Available online at www.sciencedirect.com

SCIENCE DIRECT®

Acta Materialia 53 (2005) 2607–2616

Acta MATERIALIA

www.actamat-journals.com

Microstructure control and ductility improvement of La–Al–(Cu, Ni) composites by Bridgman solidification

Y. Zhang [a,c,*], W. Xu [b], H. Tan [b], Y. Li [a,b]

[a] *Advanced Materials for Micro- & Nano-Systems, Singapore-MIT Alliance, National University of Singapore, Singapore 117576, Singapore*
[b] *Department of Materials Science, National University of Singapore, Singapore 119260, Singapore*
[c] *State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Xue Yuan Road 30, HaiDian District, Beijing 100083, China*

Received 22 December 2004; received in revised form 22 December 2004; accepted 9 February 2005
Available online 2 April 2005

Abstract

Microstructure evolutions were experimentally studied as a function of growth velocity and alloy composition in $La_xAl_{14}(Cu,Ni)_{86-x}$ alloys ($x = 57$–74). The composition–velocity ranges were determined for the formation of eutectic, amorphous, eutectic + compound, amorphous + dendrite, and eutectic + dendrite. A skewed eutectic coupled zone was found towards the compound phase. A composite structure composed of ductile La dendrites in a matrix of either eutectic or amorphous phase can be produced in hypoeutectic alloys. Compressive tests were performed on amorphous/dendrite and eutectic/dendrite composites. As the volume fraction of dendrites increases, fracture strength linearly decreases and obeys a rule-of-mixtures relationship, whereas plastic strain exhibits an exponential increase. Optimised mechanical properties can be realized through both alloy composition design and well-controlled solidification processing.

Keywords: Bulk metallic glass; Bridgman solidification; Eutectic; Composite; La based alloy

1. Introduction

Over the past few decades, bulk metallic glasses (BMGs) produced at low cooling rates have been extensively explored owing to their fundamental scientific importance and engineering application potential [1–5]. In terms of mechanical properties, BMGs have been reported to have advantages over conventional metallic alloys, in terms of higher strength, larger elastic strain limit, higher hardness and better wear resistance [2,4]. However, at room temperature monolithic BMGs have exhibited inhomogeneous plastic deformation behavior without strain hardening, during which all the plastic flow is confined in the localized regions of a few shear bands and eventually leads to catastrophic failure with little plastic strain [2,4]. To improve the ductility of BMGs, more attempts have been recently made to introduce in situ ductile crystalline phases into the amorphous matrix [6–11]. For instance, the introduction of the ductile Ta-rich solid solution particles dramatically enhanced the compressive plastic strain to be about 17% with yield strength of 1700 MPa in a Be-free $(Zr_{70}Ni_{10}Cu_{20})_{82}Ta_8Al_{10}$ alloy [9]. In a Ti-based $Ti_{50}Cu_{23}Ni_{20}Sn_7$ bulk metallic glass composite, the formation of ductile hexagonal close-packed Ti dendrites resulted in up to 6% compressive plastic strain as well as yield strength of 1190 MPa [10].

Usually, control and improvement of mechanical properties for bulk metallic glass composites can be realized by means of microstructure control, i.e., appropri-

---

[*] Corresponding author. Tel.: +86 106 233 4333; fax: +86 106 233 2508.
E-mail address: drzhangy@skl.ustb.edu.cn (Y. Zhang).

1359-6454/$30.00 © 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2005.02.020

ate design of alloy composition and well-controlled solidification processing. The appropriate design of alloy composition is of great importance in producing bulk metallic glass composites with desired microstructures. In a previous study on the La–Al–Cu–Ni multicomponent alloy system [12], the optimum glass forming ability was found to occur at an off-eutectic composition, which was proposed to be related to a skewed eutectic coupled zone. In addition to alloy design, well-controlled solidification has played a very significant role in achieving a bulk metallic glass composite with optimized mechanical properties. Until now, the most frequently used technique to prepare amorphous/dendrite composites has been copper mould casting. However, for mm-sized samples the resultant microstructures are inhomogeneous along the radius for rods, since different cooling rates are produced from the outer surface to the center. A ring-shaped alloy sample is therefore obtained, which may lead to a deviation of characterization of mechanical properties. In order to gain more insight into the microstructural development of bulk metallic glass composite and to achieve a uniform composite structure, Bridgman directional solidification was employed in the present study on La–Al–Cu–Ni multi-component alloys. The resultant mechanical properties were also characterized.

2. Experimental procedures

The ingots were prepared by arc-melting a mixture of pure La (99.9%), Al (99.9%), Ni (99.98%) and Cu (99.999%) in an argon atmosphere. The composition $La_xAl_{14}(Cu,Ni)_{86-x}$ is nominally expressed in atomic per cent, and the alloys were designated as L57, L59, L61, L62, L64, L66, L68, L72, and L74 for simplicity. Each master ingot was first melted five times, and then crushed, and remelted four times. Bridgman solidification was carried out by induction melting of the alloys in the vacuum sealed quartz tubes with 3 mm internal diameter and a wall thickness of 1 mm. The alloys were then remelted at 923 K and kept for 20 min, and subsequently withdrawn at constant growth velocities (V) in the range of 0.008–4.8 mm/s through a temperature gradient (G) of 15 K/mm into a water bath. The cooling rate (R) can be calculated as $R = GV$.

The rod samples with 3 mm diameter were mounted and polished for characterization under a scanning electron microscope (SEM) and optical microscopy (OM). An image analyzer with Leica Qwin image processing and analysis system was used to measure the volume fraction of the dendritic phase. Phase identification was carried out by a Philips X'Pert-MPD system with Cu Kα radiation of wavelength 0.154056 nm. Differential scanning calorimetry (DSC) was used to analyze the thermal properties of solidified samples at a heating rate of 40 K/min.

An Instron-5500R mechanical testing equipment was used to perform the compression test. The cylindrical samples with length of 6 mm were cut by a diamond cutter and the ends of the specimens were mechanically polished. For each type of sample, three or four specimens were tested. Strain gauges (Gauge type is FLA-05-11) were attached to the surface of the specimens to obtain one-dimensional local strains. Compressions were conducted using constant crosshead velocity of 0.06 mm/min. The resultant strain rate was $1.67 \times 10^{-4}\ s^{-1}$.

3. Results

3.1. Microstructure evolution

$La_xAl_{14}(Cu,Ni)_{86-x}$ alloys were studied by Bridgman solidification at growth velocities (V) ranging from 0.008 to 4.8 mm/s. The solidified samples have exhibited uniform microstructures throughout the transverse sections (Fig. 1). The resultant microstructures are summarized in Table 1 as a function of alloy composition and growth velocity. Fig. 2(a) shows a pseudo binary phase diagram with constant solidus temperature T_m and liquidus temperature T_l reaching a minimum of 674 K at $La_{66}Al_{14}(Cu,Ni)_{20}$. It indicates that a pseudo-ternary eutectic reaction occurs at such a composition [12,13]. The liquidus lines at both sides are very steep with similar slopes of about 18 K/at.%. Fig. 2(b) shows the resultant microstructures as a function of alloy composition and growth velocity, in which five distinct morphologies were identified as

(1) E + La: Eutectic + La dendrites;
(2) E + C: Eutectic + intermetallic compounds;

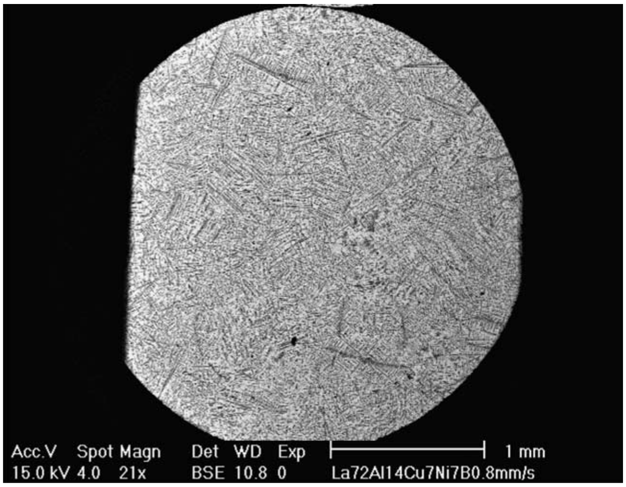

Fig. 1. SEM micrograph of the transverse section for a 3-mm rod sample prepared by Bridgman solidification.