INFLUENCE OF THE CONTENT OF Ni AS MINORITY ALLOYING ELEMENT ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AMORPHOUS AND ULTRAFINE CRYSTALLINE Al-Cu-Mg-Ni ALLOYS

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Abstract

The effect of nickel as a minority alloying element (1–3) at.% on the structure and mechanical properties of amorphous and ultrafine crystalline Al₇₅Cu₁₅Mg₉Ni, Al₇₅Cu₁₅Mg₈Ni₂ and Al₇₃Cu₁₅Mg₉Ni₃ alloys was investigated. Rapidly solidified ribbons of the three alloys were produced by chill block melt spinning (CBMS) method. It was proven that the rapid solidification produced amorphous structure in all alloys. Detailed HRTEM observations revealed zones of chemical inhomogeneity in the X-ray amorphous matrix which were identified as zones containing clusters of different atoms. A part of the ribbons were annealed until complete crystallization. The indentation hardness $H_{IT}$ and indentation modulus $E_{IT}$ of the amorphous and ultrafine crystalline Al-Cu-Mg-Ni alloys were investigated and compared using nanoindentation tests. The obtained results showed an increase of $H_{IT}$ and $E_{IT}$ with increasing Ni content in both amorphous and ultrafine crystalline samples. All ultrafine crystalline samples had higher $H_{IT}$ and $E_{IT}$ than the amorphous ones.

Key words: nanoindentation, hardness, modulus, mechanical, amorphous, Al, Cu, Mg, Ni, alloys, crystalline

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**Introduction.** The first amorphous alloy was obtained in 1960 but the interest in metallic glasses has remained high for more than eighty years because of their defect-free structure which ensures good mechanical strength, wear resistance, corrosion resistance, magnetic properties [1–3].

Alloying elements, even in minority contents, play important role in amorphous structure obtaining. The data on their influence on mechanical properties of aluminium-based metallic glass are rather limited and their part in the process of vitrification is not sufficiently studied. It was shown in [4] that alloying with more than 5% nickel improves the glass forming ability (GFA) of Al-Cu-Mg alloy and increases the hardness and strength of the metallic glass.

The effect of different Al content on the mechanical properties of (Cu_{50}Zr_{50})_{100-x}Al_x alloys was investigated using nanoindentation [5]. The method was applied in [6] and [7] to study the indentation hardness and modulus of Ce-based bulk metallic glass. In [8,9] the initiation of shear bands in metallic glass were studied by nanoindentation tests.

In our previous work [10], we used nanoindentation to investigate the effect of Zn and Zr alloying on $H_{IT}$ and $E_{IT}$ of the amorphous alloys Al-Cu-Mg-Zn and Al-Cu-Mg-Zr and their nanocrystalline analogues. We found that the alloying with less than 1 at.% Zr increased and the alloying with 1 at.% Zn reduced $E_{IT}$ in both amorphous and nanocrystalline states of the Al_{74}Cu_{16}Mg_{10} alloy.

The aim of this work is to study the influence of Ni content in the range of (1–3) at.% on microstructure transformation from amorphous to crystalline and on some mechanical characteristics of amorphous and ultrafine crystalline Al-Cu-Mg-Ni alloys.

**Materials and methods.** The studies were carried out on alloys of the Al-Cu-Mg-Ni system with Ni contents up to 3 at.%. All alloys were studied in two states: rapidly solidified amorphous ribbons and crystalline ribbons.

The ribbons 3–4 mm wide and 26–40 µm thick were produced by the CBMS method. The crystalline structure of the ribbons was achieved by annealing at 350 °C [11].

The choice of alloys composition was based on [11,12], where it was proven that composition close to eutectic is optimal for obtaining amorphous Al-Cu-Mg-Ni alloys. The content of Ni was chosen to fill the lack of data on the properties of amorphous alloys of Al-Cu-Mg system alloyed with Ni in this range. Based on the results obtained in [11] the alloys were indexed as Al_{75}Cu_{15}Mg_{9}Ni, Al_{75}Cu_{15}Mg_{9}Ni_{2}, and Al_{73}Cu_{15}Mg_{9}Ni_{3}.

High resolution transmission electron microscopy (HRTEM) observations were carried out on a JEM 2100 (JEOL Ltd., Japan) at 200 kV accelerating voltage in Selected Area Electron Diffraction (SAED) and High Resolution (HRTEM) modes to characterise the microstructure of the rapidly solidified alloys in more detail.

Nanoindentation tests were made in order to study the mechanical properties of the investigated alloys. The measurements were made using a Nano Indenter
G200 (KLA Corporation, USA) equipped with a Berkovich three-sided diamond pyramid with 20 nm tip rounding in accordance with the ISO 14577 standard [13]. Depth control method and extended time (3000 s) for finding surface were user defined because of the samples roughness (Fig. 1(a)). Up to 20 indentations were made on each sample at maximum depth of 2000 nm. The positions of the tests were selected manually. The loading history is shown in Fig. 1(b).

Results and discussions. The XRD patterns of all rapidly solidified Al-Cu-Mg-Ni alloys showed a completely amorphous (am) structure. Three types of crystalline phases were detected in the XRD patterns of the alloys after annealing – Al, Al$_2$CuMg and Ni$_3$Al. The type, quantity and dimensions of the phases are presented in Table 1. Based on the XRD results [11] the annealed Al-Cu-Mg-Ni alloys were determined as ultrafine crystalline (ufcr).

Our previous TEM results confirmed the amorphous nature of the rapidly solidified alloys. Shapeless regions with brightness varying from bright to dark were observed in TEM images, suggesting some chemical inhomogeneity of the material [11]. We conducted additional HRTEM observations and found that the interior of darker zones was divided into areas of axial shape, often triangular, several nanometres in size (Fig. 2). Parallel fringes filled the interior of these cells. The orientation of the parallel lines in adjacent cells differed, but the spac-

<table>
<thead>
<tr>
<th>Types of phases</th>
<th>Al$<em>{75}$Cu$</em>{15}$Mg$_{9}$Ni-ufcr</th>
<th>Al$<em>{75}$Cu$</em>{15}$Mg$<em>8$Ni$</em>{2}$-ufcr</th>
<th>Al$<em>{75}$Cu$</em>{15}$Mg$_9$Ni$_3$-ufcr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>35 [mass. %] 177 [nm]</td>
<td>35 [mass. %] 139 [nm]</td>
<td>37 [mass. %] 136 [nm]</td>
</tr>
<tr>
<td>Al$_2$CuMg</td>
<td>46 [mass. %] 88 [nm]</td>
<td>44 [mass. %] 88 [nm]</td>
<td>45 [mass. %] 77 [nm]</td>
</tr>
<tr>
<td>Ni$_3$Al</td>
<td>19 [mass. %] 69 [nm]</td>
<td>21 [mass. %] 44 [nm]</td>
<td>18 [mass. %] 27 [nm]</td>
</tr>
</tbody>
</table>
Fig. 2. Microstructure of the amorphous Al$_{75}$Cu$_{15}$Mg$_9$Ni$_2$-am (a) and Al$_{73}$Cu$_{15}$Mg$_9$Ni$_3$-am (b) alloys, HRTEM. Amorphous matrix with clusters of Cu, Mg/Ni atoms.

The nanoscale structure, with clusters of Cu, Mg/Ni atoms, is represented between the lines of the image. The TEM image with parallel grid lines indicates the presence of overlapping layers of ordered solid solution (Moiré pattern) [14]. This suggests that the cells are zones containing layers of different atoms—clusters, ready to form crystal phases during subsequent annealing. The absence of clusters in the bright areas of thin foils confirms our initial suggestion for chemical inhomogeneity of the amorphous ribbons.

Based on all obtained results, we can make the general conclusion that the microstructure of the three rapidly solidified alloys has an X-ray amorphous matrix with zones containing clusters of alloying atoms. Their formation during the rapid solidification precedes the formation of crystal phases during the subsequent annealing. Considering the ternary phase diagram of the Al-Cu-Mg system [15], the phase size data (Table 1), and the data on d-spacing of the detected crystal phases, it can be suggested with equal probability that these are the Al and Al$_2$CuMg phases. The formation of clusters of Ni$_3$Al is unlikely due to its high segregation temperature and the low amount of Ni in the alloys.

The indentation hardness $H_{IT}$ and modulus $E_{IT}$ of the investigated Al-Cu-Mg-Ni samples were calculated from the load-displacement curves obtained by nanoindentation tests. The approximation method of Oliver and Pharr was used [16]. Comparison of the obtained $H_{IT}$ and $E_{IT}$ of the amorphous and ultrafine crystalline samples is shown in Fig. 3.

The obtained results show higher $H_{IT}$ and $E_{IT}$ values for all ultrafine crystalline samples than for the amorphous ones.

As expected, the amorphous sample with 3% Ni has higher $H_{IT}$ (2.1 GPa) than the sample with 1% Ni (2.0 GPa) due to the higher content of hard Ni in the metal matrix. This is not the case with the sample with 2% Ni, which has lower $H_{IT}$ (1.8 GPa). We consider that a possible reason for this discrepancy could be the chemical inhomogeneity of the samples, observed by HRTEM (Fig. 2). If the indenter tip falls on a Cu or Mg rich area on the sample surface, the measurement will show higher hardness, and vice versa.
In ultrafine crystalline alloys $H_{IT}$ increases with the increasing Ni content. The lowest is the hardness of $\text{Al}_{75}\text{Cu}_{15}\text{Mg}_{9}\text{Ni}_{3}$-ufcr (3.2 GPa). Our XRD analysis showed a tendency for size decrease of the crystalline phases with increasing nickel content. According to the Hall–Petch equation [17], this can be the main reason for the $H_{IT}$ and $E_{IT}$ increase. The only observed discrepancy was $\text{Al}_{75}\text{Cu}_{15}\text{Mg}_{9}\text{Ni}_{3}$-ufcr, which had lower $H_{IT}$ (3.2 GPa) than $\text{Al}_{73}\text{Cu}_{15}\text{Mg}_{8}\text{Ni}_{2}$-ufcr (4.1 GPa). This could be due to the slightly different Mg content in both alloys and to the lower content of the $\text{Ni}_{3}\text{Al}$ crystalline phase in the $\text{Al}_{75}\text{Cu}_{15}\text{Mg}_{9}\text{Ni}_{3}$-ufcr.

The main reason for the large error bars in the $H_{IT}$ experimental values of all alloys (amorphous and crystalline) is probably the inhomogeneity of the amorphous microstructure and the high surface roughness of the ribbons. This is due to the contact of the molten metal with the surface of the copper disc on which the ribbon is cooled.

The obtained hardness results are in good compliance with the results of Farajollahi et al. [18] for samples with 1.5% Ni. We could not find any data for the $E_{IT}$ of the investigated materials in order to make comparison. We only found results for Young’s modulus, but these were obtained from tensile tests on samples produced by different methods and with higher Ni contents (6, 10, 15% Ni) [19].

The $E_{IT}$ values of the amorphous samples with 1, 2, and 3 at.% Ni are 13.8 GPa, 10.7 GPa, and 15.5 GPa, respectively, and the $E_{IT}$ values of the ultrafine crystalline samples with 1, 2, and 3 at.% Ni are 26.0 GPa, 47.0 GPa and 42.4 GPa, respectively. The reasons for the deviations in the above results are analogous to those for the deviations in the $H_{IT}$ results.

**Conclusions.** Microstructural analysis and nanoindentation tests were performed on $\text{Al}_{75}\text{Cu}_{15}\text{Mg}_{9}\text{Ni}$, $\text{Al}_{75}\text{Cu}_{15}\text{Mg}_{8}\text{Ni}_{2}$, and $\text{Al}_{73}\text{Cu}_{15}\text{Mg}_{9}\text{Ni}_{3}$ amorphous and crystalline ribbons.

The chemical inhomogeneity of the amorphous ribbons, previously detected by TEM, was studied in detail by HRTEM analysis. It showed that the microstruc-
ture of the amorphous alloys consists of an X-ray amorphous matrix with zones of size less than 5 nm which contained clusters of different atoms. The clusters were arranged in parallel layers with spacing of about 0.25 nm which most likely were clusters of elements participating in the future Al$_2$CuMg or Al phases.

Nanoindentation results showed that all ultrafine crystalline alloys have higher indentation hardness $H_{IT}$ and modulus $E_{IT}$ than their amorphous analogues. The transformation of the microstructure from amorphous to crystalline causes an increase of indentation hardness in Al$_{75}$Cu$_{15}$Mg$_9$Ni, Al$_{75}$Cu$_{15}$Mg$_8$Ni$_2$, and Al$_{73}$Cu$_{15}$Mg$_9$Ni$_3$ from 1.5 to 2.3 times and an increase of indentation modulus from 1.9 to 4.4 times.

The large deviations of experimental results obtained for $H_{IT}$ and $E_{IT}$ indicate that nanoindentation is a method mainly suitable for investigating samples with a high homogeneity and a smooth surface.

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