Low-Gravity Electrodeposition of Metals and Metal/Cermet Composites

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Electrodeposition of metals and stirring experiments that provide suspensions of cermets necessary for electrocodeposition have been carried out in the low-gravity environment produced on a KC-135 aircraft. Variation of the rate of electrodeposition was not found to affect the crystalline form of the deposits with our experimental configuration. Stirring experiments carried out to determine the feasibility of suspending and dispersing diamond and chromium carbide particles in aqueous zinc sulfate demonstrated that suspension occurred, but coagulation or clumping was evident in the suspension. Aggregation in the suspension was found to increase as the concentration of the $ZnS0_4$ solution was increased. Addition of a negative wetting agent decreased clumping. Comparisons of these results to previous low-gravity electrodeposition results are discussed. Ramifications of these results on the design of apparatus for longer low-gravity experiments are presented.

Nomenclature

e^- = negative electron
g = Earth's gravity constant
$M^{n+}\ (Aq)$ = cation with formal charge n^+ in aqueous solution
$M(s)$ = metallic solid
$M(s)\cdot\text{solid}$ = codeposition surface
n = number of electron charges

Introduction

IT HAS been reported that electrodeposition in low gravity produces deposits that have differences relative to those produced in 1 g. Ehrhardt[1,2] found that nickel deposited at a high rate under low gravity over a 6-min period during a suborbital rocket flight had some peculiar properties that were indicative of an amorphous form. A major reason for the present work is to attempt to reproduce Ehrhardt's results in the low-gravity trajectories produced on a KC-135 aircraft. Another reason is to attempt to answer questions concerning particle dispersion and suspension in low gravity. This information would aid us in designing hardware and planning for future longer time low-gravity electrocodeposition experiments.

Background

We are concerned with two processes, metal deposition and codeposition in which both a metal and neutral cermet are deposited. Metallic cations with formal charge $n+$ in aqueous solution undergoing reduction at the cathode to give a metal deposit may be represented by

$$M^{n+}\ (Aq) + ne^- \rightarrow M(s) \qquad (1)$$

With codeposition, suspended solid particles are occluded into the metal matrix as it is deposited and may be represented by the following:

$$M^{n+}\ (Aq) + ne^- + \text{solid} \rightarrow M(s)\cdot\text{solid} \qquad (2)$$

Models treating electrocodeposition have been presented by Gugliemi[3] and more recently by Celis et al.[4] The treatment by the latter is somewhat more general in that hydrodynamic effects, size and type of particles, bath constituents, and conditions can be included among the modeling parameters. It is hoped that low-gravity codeposition can reduce the influence of some of these parameters.

Ehrhardt's[1,2] report that nickel can be electrodeposited in an amorphous form when electrodeposited at a high rate in low-gravity is not unreasonable since nickel has a tendency to form amorphously under high-rate solidification at low temperature and when alloyed.[5,6] Likewise, electroless nickel preparation leads to a nickel-containing phosphide that has characteristics of an amorphous state as defined by Tamura and Endo.[7] Since crystalline nickel is so widely used as a catalyst, its catalytic applications in neat amorphous form could be quite different. Cocke[6] has recently reviewed the status of amorphous materials as heterogeneous catalysts and highlights their advantages relative to crystalline materials. Grodska et al. [8] found that silver crystal deposits prepared by electrochemical displacement with copper on Skylab showed differences relative to 1-g preparations. For electrocodeposition, Ehrhardt[1,2] has reported improvements in cermet incorporation relative to 1 g. Improvements in codeposited surfaces would be important for wear resistance under abusive conditions or compatibility in biological systems.

Experimental

We have constructed apparatuses for studying electrodeposition and codeposition on suborbital and orbiting vehicles. In preparation for these flights, which will be made possible through our participation with the Consortium for Materials Development in Space at the University of Alabama in Huntsville, we made low-gravity studies on KC-135 aircraft. The KC-135 parabolas produce 20–25 s of $10^{-2}g$. A typical 3-axes accelerometer recording for these flights has been presented by Riley et al.[9] Although shorter in time and producing gravity levels, several orders of magnitude higher than suborbital

Presented as Paper 89-0308 at the AIAA 27th Aerospace Sciences Meeting, Reno, NV, Jan. 9-12, 1989; received Jan. 16, 1989; revision received Oct. 15, 1989.

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($\sim 10^{-4}g$) and orbiting vehicles ($\sim 10^{-6}g$), KC-135 experimentation has some advantages. These include direct scientist interaction, which accommodates observation, alterations, and repair over periods of several hours and monthly flight possibilites. Another major advantage is that the flight apparatus only requires modest safety documentation. We had several goals for the KC-135 low-gravity experimentation. Included were carrying out short duration low-gravity studies on electrodeposition of metals and cermet/metal composites. It was hoped that information gained from these tests would aid us in designing hardware and operational scenarios for the longer suborbital and orbital flights that would not be amenable to direct scientist interaction.

A major objective of our planned first suborbital rocket flight is to attempt to reproduce the results of Ehrhardt[1,2] in which he reported the preparation of x-ray transparent nickel when it was electrodeposited on a suborbital rocket at $10^{-4}g$. While planning that flight we attempted to duplicate his results on a KC-135 aircraft, which flew low-gravity trajectories. Figure 1 shows the simple apparatus constructed for this study. It consisted of eight 1.5-V batteries, an off/on switch, relay, and a plug-in board for electrodeposition cells at voltages of 1.5 V, 3 V, 4.5 V, 6 V, and 12 V. The two battery boxes are evident. From right to left in front are the switch, relay, and plug-in board for the cells. Three cells are shown mounted on the board. The entire apparatus which is $\sim 24 \times 10$ in. was secured by tape to the padded floor of the aircraft during flight. The cells have been described previously.[10] Since we were restricted to 20–25 s of low gravity on each parabola, multiple electrodepositions were carried out until 5.5 min of plating time was accumulated, which was comparable to that produced on a sounding rocket. Ehrhardt[1,2] used only one cell during each mission and deposited at a rate of approximately 80 mA/cm^2. Since this high rate of electrodeposition could affect the crystalline form (or lack of) a method of varying the electrodeposition rate was required. The different voltages supply this variation with the 12-V deposition, for example, corresponding to a cell current of approximately 300 mA/cm^2.

We also constructed an apparatus for viewing the suspension of inert particles in low gravity produced on the KC-135 aircraft. The need for this study resulted from KC-135 tests on our electrodeposition apparatus for orbital flights.[10] Magnification of photographs of the two codeposition cells showed that the inert particles tended to clump when suspended by the stirrers in low gravity. Figure 2 shows the apparatus constructed for viewing particle suspension in low gravity on the KC-135. It consists of a cell containing $ZnSO_4$ plus diamond dust or chromium carbide inerts and a magnetic stirring bar. Figure 3 is a schematic of the stirred cell. As mounted in Fig. 2, the top side of the cell was recessed to accept a magnet turned by a miniature motor, which could be activated by a manual switch. The switch is adjacent to the flashlight battery used to power the motor located in the lower, left corner of the photograph. With the aid of side lighting, cell activity was viewed and recorded with the video camera.

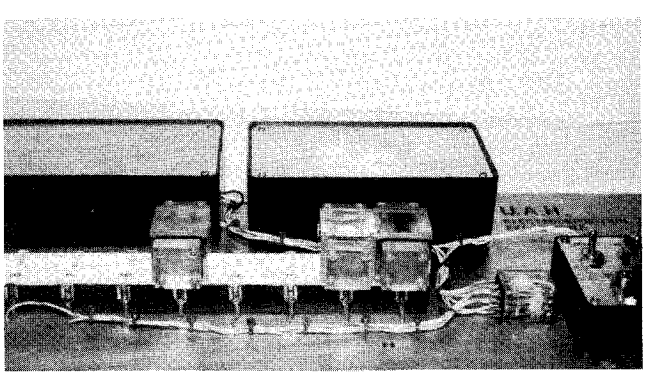

Fig. 1 KC-135 electrodeposition apparatus.

Results and Discussion

A pure amorphous state has a blurred x ray or electron beam diffraction pattern much like the liquid state. Nearest neighbors, second nearest neighbors, etc., will only contribute to the diffraction. Matsueda and Averbach[5] showed that an electron diffraction spectrum for thin film amorphous nickel prepared by the cold splat technique consisted of one large broad nearest neighbor peak and two very small second and third nearest neighbor peaks. We prepared a sample of electroless nickel from a $NiCl_2$/hypophosphite bath, which should form an amorphous Ni-P deposit.[11] It produced an x-ray diffraction pattern consisting of one broad peak. Figure 4 shows a reproduction of x-ray diffraction spectra from nickel deposited in 1 g (top) and low gravity (bottom) in experiments by Ehrhardt.[2] Except for the lack of gravity, the experimental conditions were reported to be the same. The upper spectrum for 1 g, showing intensity vs detector angle, has the typical fcc structural planes for crystalline nickel. In the lower spectrum, the peaks corresponding to those planes are gone or weak. It was interpreted as having a low-gravity deposit as nearly clear or invisible to the x rays and thus mostly amorphous in nature. Figure 5 shows the x-ray diffraction spectrum of nickel electrodeposited on a gold-coated copper plate. The deposition was carried out in the low-gravity environment produced on a KC-135 aircraft. The plating potential was 6 V; the plating time was approximately 5.5 min. Accumulations from multiple 20–25 s low-gravity parabolas were utilized to give the total electrodeposition time, which is comparable to that utilized by Ehrhardt. The peaks corresponding to the face-centered cubic (fcc) nickel crystal line planes are strong. Copper planes of the gold-plated copper cathode remain evident. There is no evidence for amorphous nickel deposition as found by Ehrhardt in this deposit or any other nickel we have deposited in the low-gravity environment produced on a KC-135 aircraft regardless of the rate of deposit.

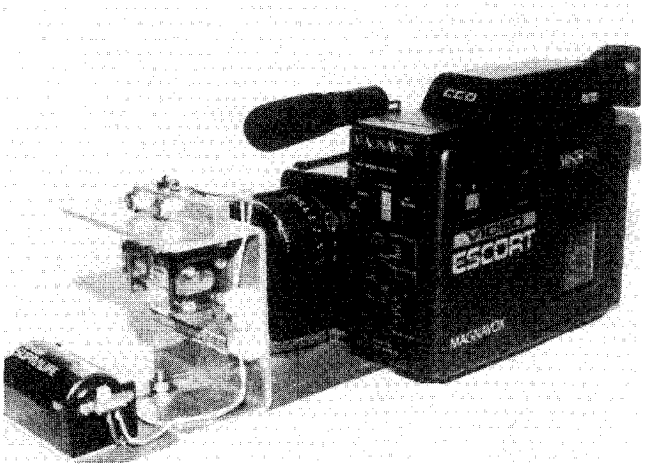

Fig. 2 KC-135 particle suspension apparatus.

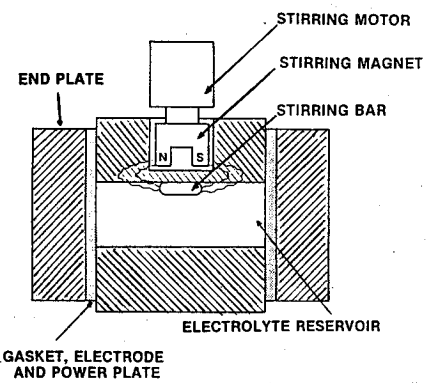

Fig. 3 Stirred cell configuration.

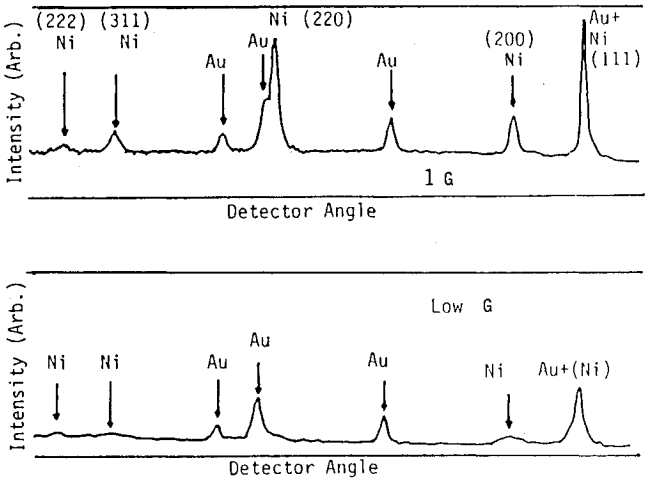

Fig. 4 X-ray diffraction spectra of Ni determined by Ehrhardt.[2]

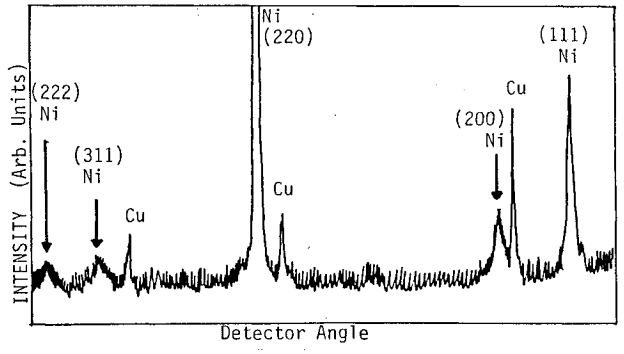

Fig. 5 X-ray diffraction spectrum of Ni deposited on KC-135.

There are several possible reasons for this disparity. The KC-135 parabola is in a 2-*g* mode just before it goes into the 10^{-2}-*g* segment. Damping times in our experimental cells in which concentration gradients are present could be significant, several seconds or greater. Also, the shorter depositing times associated with KC-135 parabolas could also lead to "imprinting" as the very thin multiple deposits accumulated continually follow the gold structure.

Table 1 shows a summary of our low-gravity inert particle/solution stirring experimental observations. Although our interest is in producing codeposits of cermets in nickel and cobalt metal matrices, $ZnSO_4$ solution was chosen for this study because it is colorless, and the Zn^{+2} ion is doubly charged as Co^{+2} and Ni^{+2} in aqueous solution. It is seen that as $ZnSO_4$ concentration increases (ionic strength increases), the coagulation of the inert particles becomes more significant. Addition of small amounts of wetting agent (surfactant) showed the negative dodecylsulfate to be the most effective. Since this coagulation is not noticeable in 1 *g*, either the strong agitation required to suspend inerts or 1 *g* is enough to overcome the attractive force while they are suspended. Regardless, it appears that stirring in low gravity leads to suspension of particles, but total dispersion is not necessarily complete.

Lack of evidence for amorphous nickel deposition on the KC-135 and conclusive proof that particles suspended in low gravity do not necessarily disperse aided in determining the configuration of the electrodeposition/electrocodeposition apparatus we constructed for suborbital low-gravity experimentation. We needed to reproduce the Ehrhardt experiment with at least 6 min of uninterrupted low-gravity deposition time, and we also needed to study the effect of rate upon the deposits. The latter was especially true when it was realized that the small thin film amounts of neat amorphous nickel

Table 1 KC-135 particle dispersion results

Cermet	$ZnSO_4$ molarity	No wetting agent	CTAB[a]	SDS[b]
Diamond	0.5	No[c]	—	—
Diamond	1.0	Yes[d]	—	—
Diamond	1.5	Yes	—	—
Cr_3C_2	0.5	No	—	—
Cr_3C_2	1.5	Yes	—	—
Cr_3C_2	1.5	Yes	Yes	No

[a]CTAB: Cetyltrimethylammonium Bromide (cationic). [b]SDS: Sodium Dodecylsulfate (anionic). [c]No: Aggregates not visible. [d]Yes: Aggregates visible.

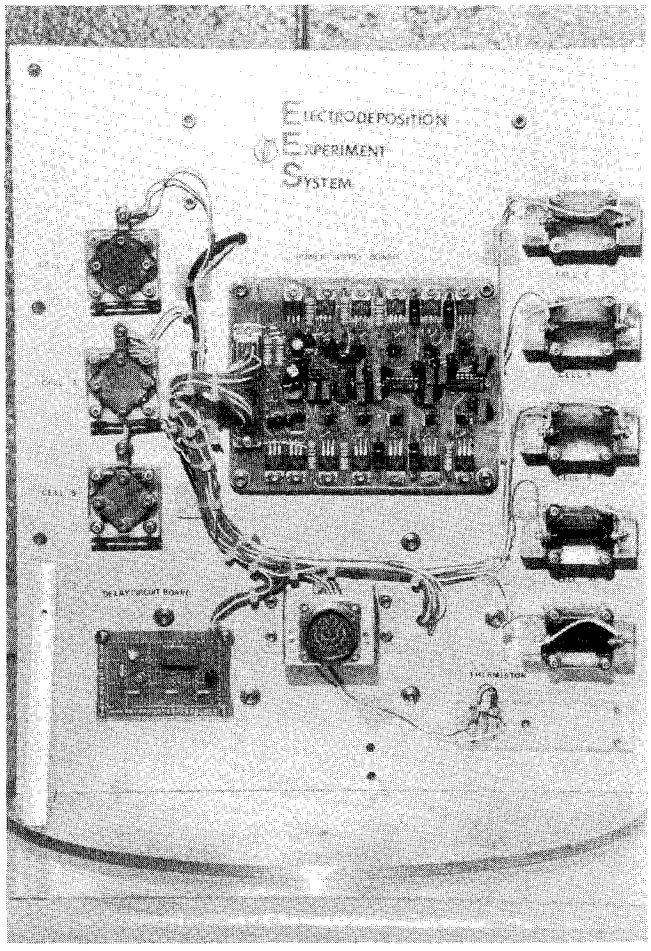

Fig. 6 Rocket electrodeposition apparatus front.

produced in the past were the result of fast condensation at low temperature.[5,7,12] It was also evident that transparent codeposition cells would be required so that pictorial data could be gathered on low-gravity codeposition and particle dispersion.

Figure 6 shows the electrodeposition side of the flight apparatus. Five electrodeposition cells are shown on the right; four will contain nickel sulfamate and one cobalt sulfate. The cells, which have been described previously, have been modified to accommodate any pressure changes that might accompany the electrodeposition. [10] A small channel has been cut in the side of each cell's liquid holding cavity and a segment of rubber tubing sealed at 1 atm placed in the channel. Any overpressure due to gas formation or heating compresses the tubing. These four nickel sulfamate cells will deposit nickel at different rates because each will be operated at a different voltage, 4.5 V, 6 V, and 9 V. The cobalt cell will be set a potential of 2.5 V and since its pH will be adjusted to about 4.2, it should deposit the B or hcp form of cobalt if it behaves as in 1 *g*. Cobalt was chosen because it is also an important catalyst, and we want to de-

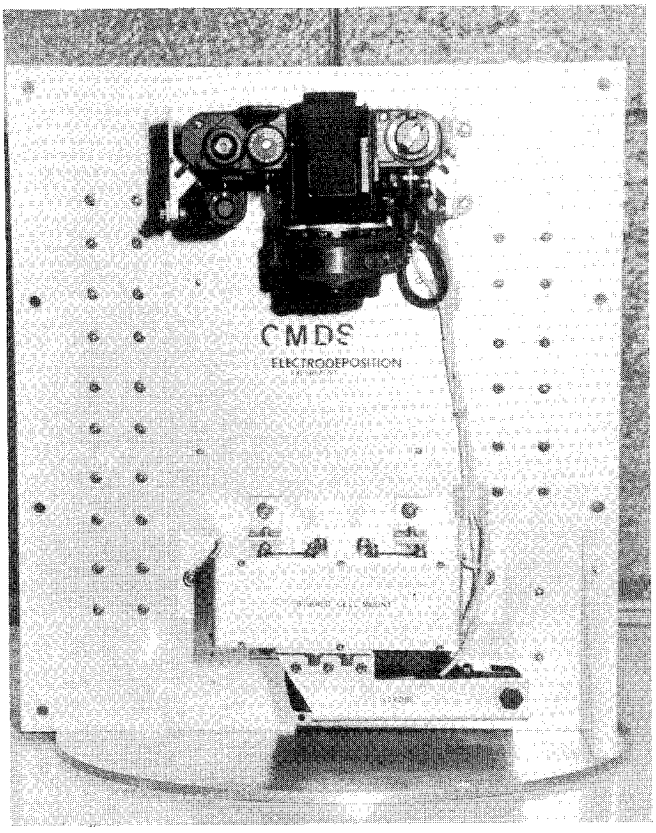

Fig. 7 Rocket electrodeposition apparatus back.

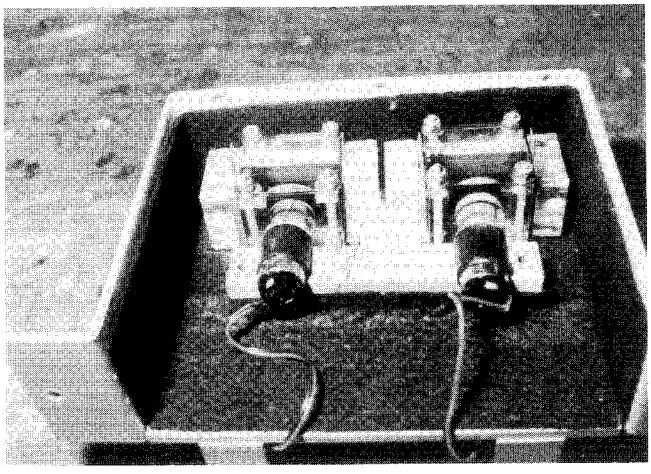

Fig. 8 Codeposition cells and stirring system.

termine if its morphology can be altered during low-gravity electrodeposition. The three cells on the left also contain nickel sulfamate. These cells have been shortened so that the distance between electrodes is one-fourth that of the other cells. Shortening the cells produces a decrease in cell resistance; therefore high currents can be obtained at only 3 V with minimal hydrogen gas production. Also in two of the three shorter cells, the cathode/anode area ratio has been decreased to one-half and one-quarter that of the remaining shortened cell to give different electrodeposition rates. Electronics boards are very evident in the lower left and center of the plate. The large board in the center interfaces with a payload central processor, which provides experimental control and will store current and temperature data at 1-s intervals for the duration of the flight. Temperature will be measured by one thermistor located in the lower right of the figure. The thermistor is mounted on a plexiglass plate so that it emulates the temperature of the plexiglass cells. Figure 7 shows the back side of the apparatus plate or the codeposition side. The two cells mounted in the compartment (see Fig. 8) will be stirred in low gravity for 15 s and damped for 10 s. Undisturbed codeposition at 2.5 will be carried out for the remaining low-gravity period. One of the stirred cells will contain nickel sulfamate with suspended diamond particles. The other will contain cobalt sulfate with suspended chromium carbide. The computer-controlled camera shown will photograph before stirring, during damping, and every 15 s into the codeposition. A back lighting strobe light is included. The cells previously depicted in Fig. 3 have internal stir bars. These are bar magnets encapsulated in glass with ridges to keep them away from the magnetic anodes (nickel and cobalt). They are turned by external two-pole cylindrical magnets attached to the shafts of small gear motors. The magnets are turned in a recession cut into the side of each cell. The codeposition particles, which are micron size, can be readily viewed through the polished plexiglas cells in the photographs after magnification by a factor of 10.

Conclusion

In summary, we have made use of the relatively short periods of low gravity produced on a KC-135 for electrodeposition experiments. We determined that it may require longer periods of uninterrupted low gravity or better quality (magnitude) to produce experimental differences in metal deposits prepared in low gravity compared to 1 gravity. We also found that particle suspension and disperion in low gravity is not as complete as expected. Lastly, relatively simple and inexpensive experiments performed on the KC-135 can lead to results that are very helpful in the design of more complex apparatus for orbital and suborbital low-gravity experiments. Based on these results, we have developed hardware for experiments to be flown on longer duration Consort rocket flights during 1989-1990. These experiments will determine if the morphology of metals can be changed when electroplated in low gravity and whether electrocodeposits are improved.

Acknowledgments

We thank NASA for its support with Grant NAGW-812 to the Consortium for Materials Development in Space at the University of Alabama in Huntsville. We also wish to thank McDonnell Douglas Space Systems Company for its support through Contract SK85A017 and Robert Shurney, Director of Marshall Space Flight Center's KC-135 Program.

References

[1]Ehrhardt, J., "Versuche zur electrolytishem Metallabscheidung under Schwerelosigheit *Galvanotechnik,* D, 7968 Sauligan 72, No. 1, 1981, pp. 13-18.

[2]Ehrhardt, J., "Dispersion Electrolysis Under Zero Gravity Under the SPACELAB Rocket Program TEXUS IV," Battelle Institute, BMFT Reference No. QV 219-AK-AN/A-ALN7910-5, April 1982; TEXUS VII, BMFT Reference No. 01QV219-AK-AM/A-SLN7910-5 November 1983; and TEXUS IX, BMFT Reference No. 01 QV014-AK/SN, November 1984.

[3]Gugliemi, N., "Kinetics of the Deposition of Inert Particles from Electrolytic Baths," Vol. 119, No. 8, Aug. 1972, pp. 1009-1012. *Journal Electrochemical Society: Electrochemical Science and Technology.*

[4]Celis, J. P., Roos, J. R., and Buelens, C.,"A Mathematical Model for the Electrolytic Codeposition of Particles with a Metallic Matrix," *Journal Electrochemical Society: Electrochemical Science Technology,* Vol. 134, No. 6, June 1987, pp. 1402-1408.

[5]Matsueda, H., and Averbach, B. L., "Sputtered Films of Nickel and Nickel Oxide," *Materials Science and Engineering*, Vol. 23, 1976, pp. 131-134.

[6]Cocke, D. L., "Heterogeneous Catalysts by Amorphous Materials," *Journal of Metals,* Feb. 1986, pp. 70–74.

[7]Tamura, K., and Endo, H., "Ferromagnetic Properties of Amorphous Nickel," *Physics Letters,* Vol. 29A, No. 2, April 1969, pp. 52–53.

[8]Grodska, P. G., Facemire, B. R., Johnstone, H. H., and Gates, D. W., "Electrochemical Deposition of Silver Crystals Aboard Skylab IV," *Journal of Crystal Growth,* Vol. 35, 1976, pp. 177–184.

[9]Riley, C., Coble, H. D., Loo, B., Benson, B., Abi-Akar, H. and Maybee, G., "Electrodeposition and Codeposition under Low Gravity/Nonconvecting Conditions," *Polymer Preprints,* Vol. 28, Aug. 1987, pp. 470–471.

[10]Riley, C., Coble, D. and Maybee, G. "Electrodeposition of Metals and Metal/Cermet Composites in Low Gravity," AIAA Paper 87-0510, Jan. 1987.

[11]Masie, J., "Guidebook Issue," *Metal Finishing,* Vol. 78, Jan. 1980, pp. 480–488.

[12]Davies, H. A., and Hull, J. B., "Amorphous Nickle Produced by Splat Quenching," *Materials Science and Engineering,* Vol. 23, 1976, pp. 193–198.

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