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The Effect of Cu on Precipitation in Al-Zn-Mg Alloys

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Abstract

The effect of Cu on the mechanical and precipitation properties of a high strength Al-2.4at.% Zn-2.1at.% Mg alloy was investigated. The results show that the addition of a relatively small amount (0.5at.%) of Cu introduces significant changes in the age hardening response of the alloy. The influence of the Cu addition goes back to changes occurring already in the initial clustering process which has been investigated here among other methods by positron annihilation lifetime spectroscopy and by 3-dimensional atom probe field ion microscopy.

1. Introduction

Al-Zn-Mg alloys have several industrial applications due to their high strength to density ratio and age hardening characteristics. The commercial alloys usually contain other alloying elements and/or different impurities. One of the main alloying constituents in these alloys is Cu, which has significant effect both on the as quenched state and on the aging characteristics of the alloy [1-3].

Al-Zn-Mg alloys show strong aging response which is due to the decomposition of the supersaturated solid solution (SSSS) and the formation of fine distribution of coherent Guiner-Preston (GP) zones and semicoherent η' precipitates [2].

It is well known that the GP zones in Al-Zn and Al-Zn-Mg alloys are three dimensional, often spherical [2-7], while those forming in Al-Cu are two dimensional, plate-like [8-11]. In Al-Zn-Mg-Cu alloys, generally two types of GP zones are formed. One, called GP(I) zone shows spherical shape and forms at relatively low temperatures. The other, called GP(II) zone forms above 70°C from vacancy-solute clusters and has an elongated ellipsoidal shape. The small GP(I) zones dissolve around 140°C while GP(II) zones are more stable and may transform continuously into the semicoherent η' phase [12].

$$\text{SSSS} \rightarrow \text{GP(I)} \rightarrow \eta' \rightarrow \eta$$
$$\text{SSSS} \rightarrow \text{VRC} \rightarrow \text{GP(II)} \rightarrow \eta' \rightarrow \eta$$

In this paper, the effect of Cu addition on the precipitation process and on the mechanical properties of an Al-Zn-Mg alloy were investigated by compression and hardness tests, as well as by positron annihilation lifetime spectroscopy (PALS), transmission electron microscopy (TEM) and three-dimensional atom probe field ion microscopy (3DAPFIM).

2. Experimental Procedures

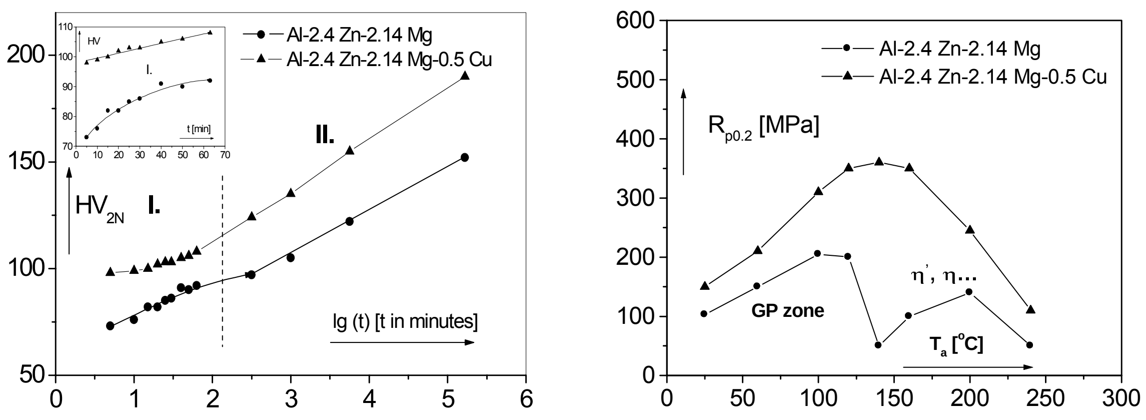
Ternary Al-2.4Zn-2.1Mg (at. %) samples, as well as samples with 0.5at.% Cu addition were prepared from 99.99% purity aluminum. Details of the sample preparation were described elsewhere [1]. Specimens were solution treated at 470°C for 30 min and water-quenched to room temperature (RT).

The specimens for the compression tests were 10 mm high cylinders of 8 mm diameter. The compression tests were performed at RT in an INSTRON machine by constant crosshead velocity of 1 mm/min. Samples for microhardness measurements were mechanically and electrolytically polished, measurements were carried out using a Shimadzu-DUH 202 depth-sensing ultra-microhardness tester with 2N maximum load.

The samples for the PALS measurements were quenched to RT water and heat treated for 1 min at RT and then stored in liquid N_2 at 78K. The PALS measurements were performed isothermally at several, gradually increasing, temperatures (78, 200, 281K). At the point (281K) where one of the samples started to change we have stopped increasing the temperature and started a new set of measurements. Further experimental details of the PALS measurements were described elsewhere [13].

The TEM investigations were carried out on a Philips CM200 electron microscope operated at 200 kV. The 3DAP measurements were made by using CAMECA's energy-compensated tomographic atom probe (ECTAP) detection system [14] installed on a locally built field ion microscope (FIM). Atom probe analysis was carried out at 25-30K with a pulse fraction of 20% in an ultra high vacuum of $\approx 10^{-10}$ Torr.

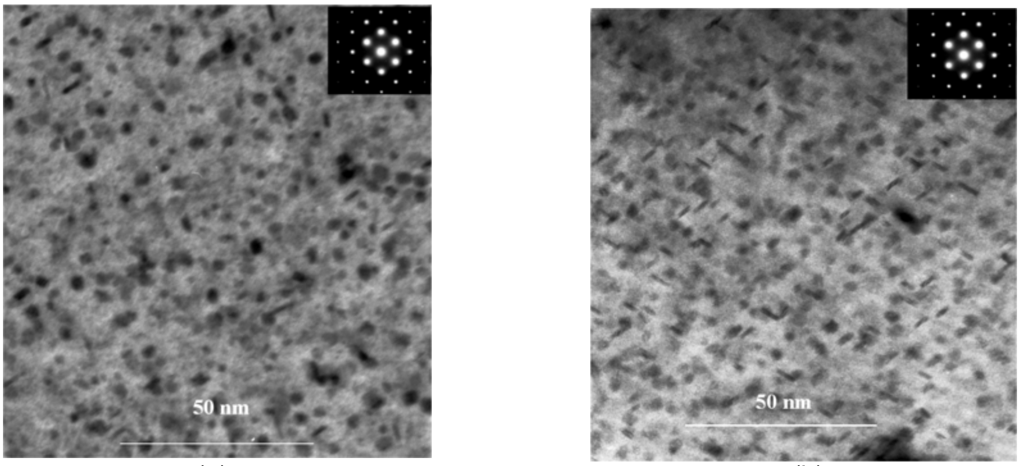
3. Results



(a) (b)

Figure 1: Mechanical characteristics of the ternary and the quaternary alloys.
(a) Vickers hardness as a function of aging time at RT.
(b) Yield stress as a function of the temperature of 2h heat treatments after quenching.

The Al-Zn-Mg alloy investigated shows strong age hardening at RT (Figure 1/a) and also at higher temperatures (Figure 1/b). The addition of Cu leads to significant strengthening already immediately after the quench.



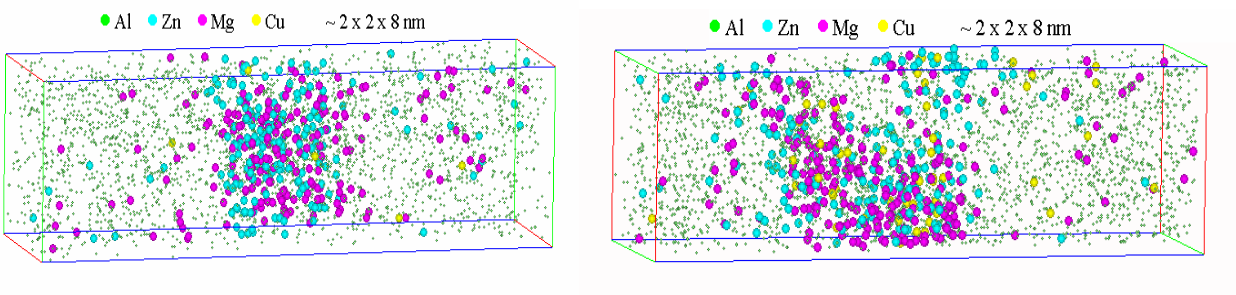
(a) (b)

Figure 2: TEM images of the ternary (a) and the quaternary (b) alloy after 2h aging at 120°C heat treatment.

The other significant difference between the ternary and the quaternary alloy is in the yield strength around 140°C, where the yield strength of the ternary alloy does not increase from the value observed after the quench while in the quaternary alloy the increase of yield strength after 2h heat treatment shows a maximum at this temperature.

Comparing the microstructure of the ternary and the quaternary alloys remarkable differences can be observed below the solvus temperature of GP(I) zones (at 120°C). The TEM micrographs in Figure 2 show the microstructure of samples aged for 2h at 120^{o}C. The tendency of the change of proof stress as a function of the aging temperature (Figure 1/b) indicates that mainly GP zones form during 2h aging at 120^{o}C. This assumption is confirmed by the diffraction pattern taken in the $<110>_\alpha$ direction (insert in Figure 2), in which no extra spots could be observed.

The TEM pictures show that spherical GP zones form with roughly the same dispersion in both alloys. This means that the Cu addition does not change the number of the spherical GP zones, the effect of Cu manifests itself rather in the aspect that in the Cu containing alloy plate-like particles in a relatively high number were also observed. While in the case of the ternary AlZnMg alloy only a few plate-like particles (about 5% of all particles) can be found in the micrograph, in the Cu-containing alloy about 30% of all observed particles were plate-like.



(a) (b)

Figure 3: APFIM images of a spherical GP(I) (a) and an ellipsoidal GP(II) (b) zones in the quaternary alloy after 2h aging at 120°C.

Results of 3DAPFIM investigations – in agreement with the TEM investigations – show higher number of particles in the Cu containing alloy. Furthermore, while in the ternary alloy only spherical zones were found, in the quaternary alloy both spherical and elongated ellipsoidal particles were observed.

Figure 3 shows selected volumes of 3DAP elemental mapping of the two types of GP zones formed in Cu-containing samples aged for 2h at 120°C. The AP measurements revealed that the particles of different shapes can also be distinguished by their Cu content. The Cu content of the ellipsoidal particles is relatively high, while the spherical particles are practically Cu-free [15]. The difference between the two alloys goes back to the early stage of the GP-zone formation, which on the other hand is strongly influenced by the quenched-in vacancies and by the formation of vacancy clusters.

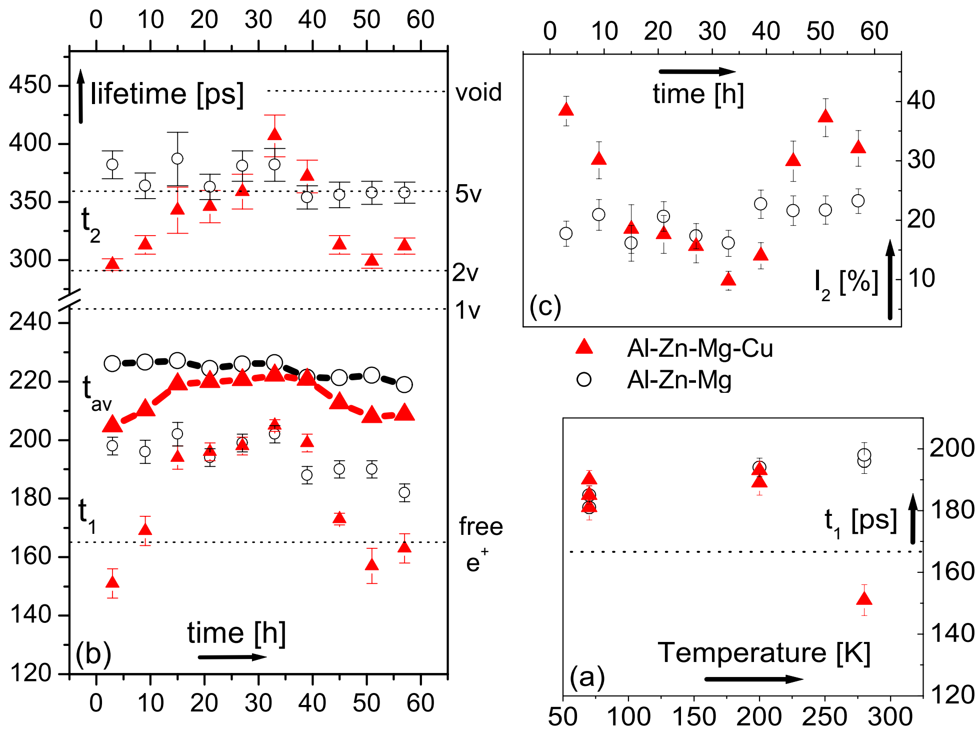


Figure 4: Summary of the PALS measurements.
(a) The lower lifetime (t_1) component as a function of the aging temperature.
(b) The lower (t_1), average (t_{av}) and higher (t_2) lifetime components as a function of the aging time at 281K, the characteristic lifetimes are shown for the pure Al alloy, mono-, di-vacancies and voids.
(c) The intensity of the higher lifetime component as a function of the aging time at 281K.

The influence of quenched-in vacancies and vacancy clusters was investigated by PALS measurements on samples water-quenched to and aged for 1 minute at RT (Figure 4). The measurements were carried out at 78, 200 and 281K, the measurement time of each lifetime spectrum took 6 hours. In the positron spectra two lifetime components could be distinguished. The lower lifetime component (t_1) is shown for both alloys as a function of the measuring temperature in Figure 4/a. At 78 and 200K the same t_1 value was detected in the ternary and the quaternary alloy. Contrary to this, at 281K a considerably shorter lower lifetime component was found for the quaternary alloy. The t_1 values obtained at the two lower temperatures are between the free positron lifetime in pure Al and the lifetime of positrons trapped by monovacancies.

The decrease of t_1 at 281K in the quaternary alloy to a value below the free positron lifetime of pure Al indicates the disappearance of the monovacancy contribution and the appearance of divacancies or small vacancy clusters. To investigate further the changes in the vacancy distribution during the initial period of aging after quenching, PALS measurements were made during different periods of aging at 281K.

In Figure 4/b the lower (t_1), the average (t_{av}) and the higher (t_2) lifetime components and in Figure 4/c the relative intensity (I_2) of the higher component are shown as a function of aging time at 281K. In the ternary AlZnMg alloy, the positron lifetime parameters are practically constant in the whole studied time interval, only a slow decrease of the lifetimes occurs even after several days. On the other hand, in the Cu containing alloy, both lifetime components increase at the beginning of the aging. Although the intensity of the longer lifetime component decreases, the mean lifetime increases, as well. This latter phenomenon indicates that, in this stage, the average size of free volume type defects increases in the sample. An opposite process starts in the sample after about 35 hours. Here the lifetimes (even the mean lifetime) decrease while the intensity of the longer component increases. So, the obtained PALS data indicate a rearrangement of free volume type defects, in which the average size decreases after 35 hours.

4. Discussion

It has been shown that the addition of a relatively small amount (0.5at.%) of Cu to the Al-2.4at.% Zn-2.1at.% Mg alloy enhances considerably the age-hardening both in natural and in artificial aging. The addition of Cu more than doubled the proof stress, $R_{p0.2}$ in the as-quenched state (from 50 to 110MPa). Taking into account that the amount of Cu is just 10% of the alloying elements, the strengthening effect of Cu addition in the as-quenched state could be explained by the incorporation of Cu atoms into the vacancy-solute clusters which form immediately after quenching [16].

The decrease of the lower lifetime at the beginning of aging at 281K (Figure 4/a) indicates that the vacancy-solute clusters containing only 1 vacancy disappear from the matrix, probably by the coagulation of small clusters leading to the formation of larger clusters. The increase of the vacancy-solute clusters goes on for 35 hours at 281K, after this both lifetime components start to decrease indicating that at this stage the emission of vacancies from the clusters set in. This formation and rearrangement of vacancy-solute clusters is faster in the quaternary than in the ternary alloy because of the higher supersaturation and because of the fast diffusion of Cu.

The TEM and 3DAP results shown in Figure 2 and Figure 3 also support the formation of Cu containing vacancy-solute clusters in the quaternary alloy. These results revealed that the addition of Cu practically does not change the size, the number density and the composition of spherical GP zones, but it enhanced strongly the formation of ellipsoidal zones containing also Cu atoms. The morphology change of the Cu-containing GP zones is most probably caused by the strain introduced by the incorporation of Cu atoms in the particles. The Cu containing complexes and GP(II) zones can assist the formation of η' precipitates in the course of subsequent agings. It should be noted that in the case of pure ternary AlZnMg alloys similar plate-like nuclei of η' precipitates are observed only after prolonged aging at higher temperatures (above 70°C) [12].

5. Summary and Conclusions

The effect of Cu on the mechanical and precipitation properties of Al-Zn-Mg alloys was investigated by compression and indentation tests, by positron annihilation lifetime spectroscopy (PALS), transmission electron microscopy (TEM) and three-dimensional atom probe field ion microscopy (3DAPFIM). The main experimental results and conclusions can be summarized as follows:

The addition of 0.5at.% Cu to the ternary Al-2.4at.% Zn-2.1at.% Mg alloy increases considerably the age hardening potential of the alloy and makes the transition from the range of Guinier-Preston (GP) zone to intermediate phase formation smoother. On the other hand, following a rapid initial hardening it reduces the rate of hardening in the early stage of natural aging.

The addition of Cu leads to the formation of new type of GP-zones in the quaternary alloy: while the GP zones formed in ternary AlZnMg alloys are spherical, in the Cu containing alloy spherical and ellipsoidal GP zones were observed. The spherical zones are free from Cu, the ellipsoidal ones contain about 0.7-1.1at.% Cu [15].

Formation of solute-vacancy complexes takes place immediately after water quenching and is the reason of the rapid initial hardening. PALS results gave insight into the development of the solute-vacancy complexes indicating that the formation and transformation of these is faster in the Cu containing alloy.

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