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Mechanical properties of cerium and a cerium–5 wt% lanthanum alloy by nanoindentation and ultrasonic velocity measurements

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ABSTRACT

This paper describes a study of the mechanical properties of cerium (Ce) and a cerium–5 wt% lanthanum (Ce–5 wt% La) alloy using nanoindentation and ultrasonic velocity measurements. The materials were also characterised using optical microscopy, energy dispersive spectroscopy, Raman spectroscopy and X-ray diffraction. Despite their propensity to oxidise rapidly in air, both unalloyed Ce and the Ce–5 wt% La alloy have been studied safely in an open laboratory. The hardness and elastic modulus values of the Ce–5 wt% La alloy were slightly higher than those of unalloyed Ce. However, the hardness values of both materials were significantly higher than other values reported in the literature; this was attributed to the presence of cerium oxide inclusions in the microstructure. Reasonable agreement was found between the elastic moduli obtained by nanoindentation and ultrasonic velocity measurements. The mean elastic modulus measured by nanoindentation was, on average, 14% higher than that obtained from the ultrasonic velocity measurements. This work has demonstrated that, with care, Ce can be handled in an open laboratory and meaningful mechanical property data obtained that appear to be free of the influence of the surface oxide layer.

1. Introduction

Cerium (Ce), one of the lanthanide (or "rare earth") elements, is a highly complex metal, most notably on account of the multiple allotropic forms it can assume. At atmospheric pressure it exhibits no fewer than four allotropic crystal structures between absolute zero and its melting temperature (1071 K). They are α-Ce, the so-called "collapsed face centred cubic (fcc)" phase, which is stable below 110 K; β-Ce, which is double hexagonal close-packed (dcph), and is stable between 45 and 275 K; γ-Ce (fcc), stable between approximately 270 and 999 K; and finally the body centred cubic (bcc) δ-Ce, which is stable between 999 K and the melting temperature at 1071 K [1]. When subjected to pressure γ-Ce will transform to α-Ce: at 295 K this occurs at 8 kbar and the transformation is accompanied by a volume change of 18% [2].

Although the uses of Ce in bulk form are limited, it has found widespread application as a constituent in stainless steels, cast irons and magnesium alloys. In stainless steels it is used as a precipitation hardening agent. Another use of Ce is as a carbide refiner in high chromium cast irons (HCCI) in which additions of Ce of up to 1.5 wt% were shown to refine the carbides in a HCCI containing 4.0 wt% C and 20.0 wt% Cr and caused the primary M_7C_3 carbides to become spheroidised [3]. The Ce was found to form as oxysulphide (Ce_2O_2S) inclusions which acted as heterogeneous nuclei for the M_7C_3 carbides. Ce has also been found to improve the cold working behaviour of Mg alloys [4,5].

Over the last few years there has been an upsurge of interest in cerium, lanthanum (La) and other rare earth elements [6] for use in electronic components and green technologies. Ce and La, which are adjacent to each other in the periodic table, are the main components of a 'mischmetal' mixture of rare earth elements that makes up the negative electrode in nickel metal hydride batteries. The increased demand for electric cars, and the elements' subsidiary roles as phosphorescents in energy-saving light bulbs, has resulted in Ce and La being placed on the US Department of Energy's (DoE) short-term 'near-critical' list for green technologies [7]. Ce and La form a continuous series of solid solutions [8] and the liquidus and solidus and the heating and cooling lines of the fcc↔bcc transformation are drawn as single straight lines connecting the two transformation points of unalloyed Ce and La. In the Ce–La phase diagram the lines denoting the transitions from β-Ce to γ-Ce are not solid lines, reflecting the uncertainty described above. The phase diagram also shows a large hysteresis in the transition temperatures between heating and cooling. Although the mechanical properties of Ce have been investigated in the past [9,10] no mechanical property data of Ce–La alloys have been found in the published literature.

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One of the difficulties in handling Ce, and lanthanide metals in general, is their rapid oxidation, especially in the presence of water. Interstitial impurities increase the oxidation rate while some solid solution additives, such as scandium, decrease the oxidation rate [11]. The rapid oxidation can present challenges in the laboratory. Zukas et al. [2] recommended that, for best results, the final polish during metallographic preparation should be completed in less than 2 min, no more than 2 min should elapse between polishing and etching and photography should be completed in 6–8 min. Even when stored in a vacuum desiccator Sheldon et al. [12] found that the surface tarnished within a day. Therefore, Ce must be stored in an air-free environment and contact with water and water-based fluids avoided.

In addition to the rapid oxidation the lanthanides are extremely pyrophoric, requiring suitable precautions during machining operations to avoid ignition of the swarf. Thin foils of Ce will readily ignite on sudden exposure to the air above 30 °C [9]. Such difficulties in machining, which can render the manufacture of mechanical test specimens problematic, may be circumvented by using nanoindentation and ultrasonic velocity (also known as "speed of sound") measurements, which are the focus of the present paper. These techniques offer the potential for the mechanical properties to be measured on simpler geometry specimens, thereby obviating the need for machining mechanical test pieces.

2. Experimental

The Ce–La alloy was produced by arc-melting at the University of Birmingham using starting materials supplied by Goodfellow Metals (Huntingdon, UK). The nominal composition was Ce–5 wt% La and energy dispersive spectroscopy (EDS) indicated a high degree of homogeneity with the La evenly distributed throughout the microstructure (for brevity, this alloy will hereafter be referred to as "Ce–5La"). Quantitative EDS across individual grains found the La content to vary from 4.0 to 6.2 wt% with mean contents between 4.8 and 5.4 wt%.

The density of the Ce–5La alloy was measured using the displacement method in ethanol in a Mettler balance, the accuracy of which was ± 0.02 mg; a density of 6.69 g cm^{-3} was recorded. For the purposes of comparison, samples of unalloyed Ce (in the form of a 12 mm diameter rod) were acquired, also from Goodfellow, and subjected to the same range of tests as the Ce–5La alloy. The density of the unalloyed Ce was measured in the same way as the Ce–5La alloy and a value of 6.78 g cm^{-3} was recorded.

Specimens were cut from the ingots and cold mounted in epoxy resin. Metallographic preparation was performed by grinding using progressively finer SiC abrasive paper with Buehler AutoMet lapping oil, the final stage being 2500 grit SiC. Owing to the softness of Ce metal, polishing by fine diamond was considered undesirable in order to avoid embedding of the diamond abrasive in the metal. Instead, the specimens were subjected to a chemical polish using a solution of 60 vol% nitric acid/40 vol% isopropanol before being washed in ethanol. After the chemical polishing stage the specimens were then examined using optical microscopy.

X-ray diffraction (XRD) was performed using a Bruker D8 diffractometer: a CuKα X-ray source was used and the voltage and current were 40 kV and 40 mA respectively. The sample was scanned through the range $2\theta = 20$–90° at a rate of 0.025° s^{-1}, making the scan lasting approximately 50 min. The specimens used were free-standing and were prepared immediately prior to XRD using the same procedure that was used for the metallography specimens (described above), including the chemical polishing. The lattice parameters of both the Ce and the Ce–5La alloy were also measured using XRD. For these measurements the samples were scanned through the range $2\theta = 20$–150° at a rate of 0.017° s^{-1}, making each scan lasting approximately 70 min.

Micro-hardness tests were performed using a Zwick Indentec ZHV2 (Zwick GmbH, Ulm, Germany), which was equipped with a Vickers (four-sided diamond pyramid) indenter. The loads used were 25, 50, 100, 200, 500 and 1000 gf., and the dwell time at maximum load was 15 s. The hardness values were determined by measuring the indent diagonals. The nanoindentation measurements were carried out using a NanoTest Platform 2 nanoindenter (Micro Materials Ltd., Wrexham, UK), which is described in detail elsewhere [13]. The specimens were glued onto an aluminium stub, which was then mounted on the specimen stage. The test machine was housed in a temperature-controlled cabinet, which also contained a damped table in order to isolate the indenter from extraneous vibrations. A Berkovich (three-sided diamond pyramid) indenter was used in all the nanoindentation tests and the distance between indents was 100 μm. A maximum load of 500 mN was used and the loading and unloading rates were 10 mN s^{-1}. In order to minimise the influence of creep the dwell time at maximum load was 120 s, which enabled the material to reach a mechanical equilibrium before the unloading of the indenter began. This is particularly important for soft metals and polymers [14]. During the unloading phase of the tests the indenter was held at 10% of maximum load for 30 s in order to assess the extent of thermal drift. The loads and depths were continuously recorded throughout the tests to generate loading and unloading curves, from which the hardness and elastic modulus could be determined. Data analysis was done using the method devised by Oliver and Pharr [15] with the analytical software provided by Micro Materials Ltd. Following the nanoindentation measurements the residual indents were imaged using an *Infinite Focus* optical profilometer (Alicona Imaging GmbH, Austria).

Ultrasonic velocity measurements were carried out using an Olympus 5073PR pulser/receiver and the time-of-flight recorded on a National Instruments NI PXI-1042 PC. A Sonatest 5 MHz transducer was used as both the pulser and the receiver, and honey was used as the coupling medium between the probe and the specimen. The experiments were controlled and made using *Labview* software, which also enabled the time-of-flight measurements to be made. The thickness of the specimens was measured using Vernier callipers.

3. Results

3.1. Microstructure

Fig. 1 shows a typical microstructure of the Ce–5La alloy, while the grain size measurements are summarised in Table 1. The chemical polish appeared to etch the surface revealing the grain structure, which rendered a separate etching stage unnecessary. Using the three-circle method (ASTM E112), G numbers of between 6.79 and 7.25 were obtained, which correspond to nominal grain diameters of between 30 and 35 μm. The sizes of individual grains were also measured from the optical micrographs and a mean grain size of 28 μm was determined for the Ce–5La alloy, which agrees well with the measurements carried out using the three-circle method. By measuring individual grains their aspect ratios (AR) can be determined. The aspect ratio is a useful measure by which the grain shape can be quantified and is defined as the ratio of the longest dimension divided by the shortest dimension of the grain (an equi-axed grain has an aspect ratio of 1.0). The mean AR of 1.46 therefore indicates that many of the grains in the Ce–5La alloy deviate from an equi-axed shape.