The Liquid-Enhanced Plasticity and Deformation Behavior of Cu–Mg–TiC Nanocrystalline Composite

Baolong Shen\textsuperscript{1}, Tohru Yamasaki\textsuperscript{2}, Yoshikiyo Ogino\textsuperscript{2}, Hisamichi Kimura\textsuperscript{1} and Akihisa Inoue\textsuperscript{1}

\textsuperscript{1}Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
\textsuperscript{2}Department of Materials Science and Engineering, Faculty of Engineering, Himeji Institute of Technology, Himeji 671-2201, Japan

Cu–Mg–TiC bulk nanocrystalline composites were prepared by mechanical alloying, HIP process and hot-rolling. Tensile tests at constant crosshead speeds were carried out using a universal testing machine at several different temperatures under an argon atmosphere. The elongation drastically increased as the fraction of melt increased, and a maximum nominal elongation of about 200% was obtained at temperature where atomic fraction of liquid phase was about 0.5 and the strain rate sensitivity $m$ was in the range of 0.8 to 1.0 for every composite. After the deformation, nanocrystalline structures with average grain sizes of about 30 nm were retained.

(Received February 26, 2001; Accepted April 26, 2001)

Keywords: Cu–Mg–TiC nanocrystalline composite, mechanical alloying, nominal elongation, liquid phase, liquid-enhanced plasticity

1. Introduction

It is known that the dislocation activity appears to continually decrease with decreasing grain size from those levels normally found in conventional metals owing to a combination of the decreased availability of dislocations and the decrease ability to create new dislocations in the increasingly confined nanophase grains.\textsuperscript{1,3} The paucity of mobile dislocations in nanophase grains has been well documented experimentally,\textsuperscript{2,3} and is simply a result of the long known and well understood image forces that act on dislocations near surfaces and hence in confined media.\textsuperscript{3,4} The difficulty in creating new dislocations within the spatial confinements of ultrafine crystallites has also long been evident from earlier researches on single crystal whiskers and wear debris.\textsuperscript{4,5} Since the minimum stresses required to activate common dislocation sources (such as a Frank-Read source) are inversely proportional to the distance between such pinning points, these stresses will increase dramatically with decreasing grain sizes into the nanophase regime owing to the limitation of the maximum distance between such pinning points. Therefore, grain size reduction can yield improvements in some mechanical properties, such as strength and hardness, but also have negative impacts on other mechanical properties, such as strain rate and ductility. The strain rate will significantly decrease when grain size decreases to about 10 nm from larger size.\textsuperscript{6,8}

On the other hand, liquid-enhanced plasticity has been applied to forming operations in rheocasting. It has also been shown in recent years that the presence of a small amount of liquid phase in some ceramics,\textsuperscript{9,10} whisker reinforced\textsuperscript{11} and mechanically alloyed (MA) aluminum alloys\textsuperscript{12} dramatically accelerates their superplasticity. So that the application of liquid-enhanced plasticity to nanocrystalline materials is particularly interesting since grain rearrangement during deformation, which involves sliding and rotation of grains, will be greatly enhanced in nanometer materials as compared with conventional fine-grained materials.

In the present study, the liquid-enhanced plasticity and deformation behavior in Cu–Mg–TiC nanocomposite prepared by mechanical alloying, HIP and hot-rolling were investigated. Magnesium was alloyed to lower the solidus and eutectic temperatures. The high-density TiC particles were dispersed for inhibiting grain growth of matrix metal in Cu–Mg–TiC nanocomposite.\textsuperscript{13}

2. Experimental Procedure

Cu–Mg(5, 10, 14 at%)–TiC(12 vol%) powder composites were prepared by ball-milling copper, magnesium and titanium powders with an addition of stearin under a nitrogen gas atmosphere. The MA composite powders were consolidated by using a hot isostatic pressing (HIP) process at 823 K (10, 14 at%Mg) and 923 K (5 at%Mg) under a pressure of 203 MPa. Then, the bulk composites were cut to many samples in thickness of 7 mm and hot-rolled at 923 K to sheets of 1 mm thickness. The tensile specimens with 5 mm gauge length, 4 mm width were electro-discharge machined from the sheets parallel to rolling direction. These specimens were then mechanically polished to an uniform thickness of 0.7 mm. Tensile tests at constant crosshead speeds were carried out using a universal testing machine at several different temperatures under an argon atmosphere.

The compositions of the samples were investigated by chemical analysis. Structural analyses were performed by X-ray diffractometry with Cu–K$_\alpha$ and electron spectroscopy for chemical analysis (ESCA). Surfaces and transverse sections of the as-rolled samples were observed by optical microscopy (OM). Fracture surfaces of the tensile-tested specimens were observed with a scanning electron microscopy (SEM). Microstructure changes of specimens before and after tensile test were observed on the sample surfaces by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The second phase particles TiC were observed by extraction replica electron microscopy. The solubility temperature of 5 at%Mg composite and the eutectic temperatures of 10 and 14 at%Mg composites were measured by differential thermal analysis (DTA).
Microstructural segregations of the constituent elements were examined by electron-probe microanalyzer (EPMA). The atomic fractions of liquid phase at the temperature above solidus or eutectic temperature were estimated from Cu–Mg phase diagram for each sample.

3. Results and Discussion

Chemical analysis of the rolled specimens is shown in Table 1. X-ray analysis revealed that the structure of the 5 at% Mg composite consisted of Cu–Mg solid solution and cubic TiC phases. In the 10 at% Mg and 14 at% Mg composites, besides Cu–Mg solid solution and cubic TiC phases, a small amount of MgCu2 phase was in equilibrium phase as shown in Fig. 1.¹¹¹⁷ precipitated during HIP. ESCA analysis revealed that about 70% of total Ti atoms were combined with C element from stearin to form TiC in all the composites. The volume fractions of the TiC particles were estimated to be about 12 vol% in all the composites. The solidus and eutectic temperatures of all the composites measured by DTA agreed with the solidus and eutectic temperature in the Cu–Mg phase diagram. The eutectic temperature is about 995 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Mg</th>
<th>Ti</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Mg</td>
<td>75.73</td>
<td>4.87</td>
<td>10.00</td>
<td>7.00</td>
<td>1.15</td>
<td>1.24</td>
<td>0.015</td>
</tr>
<tr>
<td>10 Mg</td>
<td>71.16</td>
<td>9.78</td>
<td>10.43</td>
<td>6.53</td>
<td>1.19</td>
<td>1.26</td>
<td>0.036</td>
</tr>
<tr>
<td>14 Mg</td>
<td>67.73</td>
<td>13.89</td>
<td>10.07</td>
<td>6.62</td>
<td>0.58</td>
<td>1.19</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Figure 2 shows optical micrographs of the as-rolled 10 at% Mg composite sample observed on surface and transverse section. During HIP process, copper atoms segregated into interface regions of the powder particles confirmed by EPMA observation, and formed a bright network as seen in Fig. 2. In this region, copper is enriched and titanium is depleted, composition also measured by EPMA is 90 at% for Cu, 6 at% for Mg and 4 at% for Ti, respectively. But in the dark region, which was collapsed perpendicular to the rolling direction, titanium and magnesium are both enriched; the composition is 74 at% for Cu, 13 at% for Mg and 13 at% for Ti, respectively. As seen in the extraction replica electron micrograph shown in Fig. 3, TiC particles (black point) of about 2.5 nm in diameter are densely dispersed in the Ti-rich region. In the Cu-rich (Ti-poor) region, TiC patches are seen. The grain sizes in the TiC-rich region are approximately 11, 17 and 14 nm in average diameter for the 5, 10 and 14 at% Mg composites, respectively. As a typical example, the microstructure of 10 at% Mg composite is shown in Fig. 4. In the TiC-poor region, coarse grains around 100 nm in diameter were observed by TEM.

These composites have high hardness at room temperature, e.g., Hv 490 for the 10 at% Mg composite. They are, however, brittle at temperatures below solidus or eutectic temperature. Thus, tensile tests were carried out at temperatures
above solidus or eutectic temperature where large elongations are expected. Figure 5 shows the true stress vs true strain curves obtained from the tensile tests. The tensile tests performed at initial strain rates of $1.3 \times 10^{-4}$ and $4.2 \times 10^{-3}$ s$^{-1}$ respectively. As the testing temperature exceeds the solidus or eutectic temperature, the flow stress decreases and the elongation-to-fracture increases significantly for all the composites. The largest nominal elongation of about 200% was obtained in every composite at a temperature where atomic fraction of the liquid phase is nearly about 0.4–0.5 as estimated from the Cu–Mg phase diagram. It is noted that the flow stress increases in the later stage of deformation at temperatures where large elongation is obtained. This may be due to the structural change during deformation as will be mentioned later. The fracture occurred without necking behavior in all the cases, and the shape of each specimen was almost retained even at the highest testing temperature. No cavities or micro cracks were detected after tensile tests. As shown in Fig. 6, the fracture surface has a feature of viscous flow at 1113 K where large elongation is obtained, while it becomes flat with decreasing temperature to 1003 K. The fracture appears to be initiated in the TiC-poor regions as indicated by arrows shown in Fig. 6. Because liquid pockets are formed in the TiC-poor regions as will be mentioned later.

By applying a steady creep equation, $\dot{\varepsilon} = K \sigma^n$, to a small interval of true strain around 0.2, (where $\dot{\varepsilon}$ is the strain rate, $\sigma$ is the flow stress, and $K$ is a structure and temperature-dependent constant), the strain rate sensitivity $m$ ($= 1/n$), was tested by a strain-rate-change test. Linear relations between ln $\sigma$ and ln $\dot{\varepsilon}$ were obtained at all testing temperatures in a measured range of strain rate from $4 \times 10^{-5}$ to $1.3 \times 10^{-4}$ s$^{-1}$ as shown in Fig. 7. The values of $m$ are plotted as a function of the temperature and the liquid fraction in Figs. 8(a) and (b) respectively. The strain rate sensitivity $m$ increases with increasing temperature or atomic fraction of liquid, and takes values of 0.8 to 1.0 at temperatures where the liquid fraction is 0.4–0.5. The largest elongations are obtained when the $m$ values are in the range of 0.8 to 1.0. In Fig. 9, the flow stress derived from the ln $\sigma$ and ln $\dot{\varepsilon}$ relations at a strain rate of $1.2 \times 10^{-4}$ s$^{-1}$ is plotted as a function of the liquid fraction. It can be seen that the flow stress drastically decreases as the liquid fraction increases.

It is found that the segregation of TiC particles into the TiC-rich region occurs further as the deformation proceeds,
and concurrently the fraction of the TiC-poor region increases. Also, the both TiC-rich and TiC-poor regions encroach on each other. The TiC particles agglomerate to about 10 nm in average diameter in the 10at%Mg composite after the tensile test at 1113 K, as shown in Fig. 10.

Figure 11 shows a typical microstructure of the TiC-rich and TiC-poor regions of the 10at%Mg composite, tensile tested at 1113 K. In the TiC-rich region, the grain size is very small, and about 23 nm in average diameter (Fig. 11(a)). In the TiC-poor region, large grains about 200 nm in diameter were locally seen. However, the typical grain size in the TiC-poor region is about 50 nm as shown in Fig. 11(b).

The average grain size over all the regions is approximately estimated to be about 30 nm. From these observations, it is concluded that the nanostructure is retained even after deformation in the presence of liquid. This fact may be ascribed to the inhibiting effect of TiC particles on solid-liquid interfaces as well as in grain boundaries. It was also proved by annealing the sample at 1113 K for 10.8 Ks as shown in Fig. 12, that the grain size is retained to about 30 nm even after 3 hours annealing at 1113 K.

It is difficult to identify the morphology of the liquid phase
when the liquid fraction is small. Because the contrast is very weak when the sample is just etched weakly. Here, to directly observe the liquid phase, a 10 at% Mg composite sample was annealed at higher temperatures, which is 1193 K, for 0.9 Ks. Figure 13 shows such microscopy observed by FE-SEM and nearly no etched. It is shown that grains are encircled by the white areas, which is the Cu-rich liquid phase confirmed by EDX. Therefore, this suggests that the melting took place in the deeply etched regions in Figs. 11(a) and (b), which are the triple junctions and grain boundaries. These deeply etched regions nearly are not seen when without etching, indicating that there are not any cavities or microcracks. We presume that the liquid phase existed homogeneously along grain boundaries, and then the thickness of the liquid phase is estimated to be about 3.7 nm when the liquid fraction is 0.4 and the grain size is 20 nm. In fact, the liquid can exist preferentially at triple junctions. Moreover, as seen in Fig. 11(c), the liquid phase tends to segregate into the Ti-poor regions in the later stage of deformation, resulting in a formation of liquid pockets. It is also found that the fracture surfaces show dimple patterns, which are hollows left from the agglomerates of crystalline grains after tensile test as shown in Fig. 6. Around the grains or agglomerates of grains, the liquid phase segregated as shown in Fig. 13. Therefore, as mentioned before, the fracture seems to initiate at the TiC-poor regions, where liquid pockets of large sizes would have been formed. The segregation of liquid phase may be favorable in terms of the total solid-liquid interfacial energy. It is also noted that a parallel arrangement definition of grains inclined at some $\pi/4$ to the tensile axis are seen in the TiC-poor regions as indicated by arrows in Figs. 11(b) and (c), suggesting that grain boundary sliding occurred preferentially in parallel to this direction. This fact also suggests that the deformation in TiC-

![Flow stress plotted as a function of atomic fractions of liquid phase for the 5, 10 and 14 at% Mg composites.](image1)

![Extraction-replica electron micrograph and diffraction pattern of TiC particles in the 10 at% Mg composite tensile-tested at 1113 K.](image2)

![FE-SEM micrographs of the 10 at% Mg tensile-tested at 1113 K. (a) fine-grained (TiC-rich) region, (b) coarse-grained (TiC-poor) region, and (c) a region where liquid pockets are seen. The tensile axis is vertical. The arrows in figure (b) and (c) indicate the parallel arrangement definition of grains.](image3)
poor regions is more strongly accelerated by the presence of liquid phase than in the TiC-rich regions. The segregation of liquid phase, which should be accompanied by depletion of liquid in TiC-rich regions, and also the segregation of TiC into TiC-rich regions, as shown in Fig. 10, makes it difficult to deform in the TiC-rich regions and thus increase the flow stress, as actually observed in the later stage of deformation. Therefore, it is suggested that if those structural segregations can be suppressed, much larger elongations will be obtained.

4. Summary

Bulk nanocrystalline Cu–Mg (5, 10, 14 at%)–TiC (12 vol%) composites were prepared by mechanical alloying, hot-isostatic-pressing and hot-rolling. The plasticity deformations in the presence of liquid phases of these nanocrystalline composites were investigated by tensile tests. The main results obtained are summarized as follows.

(1) The average grain sizes of Cu–(5 at%) Mg–(12 vol%) TiC, Cu–(10 at%) Mg–(12 vol%) TiC and Cu–(14 at%) Mg–(12 vol%) TiC bulk nanocrystalline composites are 11, 17 and 14 nm, respectively. These nanocrystalline composites are not almost deformed by tensile test below the eutectic temperature. While above the solidus or eutectic temperature, these nanocrystalline composites can be deformed by tension easily in the presence of liquid phase. In tensile tests, the flow stress decreases and elongation-to-fracture increases drastically as the temperature increases above the solidus or eutectic temperature, the largest nominal elongations of about 200% are obtained as the atomic fraction of liquid increases to about 0.5.

(2) The strain rate sensitivity increases with increasing temperature and takes a value of about unity at liquid fractions about 0.5, where the largest elongations are obtained.

(3) Nanocrystalline structures with average grain sizes of about 30 nm are retained even after high temperature deformation.

REFERENCES