at 40 mA/cm<sup>2</sup> to eliminate problems associated with nucleation overpotentials. Sweep rate = 5 mV/s and  $T = 150^{\circ}$ C.



Fig. 2. Alloy composition and deposit quality as a function of deposition potential for a 2:1 AlCl<sub>3</sub>:NaCl melt containing 0.25 w/o (□); 0.50 w/o (▲); 0.75 w/o (◊); 1.0 w/o (♦); and 1.25 w/o (□) MnCl<sub>2</sub>. Each reported alloy composition is the average of 12 EDS readings. Substrate was a 0.76 mm diameter copper wire. Melt temperature was 150°C.

nese deposition is positive of that for aluminum. In contrast, manganese is less noble than aluminum in this chloroaluminate electrolyte and the reduction of  $Mn^{++}$  occurs at a potential more negative than the reversible potential for aluminum deposition; consequently discrete reduction peaks for the two reactions are not seen. At low MnCl<sub>2</sub> concentrations, the curve is similar to that for pure aluminum where the entire scan is dominated by solution resistance, resulting in a linear current-potential curve in this region. As the MnCl<sub>2</sub> concentration is increased, the activation overpotential increases dramatically and dominates at the lower current densities. It is this shift from ohmic to activation control which is at least partially responsible for promoting lateral growth and eliminating the nodular and dendritic morphology.

Figure 2 is a set of curves relating alloy composition and deposit quality to deposition potential and  $MnCl_2$  concentration. The manganese content of the deposit varies from 7 to 30 w/o and increases with increasing  $MnCl_2$ . Contrary to reports in the literature (24), there is a dramatic dependence of alloy composition on potential, particularly at the higher  $MnCl_2$  concentrations. At all concentrations, the manganese content of the deposit drops slightly at a critical potential. The potential at which this occurs shifts to more negative values with increasing  $MnCl_2$ , suggesting that  $Mn^{++}$  is becoming mass transport limited. At a potential of -0.35 V/Al the deposition current is seen to approach a constant value, indicating that  $Al_2Cl_7^-$  is nearly diffusion limited as well.

The deposit quality of all of the alloys depicted in Fig. 2 is much superior to that of pure aluminum and generally improves with increasing MnCl<sub>2</sub> and at more negative potentials. Specular deposits were obtained at -0.3 V/Al for nearly all MnCl<sub>2</sub> concentrations and the alloy composition ranged from 12 to 29 w/o. At potentials negative of -0.35V/Al, deposit quality drops without an appreciable change in alloy composition. These results clearly indicate that a high manganese alloy is not required and is certainly not a sufficient condition for generating bright deposits. The deposition potential is the key to obtaining bright deposits with the favorable potential window broadening with increasing MnCl<sub>2</sub> concentration. It is also interesting to note that the standard deviation of the reported alloy compositions (average of 12 EDS readings) can be related to deposit quality. The most uniform deposits are also the brightest and were deposited at -0.3 V/Al.

X-ray diffraction patterns were measured for the electrodeposited films. Some of the patterns are shown in Fig. 3. Deposits containing greater than 27 w/o Mn have patterns consistent with that of a metallic glass structure, *i.e.*, a broad, diffuse peak is seen rather than sharp Bragg diffraction peaks. As the manganese content of the deposit is reduced, the (111) and (200) Bragg diffraction peaks for aluminum begin to appear and reveal a lattice constant



Fig. 3. X-ray (Cu-K $\alpha$ ) diffraction of electrodeposited aluminummanganese alloys.

smaller than that for pure aluminum. This lattice reduction is due to the substitution of aluminum by manganese in solid solution. The equilibrium phase diagram for the aluminum-manganese system shows that aluminum and orthorhombic Al<sub>6</sub>Mn are in equilibrium up to 25 w/o Mn, beyond which  $Al_6$  Mn and the  $\lambda$  phase (hexagonal  $Al_4$ Mn) are in equilibrium (28). The diffraction patterns in Fig. 3 indicate that the electrodeposited alloys are subject to some of the same stoichiometric limitations as those shown in the equilibrium phase diagram since fcc aluminum is not seen in alloys containing greater than 27 w/o Mn. These results suggest that the glassy structure has a stoichiometry similar to that of Al<sub>6</sub>Mn. Though metallic glasses can be expected to show short range order, none of the diffraction techniques used by us or reported in the literature (27) have positively identified this glass as the Al<sub>6</sub>Mn intermetallic.

When electrodeposits containing less than 26 w/o Mn are heat-treated to 400°C, the alloy is converted to a mixture of the Al<sub>6</sub>Mn intermetallic and aluminum. After crystallization, alloy hardness increases significantly and becomes widely scattered due to segregation of aluminum and the



Fig. 4. Knoop hardness (10g load) vs. alloy composition for electrodeposited alloys before and after crystallization.

intermetallic, Fig. 4. The intermetallic grain size was not determined and its distribution in the aluminum and crystallization kinetics are not presently known.

The potential dependence of manganese incorporation allows one to deposit some very interesting structures. Figure 5 is a set of EDS linescans from deposit cross sections showing the relative intensities for aluminum and manganese under different deposition conditions from the same melt containing 1.5 w/o MnCl<sub>2</sub>. When the potential is held constant with respect to an aluminum wire in the same electrolyte, the concentrations of the two species are constant throughout the 20  $\mu m$  deposit. Under galvanostatic control, the manganese concentration drops radially. As the deposit thickens, the surface area increases resulting in a lower current density and overpotential. In the potential dependent range, Fig. 2, the smaller cathodic overpotential causes a reduction in the manganese content of the alloy. Steeper concentration gradients are possible through computer control by stepping the potential at a rate proportional to the deposition current.

Control over composition provides a means of precisely modulating the microstructure to produce finely spaced layers alternately depleted and rich in manganese. Microstructures of this type have been shown to have significantly enhanced mechanical properties (29), and after heat-treatment, would allow one to produce alternating layers of ductile Al-Mn and Al<sub>6</sub>Mn intermetallic. Modulated structures were obtained through potential modulation between -0.3 and -0.15 V/Al. The manganese rich layers shown in Fig. 5 contain about 30 w/o Mn (EDS, quantitative analysis) while the adjacent layers contain 20 w/o. The layer spacings in this example are approximately 3 µm so they could be resolved by EDS, but much smaller layer spacings are possible. An optical micrograph of a modulated structure is shown in Fig. 6; the layers are continuous with very sharp interfaces.

### Discussion

The data shown in Fig. 2 suggest that the deposition process becomes diffusion limited in  $Mn^{++}$  at a potential dependent upon  $MnCl_2$  concentration and the deposition current indicates that  $Al_2Cl_7^-$  is diffusion limited at -0.35 V/Al. At any time during the deposition process, the alloy



Fig. 5. Distribution of manganese and aluminum radially through the electrodeposit under various deposition conditions; (a) potentiostatic, E = -0.3 V/AI; (b) galvanostatic,  $I = 40 \text{ mA/cm}^2$ ; and (c) modulated, pulsed between -0.3 and -0.15 V/AI for 5 C/cm<sup>2</sup> at each potential.

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composition can be expressed as the ratio of the partial currents

$$W_{i,Mn} = \frac{\frac{N_{Mn} i_{Mn}}{n_{Mn}}}{\frac{N_{Mn} i_{Mn}}{n_{Mn}} + \frac{N_{Al} i_{Al}}{n_{Al}}}$$
[2]

where  $N_{\rm Mn}$  and  $N_{\rm Al}$  are the molecular weights,  $i_{\rm Mn}$  and  $i_{\rm Al}$  are the partial currents, and  $n_{\rm Mn}$  and  $n_{\rm Al}$  are the equivalents per mole for manganese and aluminum. When both electroactive species are diffusion limited, the partial currents' can be expressed as limiting currents (from Fick's second law assuming conditions of linear diffusion)

$$i_{\rm Mn} = \frac{n_{\rm Mn^{++}} \mathbf{F} A D_{\rm o,Mn^{++}} C_{\rm o,Mn^{++}}}{\delta},$$

$$i_{\rm Al} = \frac{n_{\rm Al_2Cl_7} - \mathbf{F} A D_{\rm o,Al_2Cl_7} - C_{\rm o,Al_2Cl_7}}{\delta}$$
[3]

where n are the equivalents for the electroactive species,  $\mathbf{F}$ is Faraday's constant, A is the electrode area,  $D_0$  are diffusion coefficients,  $C_{o}{}^{\ast}$  are the bulk concentrations of the electroactive species, and  $\boldsymbol{\delta}$  is the diffusion layer thickness which is assumed to be equal for the two species. Since the substrate in these experiments is a 0.76 mm wire, the electrode radius is only about a factor of five greater than the steady-state diffusion layer thickness and enhanced cylindrical diffusion may be a factor. Unfortunately, an exact solution to the diffusion equation for the cylindrical case does not exist (solutions may be obtained in terms of Bessel functions chosen to satisfy the boundary conditions for the experiment). Assuming  $\delta$  is less than 100  $\mu m,$  we estimate that this contribution will be less than about 10% of the limiting current for the case of linear diffusion. Since it is assumed that the diffusion conditions are the same for both  $Mn^{++}$  and  $Al_2Cl_7^{-}$ , then  $\delta$  and the cylindrical terms will cancel and consequently will not affect the following results. Substitution of Eq. [3] into Eq. [2] yields the following

$$W_{f,Mn} = \frac{\frac{N_{Mn} n_{Mn^{++}} \mathbf{F} A D_{o,Mn^{++}} C_{o,Mn^{++}}}{n_{Mn} \delta}}{\frac{N_{Mn} n_{Mn^{++}} \mathbf{F} A D_{o,Mn^{++}} C_{o,Mn^{++}}}{n_{Mn} \delta}} + \frac{N_{Al} n_{Al_2Cl_7} \mathbf{F} A D_{o,Al_2Cl_7} C_{o,Al_2Cl_7}}{n_{Al} \delta}$$

Assuming that the diffusion coefficients for  $Mn^{++}$  and  $Al_2Cl_7^-$  are equal [reported to be  $5 \times 10^{-6} \text{ cm}^2/\text{s}$  for  $Al_2Cl_7^-$  (15)], then upon rearranging, Eq. [3] becomes

$$\frac{1}{W_{\rm f,Mn}} = 1 + \frac{N_{\rm Al} \, n_{\rm Al_2 Cl_7} - n_{\rm Mn} \, C_{\rm o, \ Al_2 Cl_7}}{N_{\rm Mn} \, n_{\rm Mn^{++}} \, n_{\rm Al} \, C_{\rm o, \ Mn^{++}}}$$
[5]

For a two electron  $Mn^{++}$  reduction and assuming the aluminum deposition reaction is that given in Eq. [1], then Eq. [5] reduces to

$$\frac{1}{W_{f,Mn}} = 1 + 0.123 \frac{C_{o, Al_2 Cl_7}}{C_{o, Mn^{++}}}$$
[6]

The concentration of  $Al_2Cl_7^-$  for melts of varying  $AlCl_3$  composition was calculated by Boxall (6) and was reported to be 3.5*M* for 2:1 AlCl<sub>3</sub>:NaCl melts. Figure 7 shows the solution to Eq. [6] as well as our data for two different deposition potentials assuming a  $Al_2Cl_7^-$  concentration of 3.5*M*. At -0.15 V/Al and high MnCl<sub>2</sub> concentration, the alloy composition is richer in aluminum than that predicted by melt composition assuming diffusion limited and alloy composition is governed by electrochemical kinetics. At low MnCl<sub>2</sub> concentrations, Mn<sup>++</sup> reduction is mass transport limited while  $Al_2Cl_7^-$  is reduced at a rate well below its limiting current; consequently, alloy composition is richer in manganese than that predicted by melt composition.

At -0.4 V/Al, alloy composition is that predicted by Eq. [6] for all melt compositions suggesting that the deposition



Fig. 6. Optical cross section of potential modulated aluminummanganese electrodeposit. Potential was modulated between -0.3 and -0.1 V/Al for 5 C/cm<sup>2</sup> at each potential. The dark layers contain 30 w/o Mn (EDS, quantitative analysis) while the adjacent layers contain 15 w/o Mn.

process is mass transport limited in both  $Mn^{++}$  and  $Al_2Cl_7^$ and that the composition of the electrodeposit is exactly what one would expect from the bulk compositions of the electroactive ions. Since we ran these experiments at a constant  $AlCl_3$  composition and never varied the  $Al_2Cl_7^$ concentration, it is possible that the process is linear only

[4]

with respect to  $Mn^{++}$ . Austin has shown however (24) that the manganese content of the electrodeposit increases with decreasing acidity which proves that the  $Al_2Cl_7^-$  concentration is indeed a factor.

It is the above mechanism which allows for the deposition of modulated alloys from a single electrolyte. When  $Al_2Cl_7$ -/MnCl<sub>2</sub> is small, manganese rich layers are obtained at potentials where the deposition process is diffusion controlled and alloy composition is therefore determined by melt composition. Layers depleted in manganese can then be achieved at small cathodic overpotentials where both electroactive species are under kinetic control and  $Al_2Cl_7$ -



Fig. 7. Dependence of alloy composition on melt composition at deposition potentials of  $-0.15 \text{ V/Al} (\square)$  and  $-0.40 \text{ V/Al} (\bigcirc)$ ; solution to Eq. [6] (\_\_\_\_\_).

is preferentially reduced. When Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>/MnCl<sub>2</sub> is large, a modulated alloy with a lower average Mn content is deposited. In this case, Mn++ reduction is diffusion limited at nearly all deposition potentials so the partial current for Mn is essentially constant. Potential modulation alters the Al partial current, thus creating layers of different composition and structure.

The effects of migration must often be considered in treating the flux of ions to and from an electrode during steady-state processes. In the case of aluminum deposition from chloroaluminates, migration would hinder the diffusion of electroactive anions to the negative electrode, thereby lowering the limiting current predicted by the diffusion equation. Transference numbers have been measured for the AlCl<sub>3</sub>-NaCl system (30, 31), and were found to be quite low for AlCl<sub>4</sub><sup>-</sup>. The mobilities of the rather large  $AlCl_4^-$  and  $Al_2Cl_7^-$  ions are quite small compared to Na<sup>+</sup>. Since these anions contribute little to the overall conductivity of the electrolyte, migration effects can be ignored.

### Conclusions

The addition of small quantities of MnCl<sub>2</sub> (0.25-1.5 w/o) to acidic mixtures of AlCl<sub>3</sub> and NaCl dramatically increases the activation overpotential for the deposition of aluminum, thereby promoting lateral growth and eliminating the tendency to form dendrites. The mechanism for nucleation and growth normally operative during Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> reduction changes dramatically; the extent of which is not presently known. Alloys containing up to 30 w/o manganese have been deposited and alloy composition is dependent upon potential and MnCl<sub>2</sub> concentration of the melt. At small cathodic overpotentials, the deposition process, with respect to alloy composition, is kinetically controlled for both species. At a potential dependent upon MnCl<sub>2</sub> concentration, it then becomes mass transport limited in  $Mn^{++}.$  At potentials approaching -0.35 V/Al,  $Al_2Cl_7^-$  also becomes diffusion limited. In this region, alloy composition is exactly what one would expect from the bulk compositions of the electroactive ions assuming linear diffusion to the electrode. The most specular, homogeneous deposits were obtained at a potential of -0.3 V/Al; however, the potential dependence of alloy composition allows one to create graded and modulated structures from a single electrolyte.

Deposits containing greater than 27 w/o Mn have x-ray diffraction patterns similar to that observed for metallic glasses. As the manganese content of the deposit is reduced, supersaturated aluminum is detected in addition to the glassy material. The structure of the glassy phase has not been directly determined, but data suggest it has a stoichiometry similar to that of the Al<sub>6</sub>Mn intermetallic. Heating to 400°C converts the glass to Al<sub>6</sub>Mn and results in increased alloy hardness, possibly through a dispersion/ precipitation hardening mechanism.

Our ability to form a variety of structures (homogeneous, graded, and modulated) coupled with the materials potentially inherent strengthening mechanisms might lead to the electrodeposition of alloys with very interesting mechanical properties. The ability to electrodeposit intermetallic compounds on a near atomic scale presents interesting possibilities for high temperature alloys.

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