Microstructure Characteristics of Spray-Formed and Melt-Spun Al85Nd5Ni10 and Al89La6Ni5 Bulk Hybrid Composites

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Abstract. The microstructure characteristics of the spray-formed and melt-spun Al85Nd5Ni10 and Al89La6Ni5 alloys were studied. The spray forming process was demonstrated to produce a bulk scale hybrid composite consisting of amorphous and nanostructured phases directly without the need of an amorphous precursor. The spray-formed Al89La6Ni5 deposit (~1 mm in thickness) were partially amorphous, and the amorphous phase came from the undercooled liquid droplets upon deposition. The as-spray-formed Al85Nd5Ni10 deposit (~20 mm in thickness) was completely crystallized due to the devitrification of the retained amorphous phase to nano-scale secondary crystals upon deposition. Primary crystals (~1 µm) are dispersed uniformly in the bulk spray-formed amorphous/partial amorphous composites and many distinctive deformation twins also are observed in the crystals, however, not twins found in the corresponding completely devitrified ribbon. This is mainly because of the stirring and impacting force offered by high velocity droplets during spray forming and the mismatch of thermal expansion coefficient between primary crystals and adjacent amorphous matrix.

Introduction

Since 1988[1-5] many ultra-high strength (>1GPa) nanostructured aluminum composites have been developed by proper annealing [6-7] the amorphous Al-RE(rare earth)-TM(transition metal) alloys. Generally, the synthesis of nanostructured Al-RE-TM composites needs amorphous phases (e.g. ribbons) as precursors. In this study, spray forming process was employed as a new way to fabricate a nanostructured Al-RE-TM composite without precursors.

Many composites have ever been produced by spray forming process [8-12], e.g. Al-10Ni-5Mm
(Misch metal) [13], Al-8Y-5Ni-2Co [14] and Al-3Y-8Ni-4Co-1Zr nanocomposites [15]. These previous studies concluded that the in-situ crystallization was due to heat accumulation during deposition. Thus, a liquid nitrogen (LN) cooled copper substrate was employed in this study to increase the heat dissipation during deposition.

Two alloys (Al₈₉La₆Ni₅ and Al₈₅Nd₅Ni₁₀) were selected in this study for spray forming based on Inoue’s glass forming ability maps [16-17]. Both of them are Al-rich (>85 at.%) alloys with good glass formation ability and can be produced as ductile amorphous ribbons at much more reduced cost than that of most bulk metallic glasses with RE-rich composition. These alloys are suitable candidates for structural application. Some previous studies [18-19] mainly focused on crystallization of ribbons, however, in this study the two alloys was fabricated via the spray-forming and melt spinning processes. Microstructure evolution of spray-formed composite and melt-spun ribbons is also compared.

**Experimental**

Molten metal was atomized with N₂ and deposited on a LN-cooled copper substrate to form a deposit of 230 mm in diameter, 3 mm in thickness, and 1 kg in weight. Some materials cut from the deposit was remelt and melt-spun with 30ms⁻¹ under Ar to form ribbons of 20-30 μm in thickness and 2-3 mm in width. The spray-formed deposit was designated as SD and melt-spun ribbons as MS30. Quantitative wave-length diffraction spectrum (WDS) analyses and back-scattered electron imaging (BEI) were performed to evaluate the chemical composition and phases transition (JEOL™ JXA-8900R). Differential scanning calorimeter (Perkin Elmer Pyris1) determined the reactions during heating. The structure evolution of ribbons and deposit were conducted by transmission electron microscopy (TEM) (JEOL AEM3010) equipped with a nano-volume energy dispersive spectrometry (EDS) system. TEM samples were prepared by ion milling (Gatan 691) with angles of 8-4 and with beam energy 4.5 kV and 25 μA.

**Results and Discussions**

Fig.1 shows the XRD diffraction patterns of the as-melt-spun ribbon (MS30) and the as-spray-formed deposit (SD) for Al₈₉La₆Ni₅ alloys. The MS30 specimen exhibits typical amorphous halo peak, and the SD specimen shows quite similar pattern with small characteristic peaks of fcc-Al, Al₃Ni, Al₁₁La₃ and some unknown phases. Fig.2 shows the DSC traces of the MS30 and SD specimens Al₈₉La₆Ni₅ alloy. Only the MS30 specimen exhibits multi-exothermic reactions, which correspond to three devitrification stages with onset temperatures of 548 K, 593K and 643 K respectively. The SD specimen shows only the third stage (565 K), suggesting that only a partial amount of amorphous phases exists in it.

Table 1 shows the enthalpies released for the SD and the MS30 specimens for Al₈₉La₆Ni₅ during continuous heating in DSC. The total enthalpy released (from R.T. to 823K) from the MS30 specimen is 108 J/g, and the total enthalpy released from the SD specimen is 39 J/g. For the convenience of calculation, the MS30 specimen was assumed to be in the fully amorphous state (as the baseline for 100%), even though it contained a small amount of crystalline phases. Therefore, the percentage of amorphous phase of the SD specimen could be determined to be 39/108 = 36% [20], while the other 64% correspond to crystalline phases. Since the 1st + 2nd exothermic peaks of the SD specimen are completely absent during deposition, this also indicates that the corresponding phases have completely precipitated.
Fig. 1 XRD patterns of the MS30 specimen (Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5} ribbon) heated in DSC to 548 K, 593 K, 643 K and 823 K, and XRD patterns of the SD specimen (Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5} deposit).

Fig. 2 DSC trace of the MS30 specimen (Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5} ribbons) and that of the SD specimen (Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5} deposit).

Table 1 Enthalpies released during continuously heating the Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5} alloys (MS30 and SD) in DSC at 40 K/min.

<table>
<thead>
<tr>
<th></th>
<th>1st peak + 2nd peak</th>
<th>3rd peak</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS30</td>
<td>60±2</td>
<td>47.5±3</td>
<td>108±3</td>
</tr>
<tr>
<td>SD</td>
<td>0</td>
<td>39±2</td>
<td>39±2</td>
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Fig. 3 shows the microstructure of the SD specimen for Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{5}. The angular shaped micro-scale primary phases precipitated in the liquid, about 1-2 \(\mu\text{m}\), were designated as primary crystals, and the nano-scale phases formed during the later solid state reaction as secondary crystals. During the spray forming process, undercooled liquid droplets directly impacted the free surface of LN-cooled substrate and subsequently accumulated into a deposit with a thickness of 1 mm. Previous studies [14-15] reported that, in BEI image, amorphous regions exhibited featureless morphology, which were significantly different from the adjacent crystalline region. In this study, the SD specimen shows many featureless regions (arrowed in Fig. 3), which are believed to be amorphous phases, coexisting with other regions full of primary crystals. Fig. 2 also confirms that there is an exothermic peak in the SD specimen, showing that amorphous devitrification did happen during heating in DSC. Therefore, the microstructure of the SD specimen is a hybrid composite consisting of amorphous phases, primary crystals and secondary crystals. Intermediate Al\textsubscript{11}La\textsubscript{3} phases in the SD specimen contained minor Ni quantities (about 5 \%) to become Al\textsubscript{11}La\textsubscript{3}(Ni), due to the higher solubility of Ni in Al by rapid solidification.

Fig. 4 shows bright field (BF) and dark field (DF) images of the SD specimen (Al\textsubscript{89}La\textsubscript{6}Ni\textsubscript{3}). A large amount of fcc-Al secondary crystals (< 5 nm) are shown to disperse uniformly in the amorphous matrix. The angular (about 1-2 \(\mu\text{m}\)) primary Al\textsubscript{11}La\textsubscript{3}(Ni) phases, containing of many deformation twins, dispersed in the amorphous matrix.

Fig. 5 shows the XRD patterns of the SD and MS30 specimen (Al\textsubscript{89}Nd\textsubscript{5}Ni\textsubscript{10}), together with the patterns of the MS30 heated to various temperatures. The MS30 specimen also exhibits an amorphous halo peak. The SD specimen shows a completely crystallized pattern, consisting of the \(\alpha\)-Al, Al\textsubscript{3}Ni, Al\textsubscript{11}Nd\textsubscript{3}-like and some unknown phases. The completely devitrified MS30 specimen shows a quite similar pattern as that for the SD specimen.
Fig. 3 Microstructure of the as-spray-formed SD specimen (Al89La6Ni5).

Fig. 4 Bright field (BF) and dark field (DF) images of the as-spray-formed SD specimen (Al89La6Ni5).

Fig. 5 XRD patterns of the SD and MS30 specimen (Al85Nd3Ni10), together with the MS30 heated in DSC to 548 K, 609 K, 634 K and 823 K.

Fig. 6 shows DSC traces of the SD and MS30 specimen (Al85Nd3Ni10). The MS30 specimen exhibits multi-exothermic reactions, which correspond to three devitrification stages with the peak temperatures of 548 K, 609K and 643 K, respectively. The SD specimen shows nearly no exothermic reaction, indicating it’s a fully crystallized structure.

Fig. 7 shows the micrographs of the back-scattered electron images (BEI) of the SD specimen(Al85Nd3Ni10). Fig. 6 shows that no exothermic peak observed in the DSC trace of the SD specimen, which implies that no retained amorphous phase exists. The SD specimen is a bulk hybrid composite consisting of primary crystals and secondary crystals. The compositions (at.%) of the primary crystals measured by the WDS technique were 72.5(±2) for Al, 9.7(±3) for Nd and 17.8(±1) for Ni, so the primary crystal was determined to be Al7NdNi2.

During spray forming, the severe temperature gradients and the large stirring and impacting during droplets depositing, together with the mismatch of the thermal expansions between the primary crystals and adjacent amorphous matrix, are sufficiently large to trigger the formation of deformation twins in the primary crystals at low temperature.

A great amount of deformation twins were surely observed in most of the primary crystals in SD specimen, ex. Al7NdNi2 in Al85Nd3Ni10 alloy and Al11La3(Ni) in Al89La6Ni5, as shown in Fig. 4 and Fig. 8. However, no deformation twins were found in the secondary crystals of the completely devitrified MS30 specimen for either Al85Nd3Ni10 or Al89La6Ni5 alloy. This is because that there was no large stirring involved, and the CTE mismatch between the nano-scale secondary crystals and adjacent nanocrystalline matrix is much smaller.

Fig. 6 DSC traces of the SD and MS30 specimen (Al85Nd3Ni10), showing distinct crystallization stages.

Fig. 7 Microstructure of as-spray-formed SD specimen (Al85Nd3Ni10)

Fig. 8 TEM, bright field (BF) images of the primary crystals in the SD specimen (Al85Nd3Ni10).
Conclusions

1. The spray-formed Al$_{89}$La$_6$Ni$_{15}$ is a bulk hybrid composite consisting of 36% amorphous phase, and nanostructured phases, including primary crystals of mostly Al$_{11}$La$_3$(Ni) phases, and a large amount of nano-scale Al secondary crystals dispersed uniformly in the amorphous matrix.

2. The spray-formed Al$_{85}$Nd$_5$Ni$_{10}$ deposit is a bulk hybrid composite consisting of nanostructured phases, including Al$_7$NdNi$_2$ primary crystals and Al$_3$Ni, Al$_7$NdNi$_2$ secondary crystals, dispersed in the nanocrystalline α-Al matrix.

3. Deformation twins were observed in the primary Al$_{11}$La$_3$(Ni) crystals in Al$_{89}$La$_6$Ni$_{15}$ deposit and Al$_7$NdNi$_2$ primary crystals in the Al$_{85}$Nd$_5$Ni$_{10}$ deposit, which were produced during the growth of the primary crystals due to the large impacting and stirring during spray forming, and the thermal expansion coefficient mismatch between the primary crystal and adjacent amorphous phase.

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Reference


