GROWTH OF SECOND PHASE PARTICLES
IN A COPPER-BERYLLIUM ALLOY

FINAL TECHNICAL REPORT

on

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ABSTRACT

Growth of second phase particles from a solid solution of copper-beryllium was studied to determine this alloy's suitability for acoustic emission testing. Optical and Scanning Electron microscopes were used to study the microstructure. Micro and macro hardness tests were also performed. A hardness curve for aging at 550°F was determined. Microscopic examination revealed the presence of large inclusions which make this alloy unsuitable for the acoustic tests envisioned.

INTRODUCTION

The subject of this study is the formation of second phase particles in a copper-beryllium alloy. This study is important because copper-beryllium alloys are being considered for use in evaluating a current model of acoustic emission generation. This model assumes that emission is the result of dislocations unpinning during plastic deformation of the lattice. The energy released from unpinning has been shown to be proportional to the distance between pinning points. Previous studies indicate that particles act as pinning points. [1]. Since Cu-Be possesses the ability to exist in states ranging from a solid solution to a two phase solid, containing dispersed precipitates, it is an obvious choice for testing the assumed relationship between dislocation unpinning and acoustic emission.

In this study, the focus of my investigation has been the effect of various aging times on the physical properties of the alloy. Originally it had been hoped that a scanning electron microscope (SEM) study of the material would provide an insight into the size, shape, and dispersion of the second phase precipitates. However, it was found that the magnification ($\sim 50K$) and resolution of the SEM was insufficient to resolve these structures.

Because direct observation was not possible, Rockwell hardness tests were used to detect the growth of these particles indirectly. Hardness tests were employed because the hardness in Cu-Be alloys is a function of the size and structure of the second phase particles. This method of investigation should reveal the specific time and temperature required to produce peak hardness.

Establishment of the heat treatment necessary for maximum hardness will provide a reference point for the preparation of acoustic emission test specimens. To determine the maximum hardness heat treatment, samples of Cu-Be were heated at constant temperature for time periods ranging from 20 minutes to 9 hours. The microstructure of several samples was examined at various magnifications with both optical and scanning electron microscopes.

REVIEW

In 1974, Hamstad and Mukherjee [2] proposed a model for metals which postulated the existence of a half-power relationship between strain rate and "continuous" acoustic emission (measured as the rms value of the signal produced). The basic assumption of this model is that continuous emission is produced by unpinning of dislocations. During plastic deformation, strain energy is accumulated in dislocations. For a line dislocation this occurs as it bows out between pinning points (Fig. 1). When the stress generated by the strained dislocation exceeds the pinning particles strength, the dislocation breaks loose sweeping through the matrix until becoming pinned by another particle [1]. Hamstad and Mukherjee suggest that the energy released by the rapid unpinning produces the pressure waves which give rise to acoustic emission.

The amount of energy stored by pinned dislocations is proportional to the strength and distance between pinning points. Controlling these variables would provide a means of verifying the half-power relationship.

Table 1. Composition of Copper Alloy
(weight %)

Be	1.85	Ag	0.015
Co	0.25	Mn	0.01
Si	0.10	Ni	0.01
Al	0.07	Sn	0.01
Zn	0.06	Cr	0.003
Fe	0.05	Pb	0.001

Cu 95.57

Figure 1. Looping of a Dislocation Past a Set of Precipitates of Spacing λ

$$\text{rms} = KV^{1/2} \epsilon_p^{1/2} (d\phi/d\epsilon_p)^{1/2}$$

V = volume

ϵ_p = plastic strain rate

K = constant

$\phi(\epsilon_p)$ = density of dislocations unpinned by strain rate up to ϵ_p

Copper-beryllium is an age hardened alloy because it is endowed with certain special properties. Firstly, it forms a solid solution when rapidly quenched from annealing temperatures (solution treatment). Secondly, at room temperature this alloy is supersaturated with Be, however precipitation does not occur because of insufficient solute atom diffusion. Precipitation will occur when the solution treated alloy is heated to moderate temperatures (aging).

Initially pre-precipitate clusters rich in Be form. These are coherently aligned with the matrix from which grow. Coherency, in this context, means that the atomic arrangement at the interface between cluster and matrix is nearly the same. Due to the difference in atomic

spacing between the matrix and the equilibrium precipitate, a state of stress occurs as interfacial atomic layers strain to maintain coherency as the precipitate grows. This stress generates a strain field which extends into the matrix. This strain field increases as the size of the precipitate increases until coherency is lost. At this point the strain field about the precipitate becomes localized.

Strain fields surrounding coherent particles actively pin dislocations, therefore a coherent particle will be a stronger pinning point than its size would indicate. Since a finite amount of Be is available for particle formation, the growth of large precipitates will reduce the total number of particles and increase the distance between them. Thus many strong pinning points can be introduced into the matrix by aging up to peak hardness and fewer, weaker points can be produced by aging beyond this point.

Hardness is the measure of a material's resistance to plastic indentation [3]. Hardness tests involve complicated stress patterns and cannot be used as a direct measure of strengthening. However, such tests do provide a means of qualitatively assessing an alloy's resistance to plastic deformation. As expressed previously, plastic deformation is the result of dislocation movement, and therefore an indirect indication of second phase precipitation.

MATERIAL AND METHODS

The material used in this study was a copper-beryllium tensile test specimen (untested) supplied by Lawrence Livermore Labs. The primary alloying elements of this specimen are 1.85% Be, 0.25% Co, and 0.10% Si by weight. Other elements are present in trace amounts only (see Table 1).

This tensile specimen had been solution treated and aged for 1 hour at 550°F prior to delivery. This specimen was sectioned to provide the many smaller samples used for this study.

Samples used for pitical and SEM observation were cut to a nominal size block with 1 0mm X 3mm X 3mm sides. Each sample was heated within a Lindberg Hevi-Duty tube furnace equipped with an argon gas supply. A positive pressure of argon was maintained within the furnace to prevent oxidation. Heating times ranged from 1 to 8 hours, with the temperature held constant at 550°F $\pm$ 10°F.

The aged samples were prepared for microscopic examination by a series of 4 sanding steps starting with 240 grit paper and subsequent sanding with 340, 400, and 600 grit paper in that order. Final surface finishing was performed on a rotating disk polisher using a general purpose polishing cloth with first 6 μ m and then 1 μ m diamond abrasive compounds. As a final step, bichromate etching solution was applied to the polished sample for 40 sec. followed immediately by a water rinse. This etching treating made the microstructure clearly vizable.

Optical studies of the samples was performed on two Leitz microscopes, one of which is equipped with a camera attachment. Samples were viewed at magnifications ranging from 200 to 650, in an effort to detect microstructural changes due to aging. Some of these samples were also studied with a Cambridge Scanning Electron Microscope. Magnifications used in this work ranged from 500 to 32K.

Samples used for microstructural observation were also used in tests using a Tukon Microhardness Tester. Tests were performed using a 100 gm indenter load and a pyramid shaped indenter. Three to four test sites were picked at random within each sample.

Two pieces approximately 45 mm X 10mm X 10 mm, cut from the original tensile specimen, were heated to $1450^{\circ}\text{F} \pm 10^{\circ}\text{F}$ for 3-1/2 hours in argon and then rapidly quenched to room temperature. This heat treatment constitutes solution treatment, which is necessary to redissolve any precipitate structures which might have formed during the initial 1 hour age treatment [4].

A second set of 10mm X 3mm X 3mm samples were cut from one of these 45mm pieces. These samples were aged at $650^{\circ}\text{F} \pm 10^{\circ}\text{F}$, for times ranging from 1 to 9-1/2 hours. These samples were treated and observed in exactly the same manner as the samples aged at 550°F .

A third group of samples were cut from the remaining 45mm solution treated specimen. Nominal size for these samples is 10mm X 3mm X 7mm. Samples from this group were aged for times ranging from 20 minutes to 110 minutes, with 10 minute intervals between each successively aged specimen. The temperature was held constant at $550^{\circ}\text{F} \pm 10^{\circ}\text{F}$. Each sample was tested on a Wilson, Rockwell hardness tester. A 1/16 inch ball type indenter and an impact load of 40 kg was selected because of this alloys relative softness. Load and indenter correspond to the Rockwell F scale.

Six well spaced indentions were made in the 10mm X 7mm face of each sample. The average hardness value and the standard deviation of hardness values was determined for each sample tested.

RESULTS

Nucleation and precipitate growth is promoted by imperfections within the grains and by the grain boundary. Imperfections can be

impurities or dislocations. Solute clusters and stable precipitate structures within the grain is more desirable for preparation of acoustic emission test specimens. Microstructural examinations were performed to determine the amount of intra-grain vs. grain boundary precipitation.

Theoretically, solution treated samples should not contain any second phase particles. In fact, second phase particles should only be observable in overaged specimens. Microstructural comparison of overaged to solution treated specimens should, therefore, provide a means of determining the amount of precipitation in both the interior and boundaries of the grains.

Initial optical microscopic examination of solution treated specimens and specimens aged at 550°F for 1, 2, 3, 5, and 7 hours all showed the presence of large smooth particles, usually rectangular in shape and 30μm to 60μm long (see Fig. 2). SEM inspection revealed the presence of a second group of particles. These particles are spherical and 1μm to 2μm in diameter (see Fig. 3).

The presence of these particles in both the solution treated and aged samples indicates that these particles are not Be precipitate structures. The presence of these particles in the solution treated specimen indicates that they are insoluble intermetallic compounds. Such compounds are formed from alloying impurities at the time of manufacture.

True precipitate structures were not observed in any aged sample. However, one sample which was heated to annealing temperature (1450°F) and allowed to cool slowly, showed evidence of the formation of Widmanstätten structures (Fig. 4). Widmanstätten structures are caused by the formation of precipitates along certain energetically favorable crystallographic planes.

Figure 2. Large inclusions in Cu-Be alloy.

3a.

3b.

Figure 3 a. Solution treated Cu-Be, X 2.7K.

b. Aged 9.5 hours @ 650°F, X 1.5K.

Fig. 4 Widmanstätten structure in annealed and slow cooled Cu-Be, X 7.3 K.

The accumulated data indicates that this particular alloy is incapable of forming a pure solid solution. However, the fact that no aging precipitates were observed does not mean they don't exist. Sample aging times and the prediction of visible sizes were extrapolated from data for similar but not identical Cu-Be alloys.

The second phase of my investigation focused on the determination of an aging time vs. hardness curve. Theoretically, hardness will initially increase with increasing aging times. This corresponds to the formation of solute clusters and the nucleation of coherent precipitates. For most copper-beryllium alloys, maximum hardness will be reached at approximately 2 to 3 hours aging time if the temperature is held constant at 550°F. [4]. Maximum hardness corresponds to the formation of the largest coherent precipitates. Additional aging should reduce hardness because the particles grow too large to maintain coherency.

Microhardness tests performed on samples aged at 550°F $\pm$ 10°F, for 1, 2, 3, 5 and 7 hours produced results which seemed to conflict with age hardening theory. Hardness for these tests is inversely proportional to the values of indentation diameter which are listed in Table 2.

Table 2. Microhardness of Cu-Be Aged at 550°F.

Aging time (hr.)	Indentation diameter
1	49.3
2	52.8
3	49.9
5	50.2
7	52.7

The aiming device on the microhardness tester used was inaccurate and could not be relied on to indent within any specified grain. This forced the use of testing of random indentation locations. Thus, the

discrepancy between my results and theory is probably the result of using too few indentions per sample to adequately average the affects of grain orientation hardness differences. Due to the failure of these tests, macrohardness (Rockwell) tests were performed.

Rockwell hardness tests indicate that the maximum hardness in this Cu-Be alloy is produced by aging for 100 minutes at 550°F. A graphical summary of the Rockwell tests is contained in Figure 5. These tests confirm this alloy's ability to age harden. Unfortunately macrohardness tests do not differentiate between precipitation at the grain boundary and precipitation within the grain.

DISCUSSION

The microscopic examination of this alloy revealed that impurities will be a consideration in the use of any alloy for acoustic emission research. Acoustic emission tests on 7075-T651 aluminum have shown that the cracking and or decohesion of large intermetallic inclusions generate emissions which are several orders of magnitude greater than those predicated for dislocation unpinning. Thus, the acoustic emission contribution from dislocation movement in the Cu-Be alloy studied will probably be undetectable [5].

The hardness tests indicate that nucleation and precipitation occurred at a significantly faster rate than similar for CuBe alloys which do not contain the assorted trace elements listed in Table 1. Two theories have been advanced regarding the effect of trace elements on precipitation. One theory suggests that their presence alters the kinetics of zone formation (Guinier-Prestion Zones are precipitate structures) so that the apparent diffusion of solute atoms is decreased.

Figure 5. Hardness vs. Age Time for Cu-Be at 550°F

A second theory states that the trace elements can assist nucleation of intermediate precipitates and thereby increase the rate of precipitation [6]. In light of the hardness data, the second theory appears to be more appropriate for the Cu-Be alloy.

Both microstructural observations and hardness tests indicate that the Cu-Be alloy used for this study is too complex to allow adequate evaluation of it's worth for acoustic emission tests with the instrumentation I have employed.

To advance this work, a study should be made to determine the feasibility of elimination of the insoluble inclusions. The composition of these inclusions can be determined by microprobe analysis. A knowledge of their composition will indicate if these impurities can be controlled during manufacture. Secondly, transmission electron microscopy, with it's potential for extreme magnification, could be used to analyze the size and distribution of the precipitate structures.

If the insoluble inclusions can be eliminated and TEM studies performed, then this Cu-Be alloy will again look promising for acoustic emission tests. Also, a study of this magnitude will help further the knowledge of precipitation mechanisms in multicomponent systems.

APPENDIX

For precipitation to occur in an age hardened alloy, nucleation must occur. Nucleation is a product of solute clustering. "Random" motion of solute atoms leads to the formation of minute regions which are high in solute concentration momentarily. Clustering is actually not due to completely random motion because the distribution of atoms within a solid is not completely random.

Clusters must attain a critical size, given by a critical radius r^* , determined by the balancing of the increased surface energy required for growth with the decrease in volume free energy (Fig. 6).

Figure 6. Relationship Between Free Energy Change and Particle Size

Nucleation is caused by the supersaturated solid solution seeking to minimize its total free energy. This process is partially rate determined by diffusion, which is a function of temperature. The Volmer-Weber theory summarizes these considerations.

(Volmer-Weber)

$$N = C \frac{e^{-\frac{Q+A}{RT}}}{T}$$

N = nucleation rate

C = constant

Q = diffusion activation energy

A = Work of nucleation under rev. conditions

K = Boltzmann's constant

T = temperature

This theory is conceptually useful but inaccurate because:

1. The strain energy always present in precipitation from a solid solution is ignored.
2. It only applies at the beginning of precipitation because supersaturation decreases and the coherency relationships probably change with the time [7].

Current theory for precipitation hardening alloys predict the formation of Guinier-Preston zones. These zones are pre-precipitates structures which do not necessarily have a shape of their own but are instead distorted solute-rich domains with no definite boundaries. These structures are completely coherent with the matrix. G. P. zones apparently only occur when the atomic discrepancy is less than 10% [7]. The atomic mismatch in the Cu-Be system is 8.8% [6]. G. P. zones are the first structures to form during precipitation because their formation is accomplished with a minimum surface energy change. Therefore the general system of precipitation in Cu-Be is probably: Solid Solution $\rightarrow$ pre-precipitate (transition) $\rightarrow$ equilibrium precipitate.

APPENDIX: MICROPROBE ANALYSIS

The large inclusions (10 - 30 μ m) have been qualitatively analyzed with an electron microprobe. The results indicate that these inclusions contain a high concentration of titanium and cobalt. Aluminum, silicon, and trace amounts of iron were also detected. Due to the physical limitations of the microprobe beryllium could not be detected (see Table 3).

Table 3. Inclusion Composition

listed in order of decreasing magnitude

Ti	20 - 40%
Co	20 - 40%
Si	
Al	
Fe	1 - 5%

Photographs of the microprobe images for each of these elements is contained in Figure 6. Light spots on these pictures correspond to areas emitting K $_{\alpha}$ wave length radiation for the particular element denoted.

a. Cobalt

b. Aluminum

c. Iron

d. Silicon

e. Titanium

f. Copper

Figure 6. Microprobe pictures of large inclusions in a Cu-Be sample.

These pictures illustrate the vast difference between matrix and inclusion composition. The light specks in the predominately dark matrix is the result of the continuous spectrum of radiation wave lengths emitted by the various elements and therefore does not necessarily indicate the presence of a particular element.

It should be noted that the presence of titanium is in conflict with the earlier data supplied in Table 1. This initial data was supplied with the test specimen.

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