Periodic Reverse Copper Electroforming from a Low Cu-content Acid Copper Sulfate Bath

K. Tajiri & T. Imamura

Copper electroforming is a useful manufacturing process for complex-configuration components that must have copper structures. A periodic reverse copper electroforming process has been developed, using a low Cu-content acid copper sulfate bath. Ductile copper deposits with tensile strength ranging from 19.1 to 30.9 kg/mm² were obtained from a bath containing no organic additives. The strength and elongation of the deposits is controlled by varying the chloride ions added to the electrolyte, because the chloride ions decisively affect the microstructure of the deposits, which in turn determines the mechanical properties of the deposited copper. Also, the deposits are so pure that they can be welded easily, forming smooth beads with few porosities. In addition, the electroforming process has a wide range of optimum current densities required in the production of complex configuration components. This technology has actually been applied to the combustion chamber of the Japanese H-II rocket's main engine.

Copper electroforming is quite useful for the production of complex components having copper structures, because the process can build up thick copper layers on various substrates. When used as a structural material exposed to high stress or high temperature during the fabrication process or in operation, the copper layer must have good mechanical properties and thermal stability. Copper deposits from the conventional acid copper sulfate bath containing organic additives do not show such high performance, however. They are usually hard and brittle and contain impurities¹ attributed to the use of organic additives, the leveling agents. G.A. Malone reported a periodic reverse electroforming process with a high Cu-content acid copper sulfate bath containing neither organic additives nor chloride ions, and showed that thick copper deposits of good mechanical properties were obtained.² Because the high Cu-content bath can only be operated in a narrow range of current densities, the process is difficult to apply to complex components. An improved periodic reverse process overcoming that problem has been expected.

The purpose of this study was to develop another periodic reverse copper electroforming process applicable to complex components, using a lower Cu-content bath known to have higher throwing power.³

Electroforming

Copper electroforming equipment consisting of a 140-L volume tank and a power supply that can provide periodic reverse current was used. The tank is equipped with systems of air agitation, carbon filtration, and thermal control of the electrolyte. Phosphorus-containing copper electrodes with surface area greater than twice the specimen's were used with bags made of polypropylene.

A low Cu-content acid copper sulfate bath without organic additives, but with chloride ions, was used for the test. The concentrations of sulfuric acid and copper sulfate (as $CuSO_4 \cdot 5H_2O$) were 135-145 g/L and 138-148 g/L, respectively.

The reason for addition of chloride ions to the bath is that more dense and smooth deposits were obtained by their presence in the preliminary test. Namely, a smooth surface was not obtained from the bath with no chloride ions at a current density of 3.3 A/dm² or less. The major electroforming test conditions are listed in Table 1. Chloride ion content, current density, and cathodic-anodic time ratio (PR ratio) were chosen as parameters. Here, current density means both cathodic current density at normal cycle times and anodic current density for reverse-cycle times and were set equal. Copper deposits more than 3 mm thick were formed on copper substrates.



Fig. 1—Mechanical properties vs. chloride ion content of deposit with 3.3 A. dm^2 and PR 20 sec cathodic, 4 sec anodic: (1) tensile strength, (2) yield strength, (3) elongation.



Fig. 2—Mechanical properties vs. current density for deposits containing about 15 ppm chloride ions at PR of 20 sec cathodic, 4 sec anodic: (1) tensile strength, (2) yield strength, (3) elongation.



Fig. 3—Microstructure variation of deposits with different chloride ion content of the bath: (a) 14.6 ppm, (b) 24.8 ppm, (c) 34.2 ppm.

Mechanical Properties & Microstructure

Two coupons of 2 mm thickness were cut from each electroformed specimen for the tensile test. Each coupon consisted of an electroformed copper layer between 0.5 mm and 2.5 mm from the interface with its substrate. The results of the tensile test are summarized in Table 2.

The values of tensile strength, yield strength and elongation

are plotted against chloride ion content and current density in Figs. 1 and 2, respectively. Figure 1 shows that the strength of the deposits decreases while elongation increases with increasing chloride ion content of the bath. At about 25 ppm of chloride ions content, however, an exceptional area with particularly low elongation exists. Figure 2 shows that the strength of the deposits increases, while the elongation decreases, with increasing current density. As for the PR ratio, no significant difference for mechanical properties was found in the range from 4 to 6. Among the parameters evaluated, chloride ion content of the bath showed the largest contribution to mechanical properties.

The cross section of a small piece of the deposited copper was observed with an optical microscope at 50X. Micrographs of some specimens are illustrated in Figs. 3 and 4. Figure 3 shows the microstructure of the deposits from the bath containing different concentrations of chloride ions; at



Fig. 4—Microstructure of deposits with different current densities: (a) 1.5 A/dm², (b) 3.3 A/dm², (c) 5 A/dm².

14.6 ppm, the microstructure is fibrous, while at 34.2 ppm it is columnar. At 24.8 ppm, the microstructure is a mixture of fibrous and columnar crystals, starting with fibrous crystals and turning to columnar crystals with the growth of the deposit. Figure 4 shows the microstructure of the specimens deposited at different current densities from the bath containing about 15 ppm of chloride ions. At 1.5 A/dm², the microstructure is columnar, while at 3.3 A/dm² and 5 A/dm², the microstructure is fibrous.

By contrasting mechanical properties with microstructure, it was found that the fibrous structure provides higher strength and lower elongation, while the columnar structure provides lower strength and higher elongation. The mixed

Table 1 Electroforming Test Conditions								
Parameter Chloride ion content	Value About 15 ppm About 25 ppm About 35 ppm	Other Operating Conditions Current density & PR ratio kept constant 3.3 A/dm ² & 5, respectively						
Current density	1.5 A/dm ² 3.3 A/dm ² 5.0 A/dm ²	Chloride ion content & PR ratio kept constant (about 15 ppm & 5, respectively)						
Cathodic-anodic time ratio (PR ratio)	4 (16 sec cathodic, 4 sec anodic) 5 (20 sec cathodic, 4 sec anodic) 6 (24 sec cathodic, 4 sec anodic)	Chloride ion content & current density kept constant (about 25 ppm & 3.3 A/dm ² , respectively)						

Table 2 Results of Tensile Test

	Operating	Conditions		Mechanical Properties			
	Chloride ion	Current density	7	Tensile Strength	Yield Strength	Elongation	
Specimen	content, ppm	A/dm ²	PR ratio	kg/mm ²	kg/mm ²	%	
А	14.6	3.3	5	28.7	15.1	39.5	
В	24.8	3.3	5	24.3	10.4	34.7	
С	27.4	3.3	5	18.2	8.3	51.1	
D	34.2	3.3	5	19.1	8.1	61.5	
E	15.9	1.5	5	22.6	9.9	49.4	
F	13.3	5.0	5	30.9	15.7	37.2	
G	24.5	3.3	4	27.3	13.5	35.4	
Н	25.1	3.3	6	28.7	14.8	39.3	
Ι	16.2	3.3	5	16.5	31.8	37.6	



Fig. 5--Cross section of electrobeam-welded copper deposit, polished and etched.

grain structure observed at 24.8 ppm of chloride ion content shows particularly low elongation. Owing to this relation between the mechanical properties and the microstructure, we can control the mechanical properties of the deposits by controlling the microstructure, which is determined by chloride ion content of the bath and current density.

Impurities & Thermal Stability

It is known that copper electrodeposits from the conventional acid copper sulfate bath contain impurities that cause outgassing at high temperatures.1 Such impurities make it impossible to apply welding or brazing processes to the deposits. Because the impurities have their origin in organic additives contained in the bath, the deposits from the bath containing no organic additives are expected to be free from such impurities and thermally stable. We analyzed the impurities of our deposit and examined the weldability of the deposit. Copper deposits produced from the bath containing about 15 ppm chloride ions at a current density of 3.3 A/dm² and at the PR ratio of 5 were used for both tests. Small pieces of the deposits were melted in ceramic dishes, and the liberated gases were analyzed by gas chromatography. One ppm of hydrogen, 26 ppm of carbon and 8 ppm of oxygen were detected. Nitrogen was not detected (< 1 ppm). These are very small values compared with the reported total impurity content, 220 and 1500 ppm,¹ for the deposits from the conventional acid copper sulfate bath.

A copper deposit on a copper substrate was electron-beam welded to a piece of inconel. The bead formed was smooth and continuous, showing no damage from gas generation. Figure 5 shows the magnified cross section view of the welded area, polished and etched. No cracks or porosities are observed. This fact demonstrates that the copper deposit is pure enough for welding.

Discussion

Reverse Cycle & Electrodes

It is a concern whether electrolytic copper plated onto electrodes corrode uniformly or not. The answer is yes. More particles caused by non-uniform anode corrosion were not observed in bags covering the copper electrodes. Also, we found no visible particles suspended in the electrolyte. If an inert electrode or an electrode with smaller surface area than the surface being treated can be used, the PR copper electroforming would be more desirable. Such electrodes were proved valid by our subsequent study.⁴

Effect of Chloride lons

A high Cu-content bath, Malone's bath,² contains no chloride ions. Chloride ion, however, is an indispensable constituent of our low Cu-content bath. Chloride ions widen the range of operating current density for the low Cu-content bath.

It was suspected that chloride ions would somehow be absorbed on the treated surface during reverse cycle, but we could not make clear the mechanism by which chloride ions affect the microstructure of the deposits. The effect of current density on microstructure, turning the structure from fibrous to columnar at low current density, may be attributed to large crystals deposited at low direct-current densities.

Applicability

Table 2 shows that our periodic reverse electroforming process can provide copper deposits ranging from 19.1 to 30.9 kg/mm² tensile strength, from 8.1 to 15.7 kg/mm² yield strength and from 37.2 to 61.5 percent elongation. The deposits are divided into two categories: the higher strength deposits from the bath containing around 15 ppm chloride ions, and the higher elongation deposits from the bath containing around 35 ppm chloride ions. The chloride ion content of the bath must be controlled strictly to get constant strength and elongation. As for the concentrations of sulfuric acid and copper sulfate, no significant effect on the deposits was observed for both the appearance and mechanical properties over the concentration ranges tested: 135-145 g/L for sulfuric acid and 138-148 g/L for copper sulfate. These ranges fully cover the changes in the sulfuric acid concentration and the copper sulfate concentration during electroforming, which makes the electroforming process quite stable.

As stated above, the effect of current density on the mechanical properties was evaluated for the bath containing about 15 ppm chloride ions (Fig. 2). Although there is not much difference in strength and elongation between 3.3 A/dm² and 5 A/dm², the strength becomes much lower and the elongation becomes much higher at 1.5 A/dm². This effect must be taken into consideration in designing the electroformed structure of components.

Smooth and dense copper deposits can be obtained over a wide range of current densities from 1 to 5.5 A/dm^2 , which makes this electroforming process applicable to considerably complex components. Because of excellent mechanical and thermal properties of the deposits and broad operating conditions, our periodic reverse electroforming process has been applied to the combustion chamber of the Japanese H-II rocket's main engine and to a high-field electromagnet.⁵

Summary

A periodic reverse copper electroforming process using a low Cu-content acid copper sulfate bath has been developed. Thick copper deposits with tensile strength, yield strength, and elongation ranging from 19.1 to 30.9 kg/mm², from 8.1 to 15.7 kg/mm², and from 37.2 to 61.5 percent, respectively, were obtained by this process. Those differences are a result

of the difference of microstructure determined by chloride ion content of the bath and current density. Fibrous grain structure produces higher strength, but less elongation, while columnar grain structure produces lower strength and greater elongation. The copper deposits are so pure that they can be welded easily, forming smooth beads with few porosities. The wide range of operating current density from 1 to 5.5 A/dm^2 makes the process largely applicable to complex configuration components.

References

- 1. W.H. Safranek, *The Properties of Electrodeposited Metals* & *Alloys*, 2nd ed., AESF, Orlando, FL, 1986; p. 111.
- 2. G.A. Malone, *NASA CR-134959*, NASA Lewis Research Center (1975); p. 10.
- 3. A.C. Hamilton Jr., *Plat. and Surf. Fin.*, 84, 47 (Aug. 1977).
- 4. K. Tajiri, T. Nakamura, Z. Kabeya, Y. Yamanaka, F. Naito, T. Kato & E. Takasaki, *15th Int'l INTERFINISH Congress*, Germany, (Sept. 2000).
- K. Tajiri, Y. Yamanaka, F. Naito, T. Kato & E. Takasaki, *Proc. AESF/SFSJ Advanced Surface Technology Forum*, 145, AESF, Orlando, FL (1998).

About the Authors



Keisuke Tajiri* is manager of the Chemical Research Section, Mitsubishi Heavy Industries, Ltd., Nagoya Aerospace Systems Works. 10, Oye-cho, Minato-ku, Nagoya 455-8515, Japan. His responsibilities are research and development of surface treatments, including electroforming for aircraft, rockets and particle accelerators. He is a graduate of Kagoshima University and is especially

interested in electroforming and electropolishing. He holds a U.S. patent and has contributed to technical journals and forums.



Tsugio Imamura is director of the Engineering Research Dept. of Nagoya Aerospace Systems Works, Mitsubishi Heavy Industries, Ltd. He is a graduate of Kuushuu University, Japan. His technical interests include delayed failure mechanics of ultra-high tensile steel and aluminum alloys.

* To whom correspondence should be addressed.