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Age Hardening in Rapidly Solidified and Hot Isostatically Pressed Beryllium-Aluminum-Silver Alloys

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Abstract

Three different alloys of beryllium, aluminum and silver were processed to powder by centrifugal atomization in a helium atmosphere. Alloy compositions were, by weight, 50% Be, 47.5% Al, 2.5% Ag, 50% Be, 47% Al, 3% Ag, and 50% Be, 46% Al, 4% Ag. Due to the low solubility of both aluminum and silver in beryllium, the silver was concentrated in the aluminum phase, which appeared to separate from the beryllium in the liquid phase. A fine, continuous composite beryllium-aluminum microstructure was formed, which did not significantly change after hot isostatically pressing at 550 °C for one hour at 30,000 psi argon pressure. Samples of HIP material were solution treated at 550 °C for one hour, followed by a water quench. Aging temperatures were 150, 175, 200 and 225 °C for times ranging from one half hour to 65 hours. Hardness measurements were made using a diamond pyramid indenter with a load of 1 kg. Results indicate that peak hardness was reached in 36-40 hours at 175 °C and 12-16 hours at 200 °C aging temperature, relatively independent of alloy composition.

1 Introduction

Beryllium exhibits an attractive combination of properties, including a very low density and high specific modulus. Unalloyed beryllium is used in many applications, including weapons, spacecraft, nuclear reactor reflector segments, neutron sources, windows for x-ray tubes and radiation detection discs, precision instruments and mirrors. Be has a lower density than Ti or even Al. Its melting point is relatively high, indicative of its high elastic modulus. Its thermal expansion coefficient is relatively low, making it dimensionally stable during temperature changes. This is an important feature, especially during composite processing. Its relatively low ductility at room temperature has limited its use in many

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structural applications such as in the aerospace industry, where its high specific strength and stiffness would be very advantageous.

The possibilities of combining Be with Al, in order to take advantage of the good ductility of Al have been recognized for many years. Lockheed Missiles and Space Company undertook an extensive study of the beryllium-aluminum system, and by 1964 had developed an alloy known as "Lockalloy." This alloy generally contains 38 wt% aluminum and is produced as extrusions and sheet hot-rolled from extruded bar stock. This composition was chosen because it gave a rule-of-mixtures elastic modulus of the composite equal to that of steel. Lockalloy combines the ductile properties of aluminum with the high strength, low density, and stiffness of beryllium. It has excellent thermal characteristics and also exhibits good formability and machining characteristics, resulting in its use in several aerospace applications. This was the first Be-Al product to reach commercial development, and was successfully used in military applications such as extruded skin stiffeners for missiles.

An age hardening study of one such alloy currently under development, Be-50Al with additions of silver, is presented in this work. A review of the processing and mechanical properties of this series of alloys is presented elsewhere [1, 2].

2 Theory

2.1 Liquid phase separation

The Be-Al phase diagram is a simple eutectic with no compounds. There is little or no solubility of Be in Al, or of Al in Be. The size and morphology of the resulting two phase alloy therefore depends on the solidification rate and processing history.

Various researchers [3, 4] have found a submerged metastable liquid miscibility gap in the Be-Al system, depicted on Figure 1 [5]. This can be used to produce liquid phase separation, resulting in unique microstructures at rapid rates of solidification. Spinodal decomposition occurs between the inflection points on the free energy versus composition plot. Within this range, there is no nucleation barrier to the separation of phases, and the resulting phases are continuous. The optimum ratio of Be-Al may occur between 40 and 60 wt% Al. Using a thermodynamic approach, Murray and Kahan [5] calculated the critical point of this miscibility gap as 1100 °C at 68 at% Be.

This liquid phase separation can be accessed in the Be-Al system when processing by rapid solidification. The metastable reaction occurs when the liquid phase greatly undercools and a new solidification pathway is followed. For liquid phase separation to occur, the liquid must undercool to a point where it reaches the metastable miscibility gap. The resultant morphology is of a continuous, nearly pure beryllium phase filled initially with a liquid composed of Al and Ag. Upon complete solidification two intimately interwoven phases exist. The resulting microstructure, depicted in Figure 1, can be described as a three-dimensional interpenetrating composite.

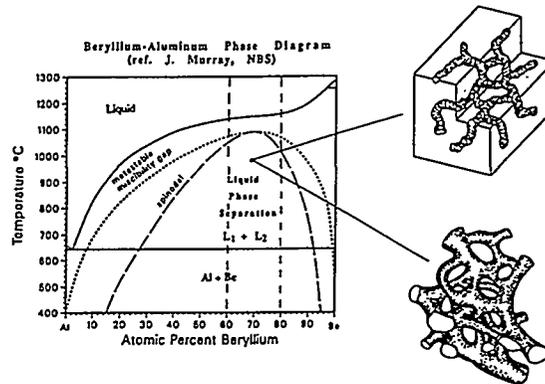


Figure 1: Beryllium-aluminum phase diagram and depiction of beryllium-aluminum three-dimensional interpenetrating composite morphology

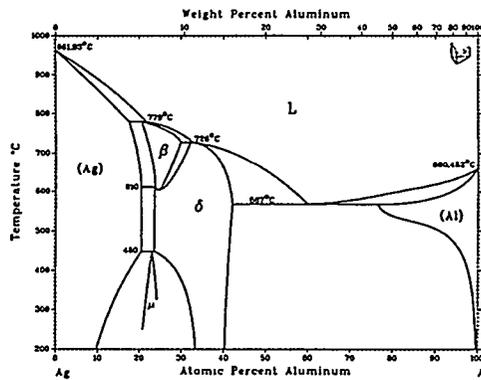


Figure 2: Aluminum-silver phase diagram

2.2 Age hardening

Among alloys demonstrating precipitation hardening, the aluminum-silver system is one of the most thoroughly studied. The driving force behind the growth of precipitates can be seen in the Ag-Al phase diagram (see Figure 2). The feature which favors precipitation hardening is the large region of solid solubility of Ag in Al near the eutectic temperature. As a result, an alloy can be held at an elevated temperature and all of its silver will be in solid solution. Upon quenching, the silver is trapped in a supersaturated solid solution. As this state is contrary to the equilibrium phase diagram, the thermodynamic driving force for precipitation of silver exists.

Walker and Guinier described the age hardening of Al-Ag alloys as having two distinct stages [6]. During the quench from a region of solid solubility, silver atoms are grouped into small, nearly spherical clusters. The size of these clusters

depends on the rapidity of the quench; the clusters in a rapidly quenched sample will typically contain on the order of 100 Ag atoms. With annealing, the clusters coarsen, absorbing silver atoms from the bulk and from smaller clusters.

As the aging continues, the number of clusters decreases and the average size of the clusters increases. The hardening associated with this initial phase is limited, though. Eventually, the clusters will become so large and widely spaced that additional annealing actually causes a decrease in the hardness.

In Al-Ag a second stage of age hardening exists. With prolonged exposure to elevated temperatures the silver will react with the aluminum to form Ag_2Al . Walker and Guinier noted that this intermetallic compound must necessarily form at the silver clusters, as all of the Ag atoms can be found there. The Ag clusters serve as nucleation sites, while the growth is characterized by the formation of Ag_2Al platelets perpendicular to the (111) planes in the alloy.

The first extensive study of the times and temperatures required for each of the two hardening phenomena was conducted by Köster and Braumann in 1952 [7]. Their best data for showing the two hardening mechanisms was obtained on Al-10 wt% Ag alloys. The curves they plot for aging conducted at 200 °C and 250 °C show two increases in hardness. One is at very short times and corresponds to formation of Guinier-Preston (G-P) zones from the super-saturated solid solution. The second is associated with the growth of Ag_2Al plates.

3 Experiment

The alloys in this study were produced by hot isostatically pressing powder made by centrifugal atomization. Fifty weight percent beryllium-aluminum alloys containing 2.5, 3, and 4 wt% Ag were fabricated. The powder was produced by a centrifugal atomization process, which resulted in a very fine microstructure. The process is described in detail elsewhere [1, 2].

Samples of each composition (2.5, 3, and 4 wt% Ag) were heat treated in a silicone oil bath at 150, 175, 200, and 225 °C for times ranging up to 65 hours for the 150 °C age. Vickers hardness numbers were determined using a microhardness tester with a 1 kg load. A minimum of five indentations were used for each combination of temperature and time.

4 Results

The results of the aging study are plotted in Figures 3–5. These plots show Vickers hardness versus aging time for all three compositions at each temperature.

The 2.5% Ag alloy displayed a significant increase in hardness after just one hour of aging at all temperatures above 150 °C. The hardness decreased until 12 hours, where it again began to increase to a peak at 16 hours at the 200 °C aging temperature. Additional decreases in hardness followed this second peak.

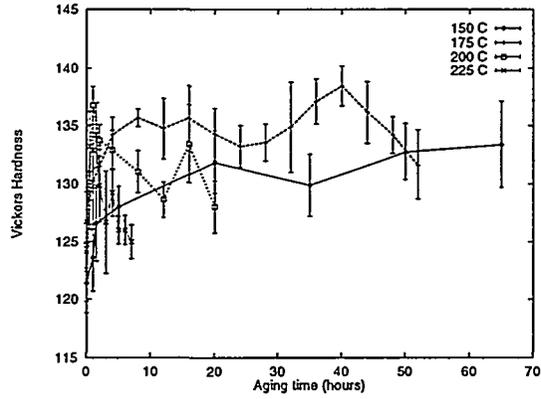


Figure 3: Vickers hardness versus aging time for 2.5% Ag composition

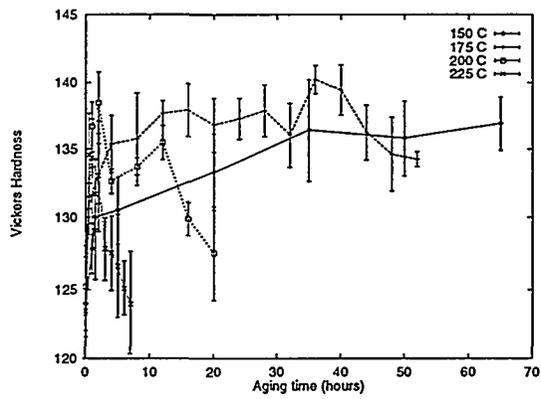


Figure 4: Vickers hardness versus aging time for 3% Ag composition

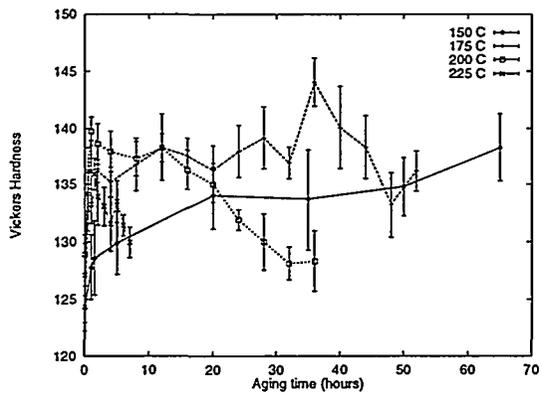


Figure 5: Vickers hardness versus aging time for 4% Ag composition

Table 1: Time to formation of Ag_2Al versus annealing temperature

| Temperature ($^{\circ}\text{C}$) | Time |
|------------------------------------|-----------------------------|
| 20 | Not observed after 3 months |
| 140 | 100 hours |
| 165 | 22 hours |
| 255 | 18 minutes |
| 300 | 3 minutes |
| 405 | 15 seconds |

A similar effect was observed in the 3% Ag alloy. For aging at 200°C , the initial peak was not observed until after two hours, and the second peak came earlier, at 12 hours.

The 4% Ag plot has more data than the previous two, but the observations are comparable. Once again, two peaks are observed for aging at 200°C , one after just one hour of aging, and the second at 12 hours. The additional data is for long times, and like the other two alloys, the main feature is continued softening.

5 Discussion

The curves plotted in Figures 3–5 consist of four main parts. The first is the initial hardening stage. The second is a slight reversion in hardness. Thirdly is another stage of hardening and finally, another decrease in hardness. Each stage can be explained according to the theories first presented by Walker and Guinier.

The first stage of hardening is associated with the formation of G-P zones. These zones can form at room temperature, given enough time, and have formed within one or two hours at 200°C . In precipitation hardening, the number and size of precipitates dictates the hardening caused by their presence. It makes sense that the alloy with the most silver realizes the most hardening from the growth of G-P zones, and that is consistent with what has been observed in these alloys.

Next the alloys actually soften a bit during a stage called reversion. This softening is caused by the dissolution of the G-P zones. Again, theory predicts what is observed in this system. Assuming that a similar amount of silver will return to solution regardless of the initial Ag concentration, alloys with less silver will experience more reversion, as these alloys will be left with fewer G-P zones than alloys richer in Ag.

A second stage of hardening follows the reversion stage. This hardening is caused by the formation of an intermetallic compound, Ag_2Al . Walker and Guinier reported data for alloys of Al-20wt% Ag concerning the time required to observe formation of Ag_2Al versus annealing temperature, listed in Table 1.

Interpolating this data for $T = 200^{\circ}\text{C}$ gives a value of approximately 3.5

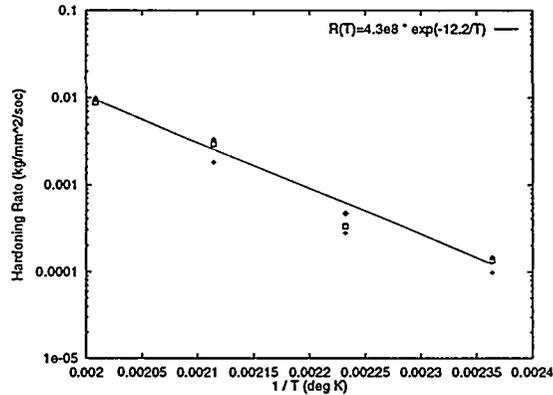


Figure 6: Initial hardening rate versus $1/T$

hours. The second peaks observed in this system occur at a higher value. Köster and Braumann's work helps explain the discrepancy. They observed that in a 38 wt% Ag alloy, the secondary peak at 200 °C occurred after just 5 hours. With a Ag concentration of 30 wt%, the peak falls between 7 and 8 hours. By the time silver is just 20 wt%, the time required for the maximum is just over 12 hours. The trend is that as Ag fraction decreases, the time required for Ag_2Al to form increases. The observed values of 16 hours, 12 hours, and 12 hours for 2.5 wt% Ag, 3 wt% Ag, and 4 wt% Ag, respectively, are therefore plausible times for hardening being caused by Ag_2Al growth. It should be noted that the silver concentration in the aluminum phase is approximately double that of the overall alloy, since there is little silver dissolved in or reacted with beryllium.

Finally, the alloys undergo a second reversion in hardness. The reasons for this stage are less well understood and currently subject to some speculation. Two possibilities exist: coarsening of the Ag_2Al platelets and coarsening of the alloy's microstructure. Were the intermetallic phase to coarsen, the hardening effect of its presence would clearly decrease. Similarly, much of the strength of the aggregate alloy can be attributed to the intimate composite microstructure. Coarsening of the microstructure would also contribute to softening.

One can also examine the initial hardening rate, and compare the slope of the hardening rate versus temperature with the activation energy for diffusion of silver in aluminum. Figure 6 is a plot of hardening rate versus $1/T$. The slope of this curve is -12.2 kJ/K, which compares nicely with the activation energy for silver diffusion in aluminum.

Mechanical properties of this Be-Al-Ag system as a function of age hardening condition have also been examined, and are presented elsewhere [1, 2].

6 Conclusions

The goal of this project was to determine the exact nature of age hardening in an unusual alloy system, Be-Al-Ag. First, the existence of age hardening was ascertained, and then aging conditions required to produce significant hardness increases were determined. The two-stage age hardening observed by Walker and Guinier 40 years ago was also observed in this ternary system.

The question, that of finding an annealing regimen to produce hard alloys has yet to be fully answered. In all cases, the hardening associated with precipitation of G-P zones exceeds the hardening caused by Ag_2Al growth. Questions as to the stability of these peaks must be raised. If the G-P zones are more likely to coarsen than the Ag_2Al platelets, then the second peak may be more desirable, despite the lower hardness. Nevertheless, for these alloys and an annealing temperature of 200 °C, the locations of the peaks have been roughly identified.

The ternary Be-Al-Ag system is a promising candidate for a lightweight, structural material. One factor that limited its use in the past was the weakness of the Al phase. With the verification of age hardening in the ternary alloy, this problem is alleviated, and the potential usefulness of the alloy is enhanced.

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