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JOURNAL OF RARE EARTHS, Vol. 33, No. 2, Feb. 2015, P. 202
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

A novel two-step processing method for fabrication of *in situ* Al_2O_{3np}/Al-$Al_{11}Ce_3$ nanocomposite

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Received 17 June 2014; revised 28 August 2014

Abstract: *In situ* Al_2O_{3np}/Al-$Al_{11}Ce_3$ nanocomposite was successfully synthesized from Al-CeO_2 system using a novel two-step processing method that combines liquid-state mechanical mixing (step-I) and sonochemistry melt reaction (step-II). The microstructural evolution and mechanical properties were investigated by optical microscopy (OM), scanning electron microscopy (SEM), transmission electron spectroscopy (TEM) and tensile tests, respectively. A good spatial distribution of CeO_2 particles in the Al melt was achieved due to reactive wetting during step-I, and the following formation of Al_2O_{3np} during step-II was attributed to the cavitation-accelerated interfacial reaction. The solidified microstructure comprised uniformly dispersed Al_2O_{3np} in the matrix and ultrafine lamellar Al-$Al_{11}Ce_3$ at the grain boundaries. Such unique microstructure endowed Al_2O_{3np}/Al-$Al_{11}Ce_3$ nanocomposite with a good balance between tensile strength (175 MPa) and ductility (18.5%). The strengthening mechanisms of the nanocomposite included grain refinement, Orowan strengthening and quench strengthening, among which Orowan strengthening contributed the most to the yield strength of the nanocomposite.

Keywords: nanoparticles; metallic composites; sonochemistry melt reaction; microstructure; tensile properties; rare earths

Nanoparticle (NP)-reinforced aluminum matrix nanocomposites (AMNCs) have received increasing attention due to their superior mechanical and physical properties[1]. Significant efforts have been devoted to this field through two major routes, namely, *ex situ* processing (e.g., powder metallurgy[2], compocasting[3–5]) and *in situ* synthesis (e.g., melt reaction[6], friction stir processing[7]). Compared with AMNCs produced by *ex situ* processing, the *in situ* AMNCs synthesized by chemical reaction between reactants and Al exhibit many advantages: the formed NPs are thermodynamically stable, free of surface contamination and more homogeneous in matrix[8]. However, it is still a challenge to control particle size at the nanoscale with respect to high temperature melt reaction. Recently, research has highlighted that melt reaction can be substantially enhanced by ultrasonic. Estruga et al.[9] used ultrasonic-assisted reduction of K_2TiF_6 and KBF_4 salts in molten aluminum to synthesize surface-clean TiB_2 NPs (~20 nm). Chen et al.[10] prepared Al_2O_3/Al nanocomposites from Al-K_2ZrF_6-$Na_2B_4O_7$ system by sonochemistry melt reaction.

In the present study, a two-step processing method that combines liquid-state mechanical mixing (step-I) and sonochemistry melt reaction (step-II) was developed to fabricate AMNCs from the Al-CeO_2 system. The following hypotheses have been taken into account: (a) during step-I, reactive wetting is expected to occur, because the uniform dispersion of CeO_2 particles in Al melt will favor the next reaction; (b) during step-II, the instantaneous nucleation of Al_2O_3 NPs (Al_2O_{3np}) could be realized when ultrasonic cavitation dominates the solid-liquid interfacial reaction. Based on the above hypotheses, *in situ* Al_2O_{3np} can be effectively incorporated and dispersed into the Al matrix by controlling the reaction process. The microstructural evolution and mechanical properties of the nanocomposite were investigated.

1 Experimental

Commercial pure Al ingot (99.7%) and analytical reagent CeO_2 powder (99.95%, average size 2 μm) were used as feedstock. The CeO_2 powder was firstly preheated at 150 ºC for 2 h to minimize its moisture level. For step-I, the Al ingot was heated up to 810 ºC inside a graphite crucible in a resistance heating furnace. Once the melt reached constant temperature, the dry CeO_2 powder was added. Then mechanical mixing was performed at 400 r/min for 10 min to produce 5 wt.%CeO_2/Al composite slurry. Subsequently, a high-energy ultrasonic horn with a diameter of 20 mm and a frequency of 20 kHz was inserted about 15 mm into the composite slurry for

Foundation item: Project supported by the National Natural Science Foundation of China (51174098) and Open Project of Key Laboratory for Ecological-Environment Materials of Jiangsu Province (EML201208)

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DOI: 10.1016/S1002-0721(14)60403-8

3 min, which was denoted hereafter as step-II. Finally, the melt was poured and cooled in a water-cooled copper mould with a cooling rate of ~5×10^2 K/s. The phase components and microstructures of the samples were inspected by X-ray diffraction (XRD, D/MAX 2500), optical microscopy (OM, Leica DM2500), scanning electron microscopy (SEM, JSM-7100F) equipped with EDS, and transmission electron microscopy (TEM, JEM-2100). The tensile properties were conducted in a universal tensile machine with a crosshead speed of 0.5 mm/min at room temperature.

2 Results and discussion

Fig. 1 shows the XRD patterns of specimens processed by different steps. Only peaks of CeO_2 and Al phases are detected in step-I specimen. However, $Al_{11}Ce_3$ phase replacing CeO_2 after step-II indicates that chemical reactions between Al and CeO_2 have taken place completely. The following reactions in Al-CeO_2 system are proposed[11]:

$$2Al+3/2CeO_2\rightarrow Al_2O_3+3/2[Ce] \quad (1)$$

$$11Al+3[Ce]\rightarrow Al_{11}Ce_3 \quad (2)$$

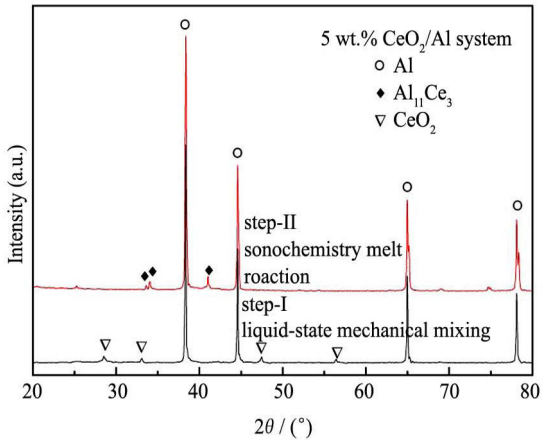

Fig. 1 XRD patterns of specimens processed by step-I and step-II

The theoretical fraction of the Al_2O_3 reinforcement is 1.4 vol.% according to reaction (1). Therefore, the absence of Al_2O_3 peaks may be attributed to the inability of XRD to detect phases less than 2 vol.%[12].

Fig. 2(a) shows the microstructure of the step-I specimen, with extraordinary uniform distribution of CeO_2 particles in the Al matrix. The fraction of CeO_2 measured by image analysis (Image-Pro Plus 6.0) is 1.6 vol.%, a little lower than that of the starting powders (1.8 vol.%). The uniform dispersion of CeO_2 particles suggests that they have a good compatibility with Al matrix. It can be speculated that reactive wetting between Al and CeO_2 probably occurs. Direct evidence can be found in the magnified image of the reacted CeO_2 particle, which is entirely different from the starting particles. The flaky shape of the starting feedstock has changed to round and the corresponding average size decreased from 2.0 to 1.7 μm (Fig. 2(b)). In addition, a thin layer containing Al, Fe and Ce elements was detected by EDS (Fig. 2(c)). The formation of the Fe-rich layer covering CeO_2 is attributed to the low diffusivity and high chemical activity of Ce that easily reacts with impurity elements in Al melt[13]. Moreover, some tiny holes are seen in Fig. 2(b) since the CeO_2 particles were readily fall or pulled out by grinding and polishing. These results confirm that the trace Ce atoms released from the initial reaction may function as an excellent surfactant.

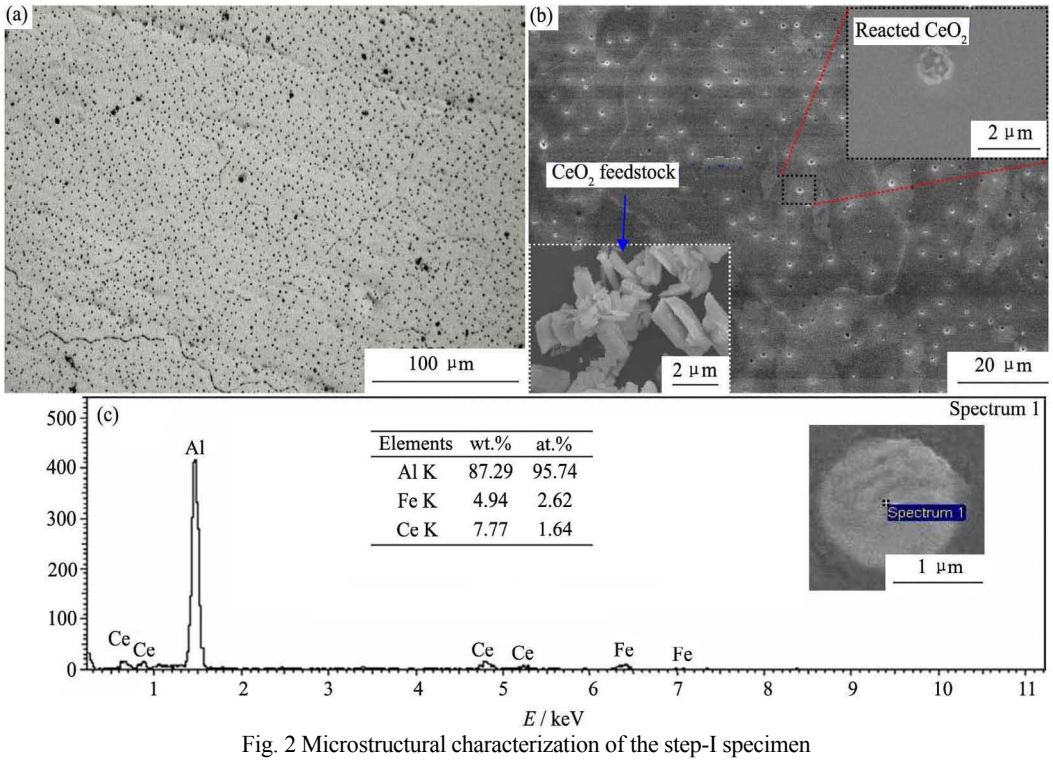

Fig. 2 Microstructural characterization of the step-I specimen
(a) OM; (b) SEM (inset images show the morphological changes of CeO_2); (c) EDS analysis of the reacted CeO_2 surface