Effect of an applied stress on discontinuous precipitation in a Cu-Ag alloy

R Monzen¹, T Terazawa² and C Watanabe¹

¹ Division of Innovative Technology and Science, Kanazawa University, Kakumamachi, Kanazawa 920-1192, Ishikawa, Japan
² Division of Mechanical Science and Engineering, Kanazawa University, Kakumamachi, Kanazawa 920-1192, Ishikawa, Japan

Abstract. The effects of an applied tensile stress on the growth rate and morphology of discontinuous precipitation (DP) product have been studied for a Cu-5wt%Ag alloy aged at 300°C. The DP cell consists of lamellae of the rod-shaped Ag precipitates and solute-depleted Cu matrix. The tensile stress accelerates the growth of DP cells along both the loading direction (LD) and transverse direction (TD) but the cell growth rate along the TD is faster than that along the LD. Transmission electron microscopy has revealed that the tensile stress is apt to produce the Ag precipitates elongated in a <110> direction nearly perpendicular to the LD in a cell, irrespective of the cell growth direction. The observed morphology of the Ag precipitates and the promotion of the cell growth, namely precipitate growth under tension can be understood through the interaction energy between the external stress and the misfit strains of precipitate. The growth of Ag precipitates toward the direction perpendicular to the LD explains the faster cell growth along the TD.

1. Introduction

The effect of an applied tensile stress on the growth rate of discontinuous precipitation (DP) cells has been first examined for six binary alloys of Cu-Ag, Cu-Mg, Cu-Cd, Zn-Cu, Ag-Cu and Pb-Sn by Sulonen [1, 2]. For the six alloys, the growth rates of DP cells at grain boundaries aligned parallel and transverse to the loading direction were different from each other. An explanation for this effect, which was based on an elastic strain energy interaction between the applied stress and the coherency stress field, was proposed. Later, Hillert [3] has provided a quantitative treatment of the experimental results by Sulonen, based on the elastic interaction between the misfit stress field around the solute atoms ahead of the reaction front and applied tensile stress. However, the effect of external stress on the DP morphology has not yet been metallographically studied.

In this study, the effects of an applied tensile stress on the growth rate and morphology of DP cells are investigated for a Cu-5wt%Ag alloy aged at 300°C. The DP cell in Cu-Ag alloys consists of lamellae of the Ag-rich β phase and solute-depleted α phase [4, 5]. We have found that the growth of DP under the tensile stress is accelerated along the loading direction (LD) and transverse direction (TD) compared with the growth of DP under no applied stress, but the growth rate of DP cells along the TD is faster than along the LD. In addition, from transmission electron microscopy (TEM) observations, it has been shown that aging under tension tends to produce the rod-shaped Ag
precipitates elongated in a $<110>_a$ direction nearly perpendicular to the LD in a cell, independent of the growth direction of DP cells. This observation accounts for the anisotropy in the cell growth rate.

2. Experimental

Ingots of a Cu-5wt%Ag alloy were prepared by melting 99.99%Ag and 99.99%Cu. The alloy ingots were homogenized at 800°C for 24 h in a vacuum, cold-rolled to 50% reduction in thickness and then spark-cut into specimen strips. The specimens had a cross-section of 3 mm $\times$ 6 mm and a gage length of 20 mm. All the specimens were solution-treated at 780°C for 1 h, quenched into water and subsequently aged at 300°C for various times either under an applied stress of 20 MPa (stress aging) or under no stress (free aging). The applied stress of 20 MPa is about one third of the yield strength of the solution-treated specimen at 300°C. Thin foils for TEM observations were prepared by slicing the aged specimens with a spark cutter and by electropolishing using a solution of 67% methanol and 33% nitric acid at -30°C and 6.5 V in a twin-jet electropolisher. Microscopy was carried out using a HITACHI H-9000NAR or a JEOL 2000EX microscope at an operation voltage of 300 or 200 kV.

3. Results

![Figure 1](image1.png)  
**Figure 1.** Optical micrograph of a tensile-stress-aged specimen. Aging was carried out at 300°C for 1 h. An arrow indicates the loading direction (LD).

![Figure 2](image2.png)  
**Figure 2.** Variation in the width of DP cells during free aging and tensile-stress aging at 300°C. LD=Loading Direction, TD=Transverse Direction.

DP cells under no stress grew randomly to all directions. In the specimen, tensile-stress-aged, the width of cells in the TD is larger than that in the LD, as exemplified in figure 1. Figure 2 shows the cell width $w$ against aging time $t$ for the specimens, free-aged (FA) and tensile-stress-aged (TSA) at 300°C. A linear relationship exists between $w$ and $t$ for these specimens. The growth of DP in the TSA specimen is promoted along the LD and TD in comparison with that in the FA specimen, but the growth rate of DP cells along the TD is faster than along the LD. The latter is in agreement with the observation by Sulonen [2] for a Cu-5wt%Ag alloy aged at 500°C for 30 min under tension.

Interpretations of the results of Sulonen [1, 2] on the effect of applied stress on DP have been put forward by Sulonen [1, 2] and Hillert [3]. When DP occurs in an elastically isotropic solid under an external stress $\sigma$ and with a coherency strain $\delta$ in the solute diffusion zone abutting a grain boundary, the elastic strain energy $\Delta G$ in the coherent zone at the grain boundary perpendicular to the LD is written as [6]

$$\Delta G = \frac{E}{1-\nu} \delta^2 \left(1 - \frac{2\nu}{1-\nu} \delta \sigma \right).$$  

(1)
Here $E$ is the Young's modulus and $\nu$ is the Poisson's ratio. If the grain boundary is parallel to the LD, the driving force for moving it (elastic strain energy) is expressed as

$$\Delta G = \frac{E}{1-\nu} \delta^2 + \delta \sigma.$$  \hspace{1cm} (2)

Since the sign of $\delta$ is plus in the present work [7], these equations predict that application of tensile stress during aging enhances the growth rate of DP cells in the TD but lowers it in the LD. However, this prediction is in conflict with the result of figure 2.

DP reactions in the FA and TSA specimens were always observed to occur in two directions from one boundary. Individual DP cells gradually grew laterally together and formed a double seam with reaction fronts. TEM observations of various DP cells in the FA specimen revealed that Ag precipitates in a cell had an elongated shape along a $<110>_{\alpha}$ direction of the Ag-depleted Cu matrix. This direction is in agreement with the elongated $<110>_{\alpha}$ direction of rod-shaped Ag precipitates in disk-shaped aggregates parallel to $\{001\}_{\alpha}$ planes in Cu-5.7wt%Ag single crystals [7]. The discontinuous Ag precipitates exhibited a cube-on-cube orientation relationship to the Cu matrix, in accordance with the previous studies on Cu-Ag alloys [8, 9]. In the FA specimen, rod-shaped Ag precipitates behind an advancing grain-boundary grew in a $<110>_{\alpha}$ direction nearly perpendicular to the boundary.

Figure 3. TEM images of rod-shaped Ag precipitates in DP cells after movement of grain boundaries, aligned nearly (a) parallel and (b) perpendicular to the loading direction (LD), in the specimen, tensile-stress-aged at 300 °C for 30 min. RF=Reaction Front.

Figures 3(a) and 3(b) depict TEM images of rod-shaped Ag precipitates in DP cells after migration of grain boundaries aligned nearly parallel and perpendicular to the LD in the specimen, tensile-stress-aged at 300 °C for 30 min. The zone axes in these figures are parallel to the [110]$_{\alpha}$ direction. In figure 3(a), the Ag precipitates are elongated in the [110]$_{\alpha}$ direction of grain A nearly perpendicular to the grain boundary. It should be noted in figure 3(b) that the Ag precipitates initially grow along the [101]$_{\alpha}$ direction of grain A relatively perpendicular to the advancing boundary, but their growth direction is changed into the [110]$_{\alpha}$ direction nearly perpendicular to the LD. This change in growth direction was often observed in the TSA specimen, irrespective of the cell growth direction. It was confirmed that the initial or final growth direction of Ag precipitates in some DP cells was a $<110>_{\alpha}$ direction nearly perpendicular to the grain boundary or the LD. The initial growth direction is unaffected by the applied stress.

4. Discussion

As mentioned in section 3, the result of figure 2 that the cell growth velocities along the LD and TD under tension are faster than that under no stress cannot be explained from equations (1) and (2). The
origin of the promotion of the cell growth velocity (figure 2) and the observed morphology of Ag precipitates (figure 3) under the tensile stress can be understood to arise through the interaction energy due to the presence of positive misfit strain $\varepsilon_{ij}$ (stress-free transformation strain) between a Ag precipitate and an external stress $\sigma_{ij}$. The interaction energy means the work done by the external stress during the growth of discontinuous Ag precipitates. The interaction energy $\Delta E$ per unit volume of the Ag precipitate is expressed as [10, 11]

$$\Delta E = -\sigma_{ij}\varepsilon_{ij} \quad (3)$$

This equation predicts that the growth of Ag precipitates, namely DP cells is promoted by applied tensile stress. This prediction is in agreement with the result of figure 2. Also, it may be expected from equation (3) that the rod-shaped Ag precipitates elongated in a $<110>_{\alpha}$ direction nearly perpendicular to the LD in a cell are produced under tension, since the misfit strains along the elongated $<110>_{\alpha}$ direction of a rod-shaped Ag precipitate and along the direction normal to the elongated direction are, respectively, $\varepsilon_{33}=0.015$ and $\varepsilon_{11}=\varepsilon_{22}=0.12$ [7]. This also is coincident with the observed morphology of Ag precipitates in figure 3. Therefore, it can be concluded that, as a consequence of the change in growth direction of the Ag precipitates toward the direction perpendicular to the LD as shown in figure 3(b), the cell growth rate in the TD is faster than that in the LD.

5. Conclusions

Application of a tensile stress during aging a Cu-5wt%Ag alloy at 300°C promotes the growth of discontinuous precipitation cells in both the loading direction (LD) and transverse direction (TD) but the cell growth along the TD occurs more rapidly than along the LD. The tensile stress has no influence on the initial growth direction of discontinuous rod-shaped Ag precipitates in a cell, which is a $<110>_{\alpha}$ direction nearly perpendicular to the advancing grain-boundary, but is prone to change into a $<110>_{\alpha}$ direction nearly perpendicular to the LD. The change in growth direction of Ag precipitates toward the direction normal to the LD and the acceleration of the cell growth, namely precipitate growth under tension can be understood through the interaction energy due to the presence of positive misfit strains between the applied stress and Ag precipitate. As a result of the change in precipitate growth direction toward the direction perpendicular to the LD, the cell growth along the TD occurs more rapidly.

Acknowledgments

A part of this work was conducted in the Kyoto-Advanced Nanotechnology Network, supported by the “Nanotechnology Network” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was also partially supported by a Grant-in-Aid for Science Research from The Ministry of Education, Culture, Sports and Technology under Grant No.19560742.

References

[1] Sulonen M S 1964 Acta Metall. 12 749
[2] Sulonen M S 1964 Acta Polytec. Scand. (a) 38 3
[3] Hillert M 1972 Metal. Trans. 3 2729
[4] Gust W, Beuers J, Steffen J, Stiltz S and Predel B 1986 Acta Metall. 34 1671
[5] Gupta S P 1998 Can. Metall. Q. 37 141
[6] Chung Y H, Shin M C and Yoon D Y 1992 Acta Metall. Mater. 40 2177
[7] Watanabe C, Monzen R, Nagayoshi H and Onaka S 2006 Phil. Mag. Lett. 86 65
[8] Liu J B and Meng L 2008 J. Mater. Sci. 43 2006
[9] Han K, Vasquez A A, Xin Y and Kalu P N, 2003 Acta Mater. 51 767
[10] Eshelby J D 1957 Proc. R. Soc. (a) 241 376
[11] Eshelby J D 1959 Proc. R. Soc. (a) 252 561