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Carderock Division
Naval Surface Warfare Center
Bethesda, Md. 20084–5000

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CARDIVNSWC–TR–61—94–06 September 1994
Survivability, Structures, and Materials Directorate
Technical Report

Modified Cu–Mn–Al High Damping Alloys

by
C.R. Wong
R.S. Venkatachalam

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ABSTRACT

Zirconium and erbium modified Cu-Mn-Al was spray formed in an effort to increase homogeneity and damping capacity and decrease impurity levels. Although the microstructure revealed that the optimum spray forming parameters have not yet been achieved, the modified alloys showed both high damping and resistance to losing that damping over time. The elemental additions also accelerated the formation of alpha manganese at the grain boundaries during aging.

ADMINISTRATIVE INFORMATION

This report was prepared under the Quiet Alloys Program, part of the Functional Materials Block Program, Sponsored by Mr. Ivan Caplan, Carderock Division Naval Surface Warfare Center (CDNSWC Code 0115). The work was supervised by Dr. O. P. Arora, DTRC Code 612. The work was performed under Program Element 62234 N, Task Area RS34S94, Work Unit 1-2812-804.

INTRODUCTION

Cu-Mn is a high damping alloy which has mechanical properties similar to bronze but dealloys even more readily[1]. Although the damping tends to decrease with time, the damping capacity was measured as relatively high in a full scale cast propeller after it had been in service.[2] High damping Cu-Mn alloys known as Incramute* and Sonoston,** have been commercially produced and characterized but the original commercial sources for these alloys are no longer available. Efforts by CanMet to cast Sonoston revealed difficulties in producing sound castings because of the reactivity of the Mn and because of the large differences in liquidus and solidus temperatures.[3] The castings often have a heavily-cored dendritic microstructure which results in a coarse banded microstructure upon hot working. Such microstructures are deleterious to both mechanical and corrosion properties. An effort by NRL to fabricate Cu-Mn alloys by rapid solidification processing (RSP) resulted in much better homogeneity but the damping capacity was very low.[4] It has been shown that an addition of a rare earth erbium (Er) to Incramute not only reduced the tendency of the Cu-Mn alloy to lose damping with time but also increased the damping by a factor of six and decreased the strain at which the damping mechanism became mobile.[5] Initial attempts to produce Er modified Incramute in 10 lb ingots were not successful

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*Trademark, International Copper Research Association, Inc.

**Trademark, Stone Maganese Marine, LTD.

because of high impurity levels. The damping mechanism in Cu-Mn alloys is dependent on the movement of antiferromagnetic domain walls.[6] Solute elements diffuse to these walls causing them to become immobile. Er additions are thought to combine with the interstitial solute elements as well as Si and S, and reduce their diffusivity. The aging times in the RSP material were accelerated due to the enhanced solute migration kinetics of fine grained materials due to grain boundary diffusion. This enhanced solute migration would also reduce the damping. Spray forming Cu-Mn-Al should result in a fine grain homogenous alloy and the addition of Er or Zr (a gettering element commonly used in copper alloy spray forming) should impart a durable high damping capacity.

APPROACH

A. *Spray Forming*

The starting materials consisting of a master alloy of 70-30 Cu-Mn with elemental additions made to achieve the desired chemistry were melted in nitrogen. The master alloy was used instead of elemental Cu and Mn because the flake shape of the electrolytic grade Mn caused arcing in the melt during the initial attempts to spray form the alloy. The resulting melt was highly viscous and did not feed through the spray nozzle readily. The materials were sprayed in about 5 lb heats at a temperature of 1035 °C using nitrogen.

B. *Characterization*

The chemical analysis shown in Table I. was obtained by inductively coupled plasma methods while analysis of selected areas was performed using energy dispersive spectroscopy (EDS) on polished and unetched samples.

Table 1 Results Of Chemical Analysis of Bulk Samples in Weight Percent

Sample	Cu	Mn	Al	Zr	Er
Cu-Mn-Al	bal.	41.65	1.99	--	--
Cu-Mn-Al-Zr	bal.	40.30	2.45	0.307	--
Cu-Mn-Al-Er	bal.	42.09	2.51	--	0.11
Cu-Mn-Al-Zr-Er	bal.	41.84	2.51	0.38	0.22

The spray formed material was cut into approximately 1 x 10 x 60 mm blocks and solution treated at 800 °C 45 minutes in an argon atmosphere. They were then aged in the Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 400 °C for 6 hours while damping measurements were continuously taken. The resulting material was underaged in order to magnify the strain aging effect.[1]

Optical microstructural analysis was performed on samples which were polished and etched with Picral and Nital. Microstructural characterization was performed on the actual pieces used for the damping testing except for the as sprayed condition in which case material adjacent to the samples was taken from the ingot.

ASTM grain size was measured from optical micrographs taken at 100x using a LECO 2001 Image Analyzer.

The damping capacity was measured using a fixed-guided cantilevered test configuration. In this configuration, shown in figure 1, the clamp on the left holds the sample to a stationary frame while the right clamp attaches the sample to the controlled drive shaft. When the samples are not firmly held, erroneous damping measurements may result due to slip between the sample and clamps. In order to minimize such errors, three-pronged clamps were used. A torque wrench was used to tighten the clamps in order to achieve consistent clamping.

The damping was measured by applying a small sinusoidal time-varying mechanical force to the drive shaft and measuring the displacement of the sample. The phase angle, δ, of the lag between the applied load and the measured displacement was calculated. The tangent of δ is a measure of the damping capacity commonly called the loss factor. All samples were tested at three distinct alternating frequencies of vibration: 0.1, 1, and 10 Hz. The load applied during the bulk of the test was sufficient to impart a maximum strain of 10^{-4}. It is important to note that a much higher load is initially applied and then reduced until the proper displacement is achieved.

RESULTS AND DISCUSSION

The bulk chemical analysis shows the composition to be close to that of Incramute in major alloying elements. The as-spray-formed material was not totally uniform. Cu rich regions were found which have a composition near the liquidus minimum shown in figure 2 as measured by

EDS. The black irregular inclusions illustrated by micrographs in figure 3 indicate that much of the aluminum oxidized and did not go into solution. The unmodified Cu-Mn-Al showed plate shaped silicon particles which did not dissolve during solution treating. Few areas high in Er were identified in the alloys which contained Er but many fine white needle shaped particles of Zr were found in the alloys which contained Zr. Figure 4 shows that in the solution treated samples the areas high in copper and most of the Zr needles dissolved into the matrix. The Al inclusions remained and EDS analysis indicated that Er or Zr was often found in the same areas as Al in the alloys which contained those elements.

The grain size measurements, listed in table 2 show that the grain size was initially very fine in the unmodified and Zr only addition alloys. After solution treatment all the alloys had essentially the same grain size.

Table 2. ASTM Grain Size

Sample	As Spray Formed	Solution Treated	Aged
Cu-Mn-Al	9.6	5.0	5.2
Cu-Mn-Al-Zr	9.7	6.5	6.6
Cu-Mn-Al-Er	5.5	5.6	5.6
Cu-Mn-Al-Zr-Er	5.0	5.5	5.8

Figure 5 shows that the damping during aging at 400°C initially decreased for one or two hours then leveled out. The higher the gettering element content, the higher the damping during aging. The higher damping also correlated to the increased formation of alpha manganese at the grain boundaries as depicted in figure 6.

The damping data shown in figure 7 illustrates the importance of continuous application of strain on the behavior of the material. In the alloys with the gettering additions, the damping was higher when the measurements were resumed after pausing for as little as 13 hours. This effect noticeably decreases over time and is not found in the unmodified alloy. The damping plotted in figure 8 corroborates the trend shown if figure 7 with the damping drastically increasing when the material was not tested for a week. Under the application of constant strain the solute elements diffuse to the area of the antiferromagnetic domain walls thus reducing their mobility. When alloy is allowed to relax, the mobile solute elements diffuse to the now stationary boundaries again reducing their mobility. This produces solute rich and solute poor regions. The initial large vibration breaks the boundaries free of the pinning elements and the walls traverse solute poor regions which results in higher damping. As long as there are mobile solute elements in the alloy the damping capacity will change with time and vibrational strain history

In all the modified alloys the damping decreased with time but the rate of decrease slowed with increasing content of gettering element. Although there is a lot of scatter in the data it is evident that the alloy with the highest gettering content maintained the most consistent damping level. The distance at which solute atoms can be attracted to a domain boundary is finite. Although the attraction is initially high, it falls over time as the solute becomes more dilute. Therefore the presence of mobile solutes can be determined by the stability of the damping capacity over time. It is evident from this data that the gettering elements were effective in reducing the amount of mobile solute elements.

SUMMARY

The spray forming parameters have not been optimized and a large fraction of the aluminum and the gettering elements were not in solution.

The sample containing zirconium exhibited the highest damping and the sample containing the highest concentration of gettering elements was the most effective at maintaining high damping.

ACKNOWLEDGMENTS

The authors are indebted to Olin corporation for spray forming the material. They would also like to express their appreciation to Albert Brandemarte and Richard Stockhausen for providing the metallographic services.

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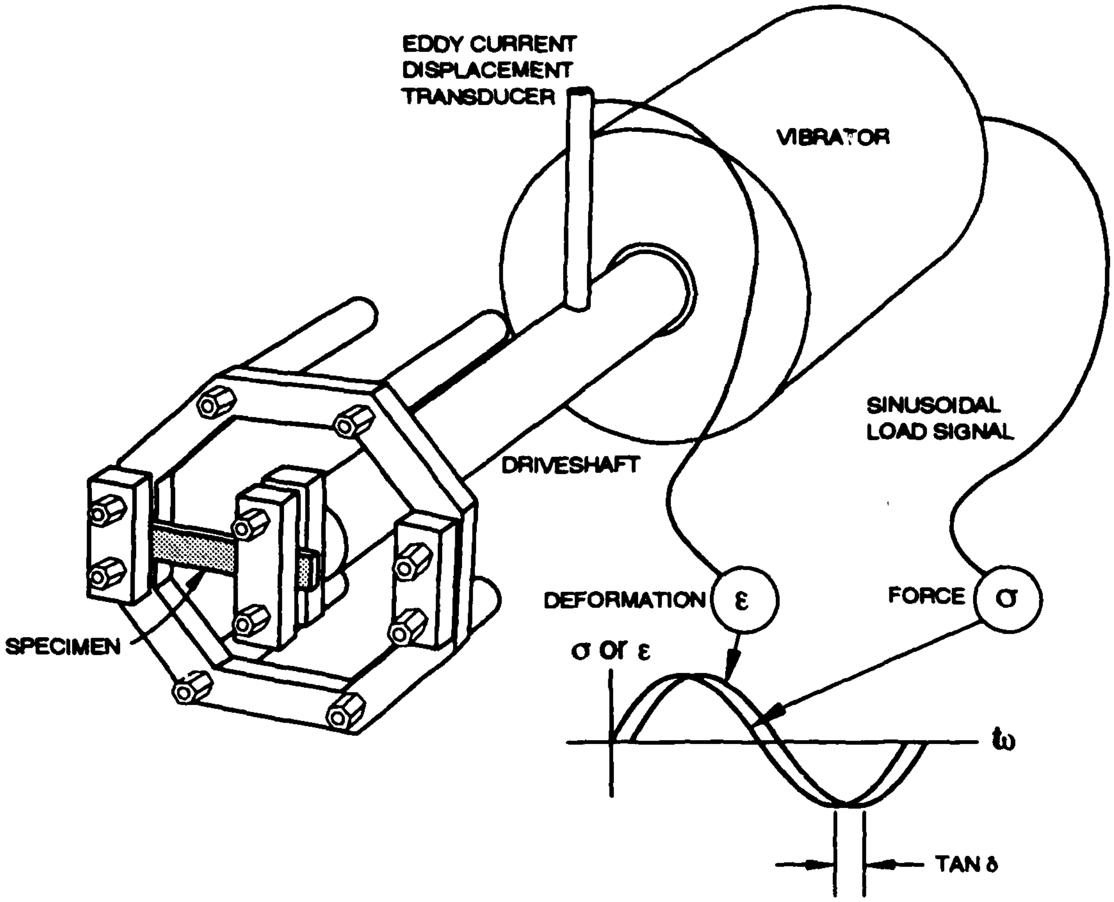


Fig. 1. DMTA Test Setup

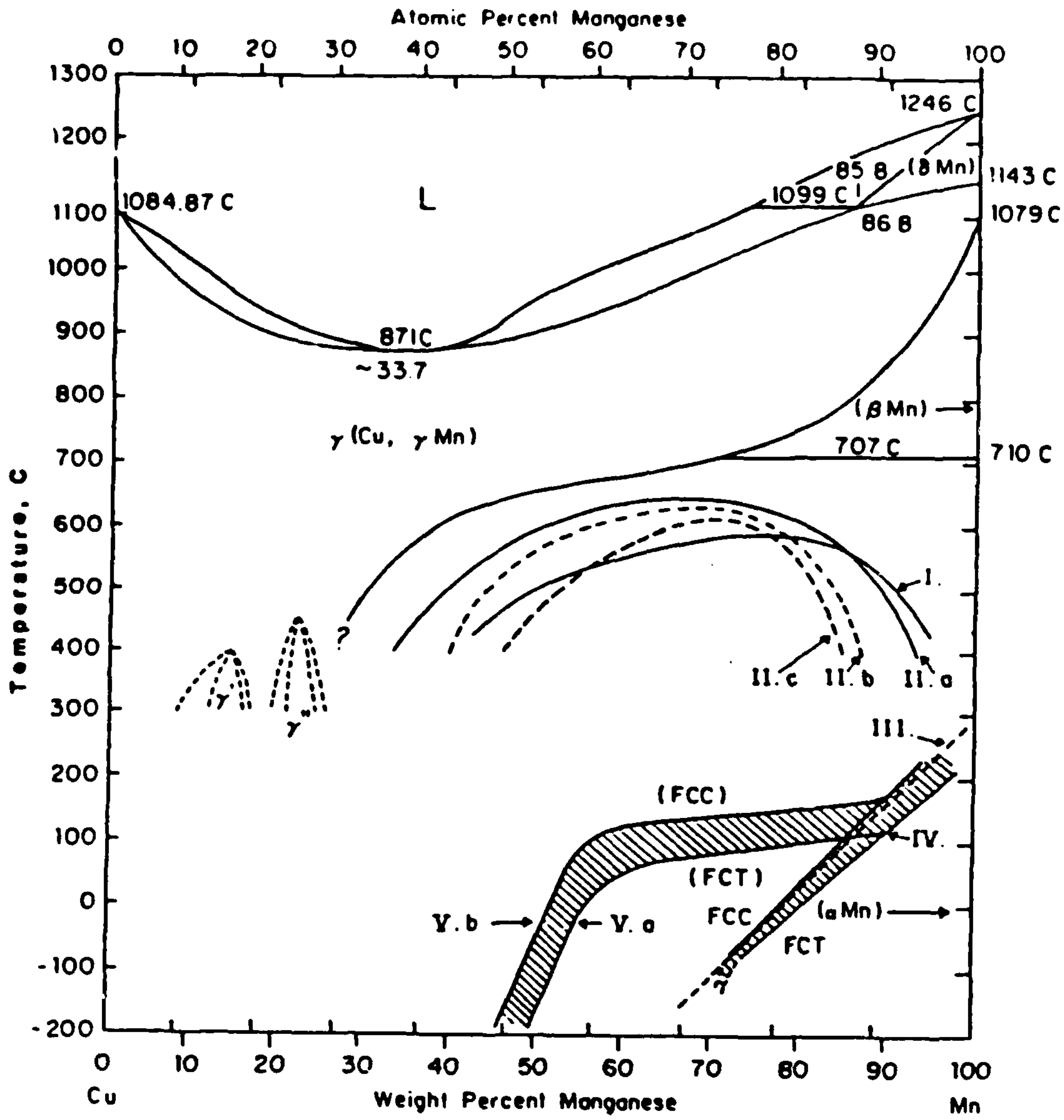
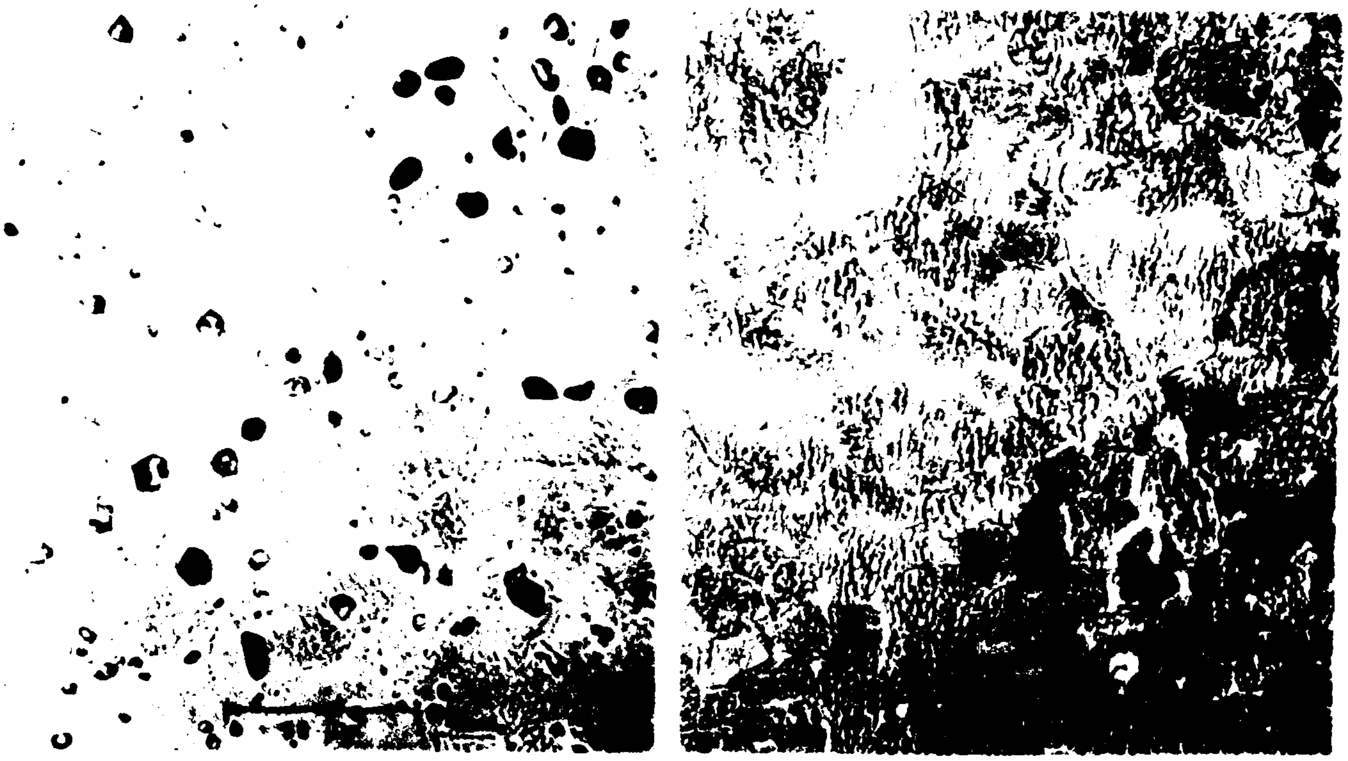


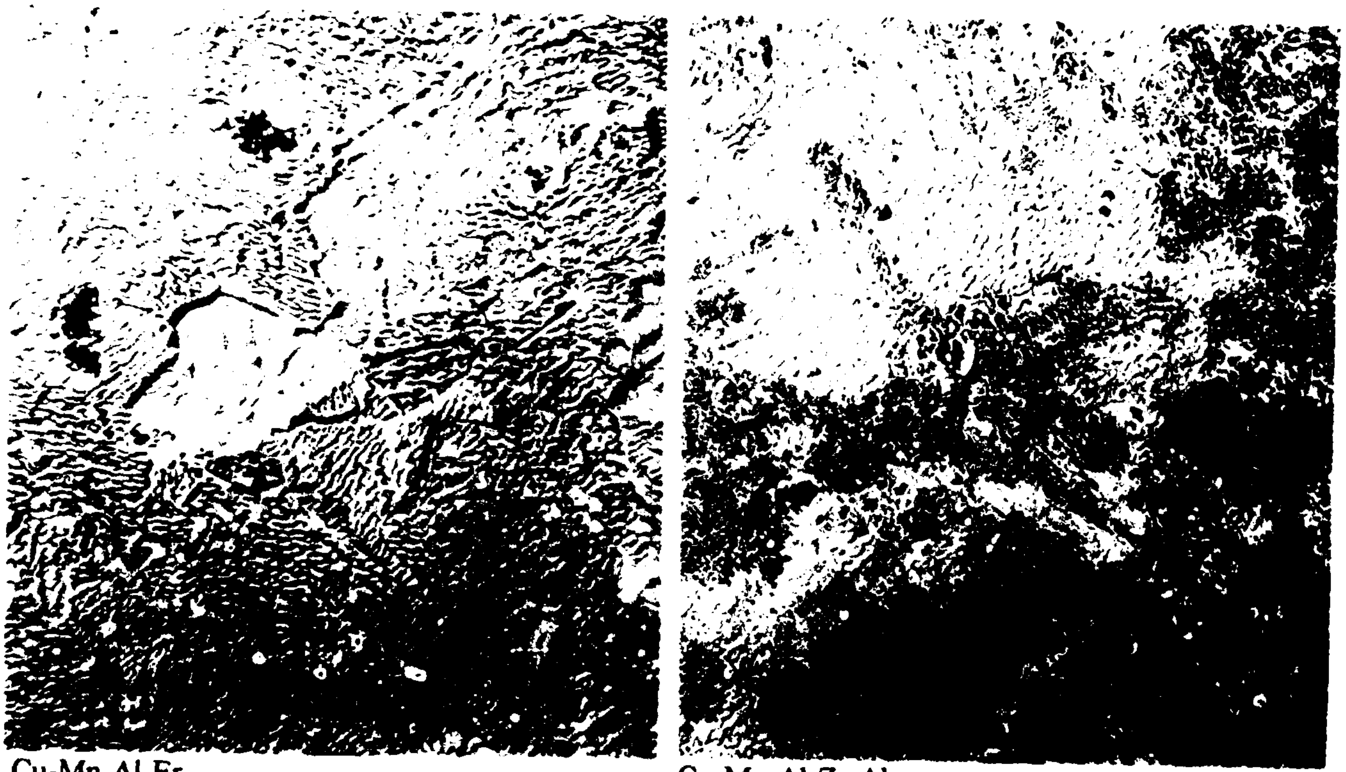
Fig. 2. Cu-Mn Phase Diagram [Ref. 7]

I. Miscibility Gap
II. Miscibility Gap
    a. Layering Range.
    B. Chemical Spinodal
    c. Coherent Spinodal
III. Neel Temperature
IV. FCC to FCT transition in quenched alloy
V. FCC to FCT transition in aged alloys



Cu-Mn-Al

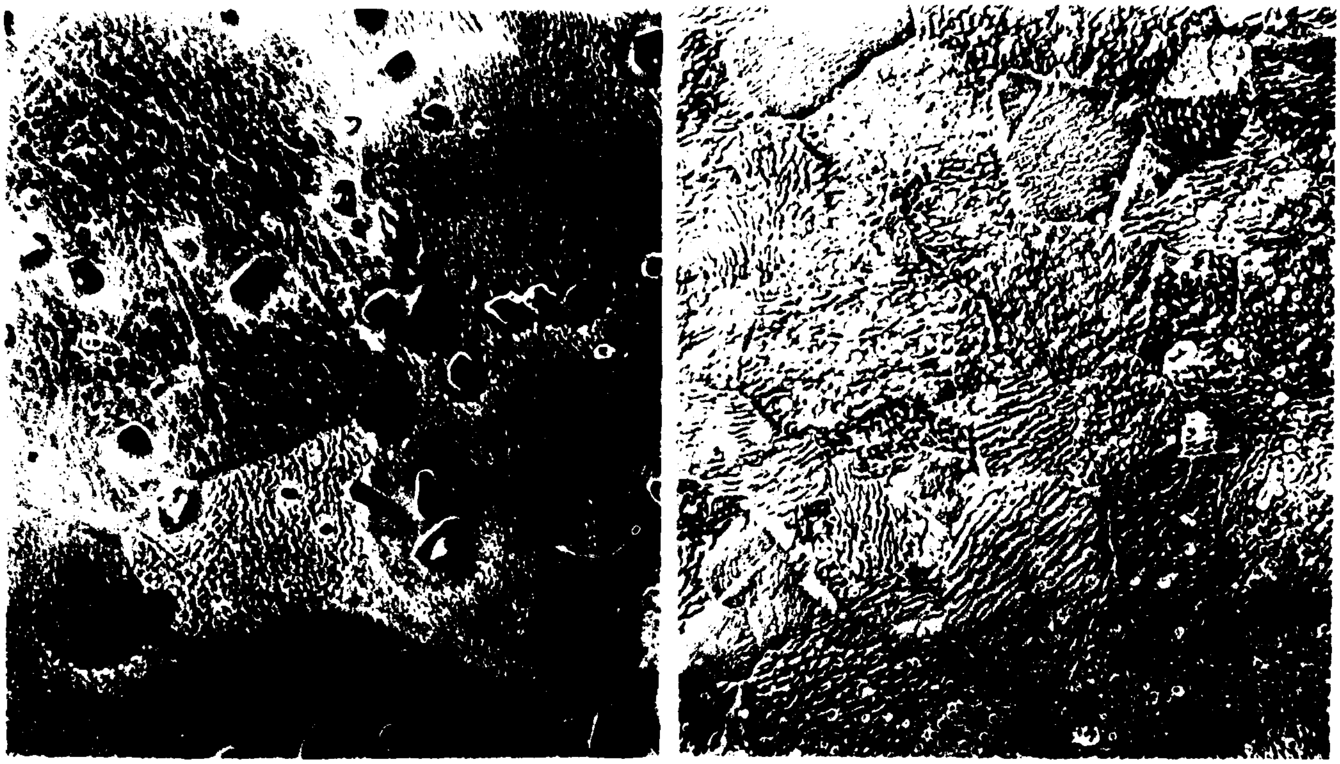
Cu-Mn-Al-Zr



Cu-Mn-Al-Er

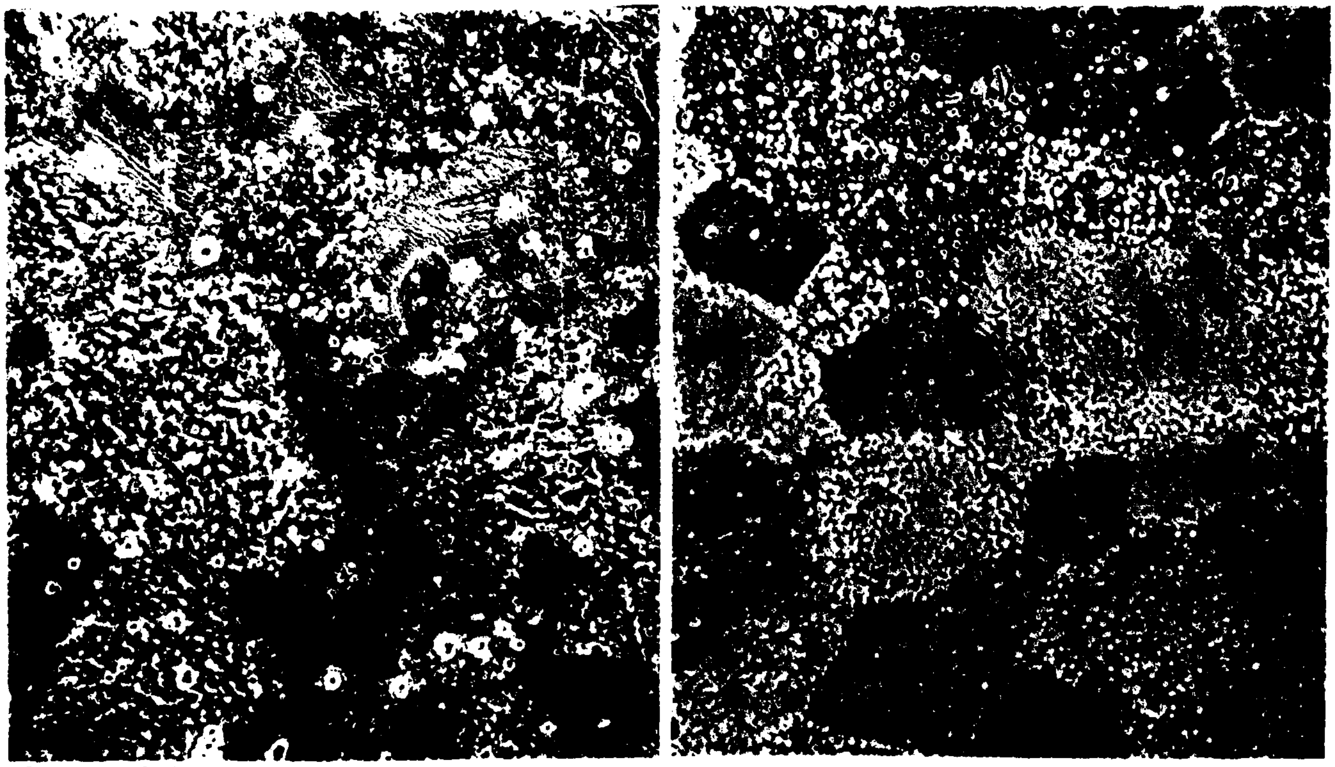
Cu-Mn-Al-Zr-Al

Fig. 3. Optical Micrographs Of The As Spray Formed Material



Cu-Mn-Al

Cu-Mn-Al-Zr



Cu-Mn-Al-Er

Cu-Mn-Al-Zr-Al

Fig. 4. Optical Micrographs Of The Solution Treated Material

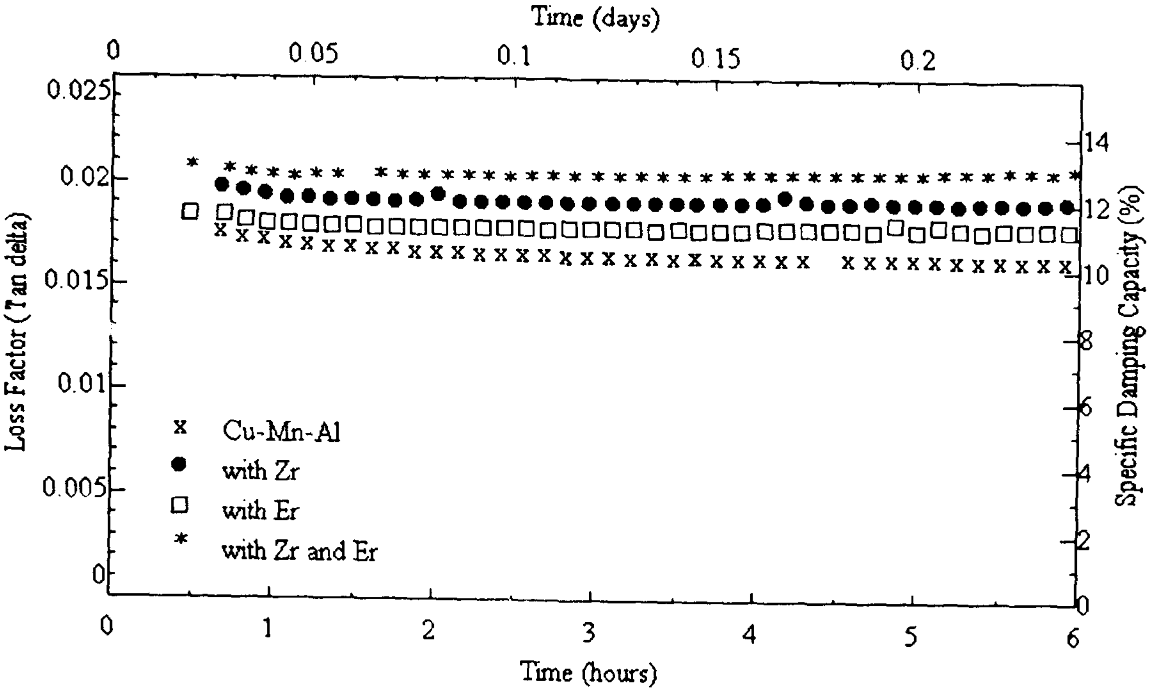
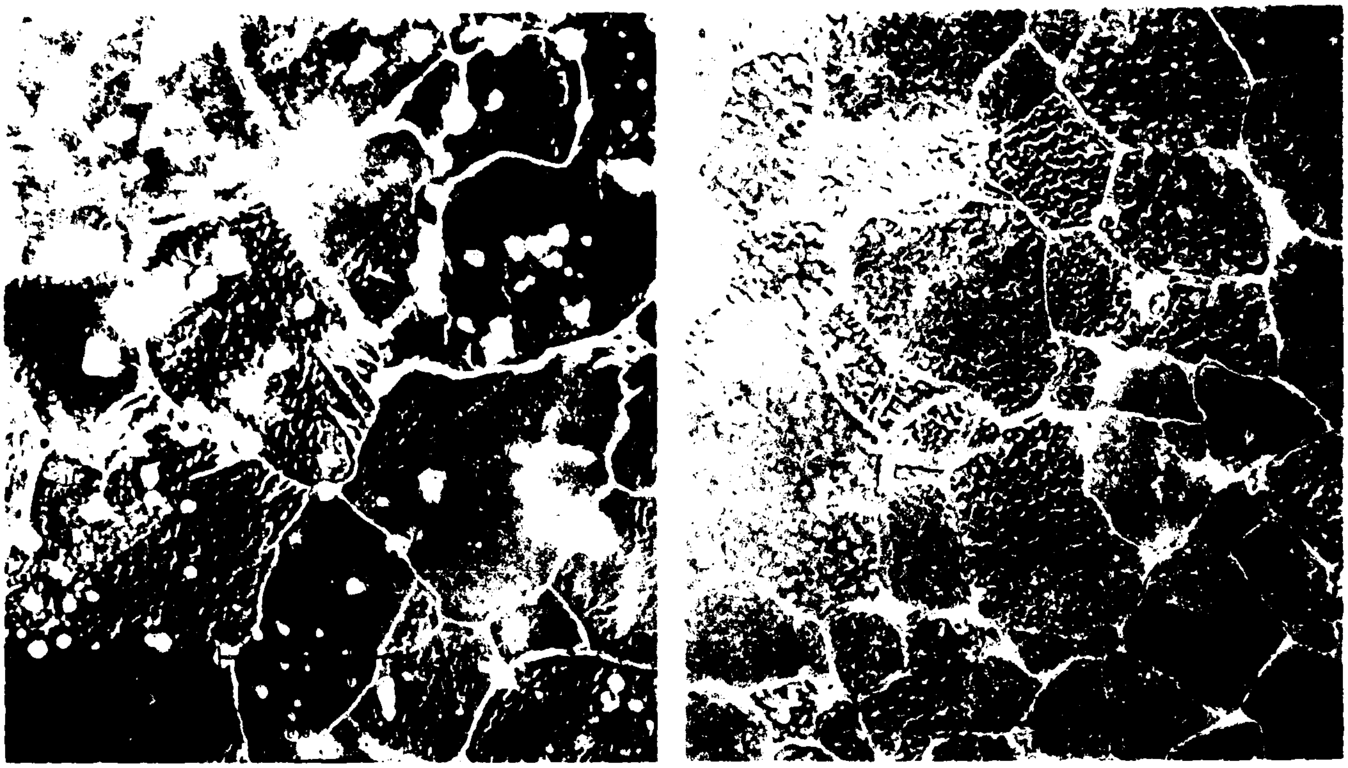
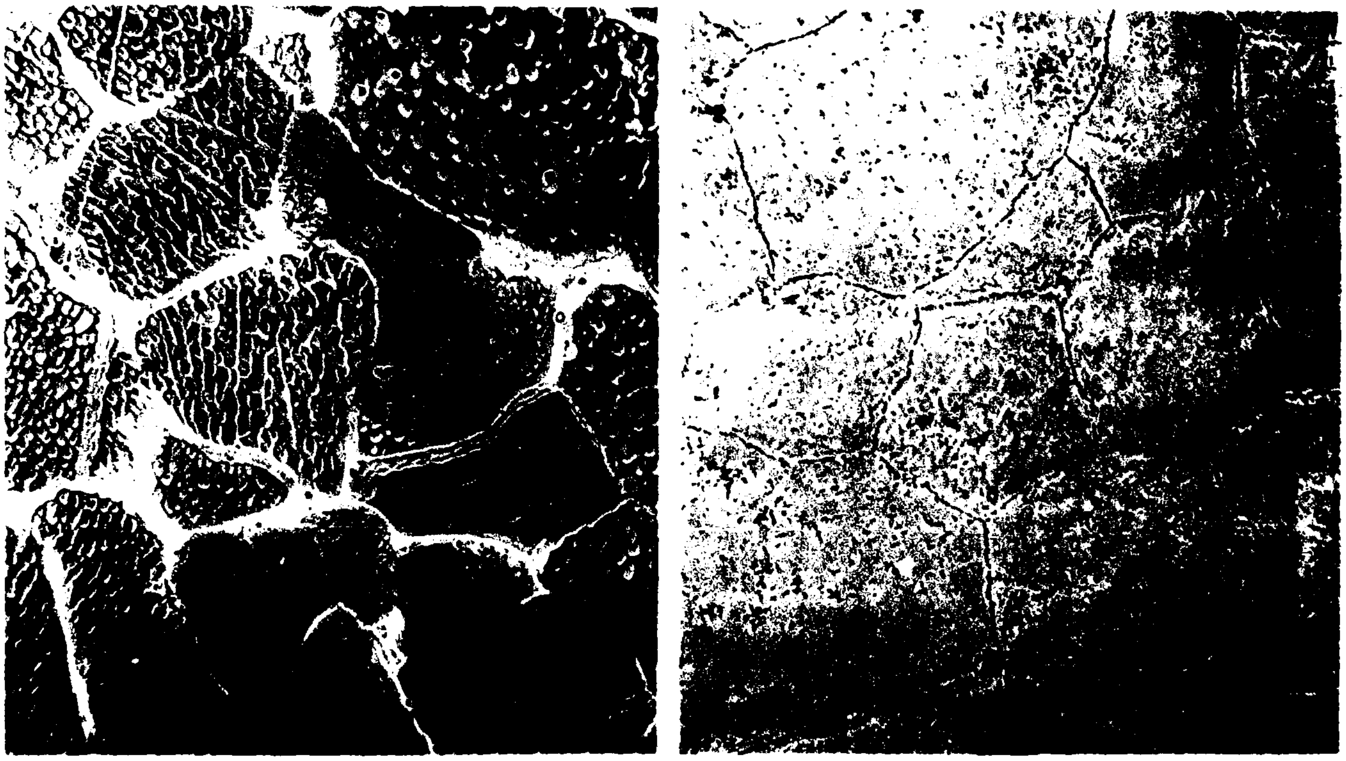


Fig. 5. Damping Capacity During Aging



Cu-Mn-Al

Cu-Mn-Al-Zr



Cu-Mn-Al-Er

Cu-Mn-Al-Zr-Al

Fig. 6. Optical Micrographs Of The Aged Material

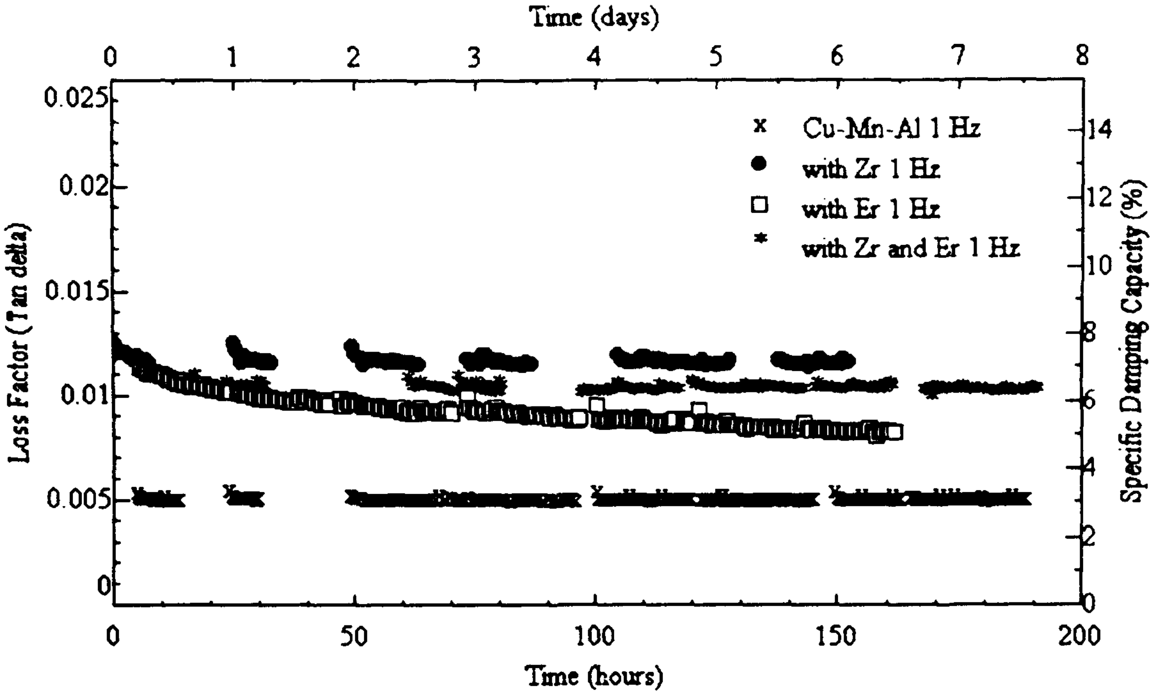


Fig. 7. Damping Capacity The First Week After Aging

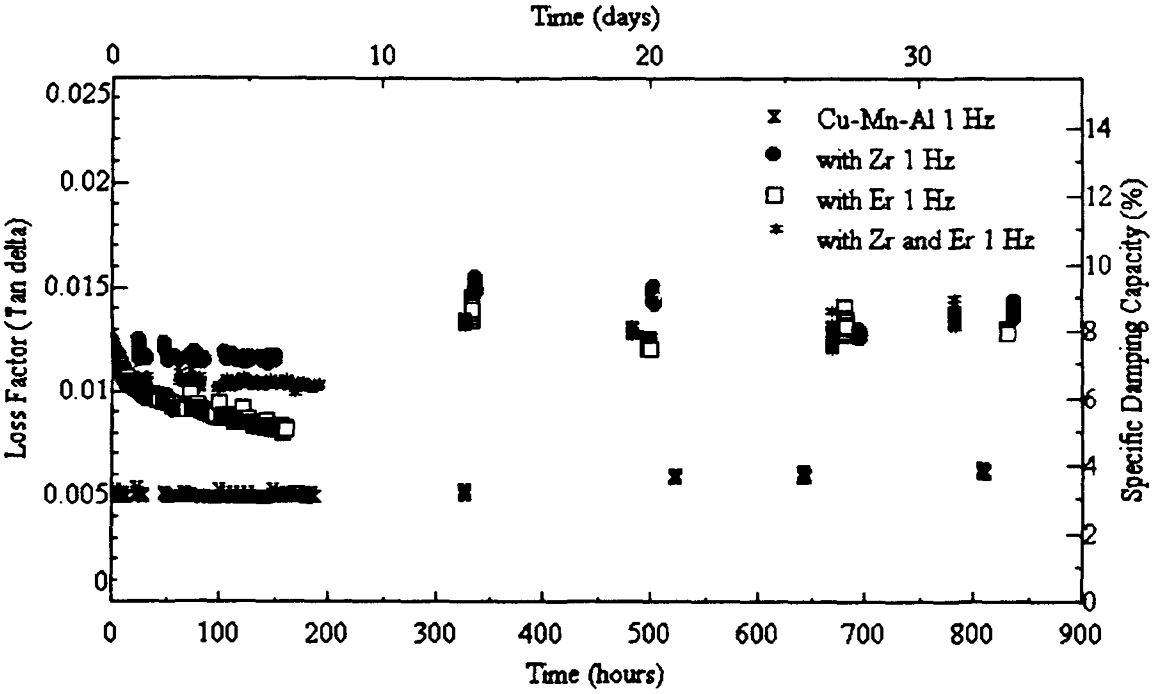


Fig. 8. Damping Capacity Five Weeks After Aging

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