Structure and mechanical properties of Ce-La alloys containing 3-10 wt. % La

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Abstract

This paper describes a study of the microstructure and mechanical properties of a range of cerium-lanthanum (Ce-La) alloys with La contents of between 3 wt. % and 10 wt. %. Ce-La alloys are regarded as non-radioactive surrogates for delta-phase plutonium (δ -Pu) alloys. The Ce-La alloys were characterised using optical microscopy, energy dispersive spectroscopy and X-ray diffraction while the mechanical properties were determined using micro-hardness, ultrasonic velocity and nanoindentation measurements. The presence of La appears to impart a degree of solid solution hardening to the alloys, as indicated by the modest increase in micro-hardness with increasing La content; a small increase in elastic modulus with La content was also seen. The hardness and elastic modulus values of the Ce-La alloys in this study are similar to those of homogenized Pu-Ga alloys in the Ga-lean part of the δ -Pu phase field. Despite the propensity of the Ce-La alloys to undergo oxidation in air, the oxide thicknesses of the alloys, which were determined by energy dispersive spectroscopy, were found to be insufficient to exert a significant influence on the nanoindentation measurements.

Keywords: cerium; mechanical properties; nanoindentation; plutonium.

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1. Introduction

Owing to the similarities between cerium (Ce) and delta-phase plutonium (δ -Pu) alloys, the former is considered as a non-radioactive surrogate for the latter [1-6]. These similarities include: (i) similar crystal structure (both being face-centred cubic at ambient temperature and pressure); (ii) relatively low melting temperature; and (iii) a tendency to transform to a different phase if cooled to sub-ambient temperatures or subjected to pressure [7,8]. Moreover, alloys of Ce and other elements – for example lanthanum (La) and neodymium (Nd) – exhibit solid-state micro-segregation in the transformation between the body centred cubic (bcc) δ -Ce and face centred cubic (fcc) γ -Ce, which is similar to that seen in plutonium-gallium (Pu-Ga) alloys during cooling through the ϵ -Pu (bcc) + δ -Pu (fcc) two-phase region [2,9,10]. According to the Ce-La phase diagram [11], Ce and La form a continuous series of solid solutions. However, while the phase transition temperatures of unalloyed Ce and La are known, there is more uncertainty concerning the exact temperatures at which the double close packed hexagonal (dcph) β -Ce / α -La transforms to the fcc γ -Ce / β -La in Ce-La alloys [11]. Moreover, for unalloyed Ce, there is a large hysteresis in the β -Ce / γ -Ce transition temperature between heating and cooling [12-15]. On cooling, the $\gamma \rightarrow \beta$ transformation in unalloyed Ce occurs at -16 °C, while the reverse transformation on heating takes place at 139 °C [11]. The magnitude of the hysteresis can be affected by both impurity levels and grain size, with higher impurity levels and larger grain sizes both contributing to a smaller hysteresis [15]. Similar behaviour is seen in unalloyed La: when heated, the dcph α -La transforms to the fcc β -La at 310 °C, although the $\beta \rightarrow \alpha$ transformation occurs at 260 °C upon cooling [11]. Rashid and Altstetter [13] showed that, for unalloyed Ce, the $\gamma \rightarrow \beta$ transformation has many characteristics of a martensitic transformation and the amount of β -Ce present at ambient temperature can be increased by repeated thermal cycling between the α -Ce and γ -Ce phases.

In recent years, Ce-La alloys have been the subject of several studies, both theoretical and experimental, examining various aspects of the Ce-La system [2,5,6,16-18]. Gibbs *et al.* [2] performed electron probe microanalysis (EPMA) to map the La distribution in Ce-La alloys that had received homogenizing heat treatments at 546 °C, 585 °C and 633 °C. The rate of homogenization was used to obtain an activation energy of 126 kJ.mol⁻¹ for diffusion of La in Ce. The oxidation behaviour of

a Ce-La alloy has also been studied by one of the present authors [18] and it was found that the addition of La to Ce resulted in an increase in the rate of oxidation compared to unalloyed Ce [19]. This was attributed to the more porous nature of the oxide structure on the alloy, such as a larger lattice parameter and elevated defect levels, which served to enhance the diffusion of oxygen through the oxide to react with the underlying metal. The surface oxide layer can also influence the hydriding corrosion of Ce and Ce alloys. Li *et al.* [6] and Wang *et al.* [20] examined the effect of La content on the hydriding reaction kinetics of Ce-La alloys with La contents of up to 10 wt. %. They found that the hydriding rate increased with La content, as indicated by decreased induction time, increased H₂ consumption rate and increased hydride nucleation rate.

In contrast to the corrosion behaviour, the mechanical properties of Ce-La alloys have been less well studied. A previous study by the present authors [16] described the use of nanoindentation and ultrasonic velocity measurements to obtain the mechanical properties of unalloyed Ce and a Ce-5 wt. % La alloy. It was found that both the hardness and elastic modulus values were significantly affected by the presence of cerium oxide (CeO₂) inclusions in the Ce-5 wt. % La microstructure. These inclusions were thought to have been formed during the arc melting process by the reaction between molten Ce and residual oxygen in the furnace. Moreover, apparent discrepancies were seen between nanoindentation hardness and micro-hardness values obtained at the same loads. This required further work to investigate in more detail. Therefore, a further study was undertaken, one objective of which was to investigate the structure and mechanical properties of a range of Ce-La alloys from a different supplier, and which is of greater purity than the Ce-La alloy previously studied [16]. The alloys used in the present study also had a greater range of compositions, which enabled the effect of La content on the mechanical properties to be examined. Another objective of the study was to compare the hardness and elastic modulus values of Ce-La alloys with those of Pu-Ga alloys. Finally, given the propensity for Ce and Ce-La to oxidise in air [18,19], the absence of CeO₂ inclusions also enabled the effect of a surface oxide layer on hardness measurements to be investigated.

2. Experimental Details

The Ce-La alloys were supplied by Ames National Laboratory (Iowa, U.S.A.) and their nominal compositions were Ce-3 wt. % La, Ce-5 wt. % La and Ce-10 wt. % La; for brevity they will hereafter be referred to as “Ce-3La”, “Ce-5La” and “Ce-10La”. The alloys were arc-melted and then cast into rods approximately 12 mm in diameter. Specimens were cut from the rods for density determination, metallographic preparation, X-ray diffraction, hardness measurements, nanoindentation and ultrasonic velocity measurements.

For metallographic preparation, specimens were cold-mounted in epoxy resin and subjected to grinding using progressively finer SiC abrasive paper with Buehler AutoMet lapping oil, the final stage being 2500 grit SiC. In order to minimise embedding of abrasive in the metal, polishing by fine diamond was not carried out. Instead, a chemical polish procedure was carried out using a solution of 50% nitric acid-50% ethylene glycol before being washed in ethanol. Following the chemical polishing stage, the specimens were then examined using optical microscopy. Further examination was also carried out using a JEOL JSM-7000F field emission scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) capability in order to study the La distribution in the alloy. EDS measurements were carried out at a minimum of ten different regions of each specimen and, on average, ten different locations at each region.

For X-ray diffraction (XRD) a Bruker D8 powder diffractometer, which was equipped with a CuK α X-ray source, was used; the voltage and current were 40 kV and 40 mA respectively. The specimens were scanned through the range $2\theta = 20^\circ - 90^\circ$ at a rate of 1 s per step; each scan lasted approximately 50 minutes. 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. For lattice parameter measurements the specimens were scanned through the range $2\theta = 20^\circ - 150^\circ$ at a rate of 0.5 s per step, making the scan lasting approximately 1 hour 15 minutes.

Density measurements were carried out using the displacement method in ethanol on a Mettler Toledo XS205 precision balance, the accuracy of which was ± 0.01 mg. 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 2 MHz transducer was used as both as the pulser and the receiver, and the coupling medium between the probe and specimen was Vaseline. The experiments were controlled and measurements recorded using *Labview* software, which also enabled the time-of-flight measurements to be made. The thickness of the specimens was measured using Vernier callipers.

The longitudinal wave velocities, together with the measured density values, were used to obtain the elastic modulus (E) values using the following equation:

$$E = \frac{V_L^2 \times \rho \times (1 + \nu)(1 - 2\nu)}{1 - \nu} \quad (1)$$

Where V_L is the longitudinal wave velocity, ν is the Poisson's ratio and ρ is the material density. In the present study, the specimen sizes of the Ce-La alloys were insufficient to enable shear wave velocities to be measured, which prevented their Poisson's ratios from being determined. In the absence of experimental values, Poisson's ratios were estimated using the rule of mixtures. Using the values of 0.248 for unalloyed Ce [21] and 0.288 for unalloyed La [22] the Poisson's ratios of the three alloys were 0.249 (Ce-3La), 0.250 (Ce-5La) and 0.252 (Ce-10La). When these values were used to calculate the elastic moduli there were no significant differences between these values and those calculated using the Poisson's ratio for unalloyed Ce.

Micro-hardness tests were performed on polished metallographic specimens using a Zwick Indentec (Zwick GmbH, Ulm, Germany), which was equipped with a Vickers (four-sided diamond pyramid) indenter. A range of loads was used, from 25 g. to 1 kg., and the dwell time at maximum load was 15 s. The Vickers hardness (HV) was calculated from the areas of the residual indents. Approximately 50 indents were made on each alloy.

The nanoindentation measurements were carried out using a Micro Materials NanoTest Platform 3 (Micro Materials Ltd., Wrexham, U.K.), which is described in detail elsewhere [23]. The specimens were glued onto an aluminium (Al) stub, which was then mounted on the specimen stage. A Berkovich (three-sided diamond pyramid) indenter was used in all the nanoindentation tests. Prior to the measurements the machine had been calibrated using a fused silica standard (also attached to an Al stub) in order to obtain the frame compliance as well as the area function of the indenter. In the nanoindentation measurements a maximum load of 500 mN was used and the loading and unloading rates were 10 mN s⁻¹. The distance between indents was 100 µm. 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 prior to unloading of the indenter. This is particularly important for soft metals and polymers [24]. 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. At least 5-10 indents were performed on each specimen. The loads and depths were continuously recorded throughout the tests to generate loading and unloading curves, from which the hardness and contact modulus (E_r) could be determined. Data analysis was done using the method devised by Oliver and Pharr [25] with the analytical software provided by Micro Materials Ltd. The residual indents were imaged using an Alicona *Infinite Focus* optical profilometer (Alicona Imaging GmbH, Austria). The elastic modulus (E) values were obtained from the E_r values using the following equation:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

Where E_i is the elastic modulus and ν_i the Poisson's ratio of the indenter; in the present study the following values were used: $E_i = 1140$ GPa and $\nu_i = 0.07$. In common with the determination of the elastic moduli from the longitudinal wave velocities, the Poisson's ratios estimated above were used for calculating the elastic moduli from the E_r values.

3. Results

3.1 Microstructure

Figure 1 shows an optical micrograph of a typical microstructure of the Ce-3La alloy; this micrograph is representative of all three alloy compositions. In each of the alloys the appearance was that of a single-phase microstructure with no obvious second phase features (e.g. CeO₂ inclusions). The morphology of the grains appears to vary through the cross-section of the specimens with equi-axed grains in the interior and more columnar grains observed at the edges. In the central region of the specimens, of which Figure 1 is an example, the grain sizes were measured using the ASTM E112 (“three-circle”) method: mean G numbers of 4.05 (Ce-3La), 3.20 (Ce-5La) and 2.94 (Ce-10La) were obtained, which correspond to nominal grain diameters (d_n) of 90 μm , 120 μm and 125 μm respectively. However, the three-circle method cannot quantify grain shape. For this reason, the dimensions of individual grains were measured to determine their aspect ratios (AR). The AR of a grain is defined as the ratio of its longest dimension divided by its shortest dimension; an equi-axed grain has an aspect ratio of 1.0. The results of these grain size measurements and aspect ratios are summarised in Table 1. The mean grain sizes are up to 20 μm larger than those measured using the three-circle method. However, in some regions, individual grains larger than 200 μm were observed, an example of which can be seen in Figure 2. These measurements were made over the entire specimen diameters and were not confined to the central region. The columnar morphology of many of the grains, particularly in the regions close to the edges of the specimens, can be seen from the aspect ratios, the mean values of which are between 1.5 and 1.9. Despite these variations in grain size, micro-hardness measurements (see below) did not record any significant variations in hardness across the microstructure of the three alloys. This was attributed to the indent sizes being significantly smaller than the grain sizes. The effect of grain size on the indentation behaviour is discussed in more detail in Section 4.2.

EDS of the alloys indicated Ce and La to be the only alloying elements present. A typical EDS spectrum is shown in Figure 3. It shows the most significant peaks to be those of Ce L α and Ce L β at 4.840 keV and 5.262 keV respectively. The La L α peak at 4.651 keV appears as a shoulder on the Ce L α peak; the La L β peak (5.043 keV)

was not visible. The presence of the O K α peak at 0.523 keV is attributed to the oxidation that occurred during the chemical polishing stage of specimen preparation (approximately 5 minutes duration) prior to transfer to the SEM. The mean La contents were 3.36 ± 0.43 wt. % La (Ce-3La), 4.49 ± 0.29 wt. % La (Ce-5La) and 10.09 ± 0.35 wt. % La (Ce-10La). These values were based on approximately 100 individual measurements per alloy. EDS line scans across individual grains (typical examples of which are also shown in Figure 3) indicated good homogeneity with typical variations of ± 0.5 wt. % La.

An XRD pattern from a chemically polished Ce-10La alloy is shown in Figure 4a. The XRD patterns obtained from the other Ce-La alloys were very similar to Figure 4a and are therefore not shown. All major reflections were those of metallic Ce with no significant reflections indicative of Ce oxide (CeO₂ or Ce₂O₃). In all three alloys the metallic Ce is in the fcc gamma phase (γ -Ce). The lattice parameter (a) values were determined from XRD patterns (not shown) that were acquired over the 2θ range of $20^\circ - 150^\circ$. The lattice parameters are plotted as function of La content in Figure 4b, together with the lattice parameter of unalloyed Ce (5.161 Å), determined in a previous study [16]. The graph shows an increase in lattice parameter with increasing La content from 5.166 Å (Ce-3La) to 5.180 Å (Ce-10La), a consequence of the larger atomic radius of La. The lattice parameter for the Ce-10 wt. % La alloy agrees well with the figure recorded by Gschneidner and Calderwood [11]. The lattice parameter increases by 0.0019 Å / at.% (although the La content in Figure 4b is given in wt.%, owing to the similarity in atomic masses between Ce and La, in Ce-La alloys 1 wt.% La $\approx$ 1 at.% La). In contrast, in delta-phase Pu-Ga alloys the lattice parameter decreases with increasing Ga content. Moreover, the magnitude of the change is also considerably greater at 0.0092 Å / at.% [26]. These differences are ascribed to disparities in atomic radii, Ga being 14.2% smaller than Pu [27] while La is 2.8% larger than Ce [28].

3.2 Ultrasonic velocity measurements

The density measurements and longitudinal wave velocities of the three alloys are listed in Table 2, which shows that the density decreases with increasing La content. The mean longitudinal velocity also increased with La content from 2217 ± 9 m s⁻¹ (Ce-3La) to 2293 ± 19 m s⁻¹ (Ce-5La) and 2354 ± 42 m s⁻¹ (Ce-10La). Using these

figures, together with the measured density values, and assuming a Poisson's ratio of 0.248 [21], gave a mean elastic modulus for Ce-3La of 28 ± 0.2 GPa. The corresponding values for Ce-5La and Ce-10La were 30 ± 0.4 GPa and 31 ± 1.0 GPa respectively. These figures show reasonable agreement with elastic moduli values for unalloyed Ce in the literature: Gschneidner and Beaudry [21] quoted a figure of 30 GPa, while the corresponding figure given by Brandes and Brook [29] is 33.5 GPa. However, as shown by the present authors in the previous study [16] the precise figure is dependent on factors such as impurity levels, notably oxide content, and the method of measurement.

3.3 Micro-hardness

Micro-hardness values of the Ce-La alloys as a function of La content are shown in graphical form in Figure 5. A modest increase in micro-hardness with increasing La content can be seen: at a maximum load of 50 g., the mean hardness increased from 24.7 HV_{0.05} (Ce-3La) to 27.9 HV_{0.05} (Ce-10La). Although Table 1 appears to show an increase in mean grain size with La content – which, based on the Hall-Petch relationship, would be expected to be mirrored in a decrease in hardness – owing to the scatter in measured grain sizes this is not significant. Therefore, the effect of grain size variations on the hardness values in the present study is considered to be negligible. The micro-hardness values listed above compare with a Vickers hardness of 22 HV for unalloyed Ce [21], although this figure was not accompanied by any details of the material (e.g. grain size, impurities, processing etc.) or on the test conditions employed (e.g. load, dwell time at maximum load etc). Nevertheless, when compared with the results in the present study, the La appears to impart a degree of solid solution hardening to the Ce lattice. The scatter in the micro-hardness values is attributed to variations in La content through the microstructure such as that seen across individual grains (discussed in a previous section): such variations will be mirrored in the extent of the solid solution hardening.

The differences in grain morphology between the edges and the centres of the specimens (discussed above) might be expected to be reflected in differences in mechanical properties. For this reason, the effect of microstructure on the micro-hardness was investigated by mapping the hardness across the diameter of the specimens. The spacing between the indents was approximately 0.5 mm. Figure 6

shows the micro-hardness across the centre of the Ce-10La alloy: there are no significant variations in hardness between the centre and edges of the specimens. Similar findings (not shown) were also observed with both the Ce-3La and Ce-5La alloys.

The micro-hardness values for the Ce-5La alloy are approximately half the values recorded ($48.1 \pm 1.8 \text{ HV}_{0.05}$) during previous work on another Ce-5La alloy [16]. However, the Ce-5La alloy used in that study [16] contained significant levels of CeO_2 inclusions, which were identified as such by both EDS and Raman spectroscopy [17]. The mean size of those inclusions was $2.9 \pm 1.5 \text{ }\mu\text{m}$, while the mean oxide volume fraction, which was determined by image analysis, was 3.5 %. The hardness of bulk CeO_2 is approximately 6.40 GPa: the presence of the CeO_2 inclusions therefore contributed to the elevated hardness values, which could be explained using a rule-of-mixtures approach [16]. However, in the alloys investigated in the present study no such inclusions have been observed, and this is reflected in the lower hardness values.

The variation of micro-hardness as a function of load was also investigated by performing measurements using a range of loads between 25 g. and 1 kg. The results are shown in Figure 7. They show a significant increase in hardness at the lowest loads. The extent of this increase is most apparent in the Ce-10La alloy. Also included in Figure 7 are hardness data for various Pu-Ga alloys for comparison: the differences between Ce-La and Pu-Ga alloys are discussed in Section 4.1.

3.4 Nanoindentation

A typical load-depth curve from the indentation of Ce-5La is shown in Figure 8. The plateau in the curve at maximum load is indicative of creep, which is often observed in room temperature indentation tests, particularly in soft materials. Creep of the indenter during the dwell time at maximum load represents a potential source of errors in the determination of both hardness and elastic modulus. In the present study, the dwell time at maximum load was 120 s. The purpose of the dwell time is to allow the material to deform sufficiently for creep deformation to be insignificant during unloading [30]. If this is not done, then the initial unloading gradient is often found to be non-linear, with resultant inaccuracies in the elastic modulus values

derived from this gradient [31]. To avoid such an outcome, Chudoba and Richter [32] recommended that the dwell time should be sufficient that the creep rate has decreased to a value where the depth increase in 1 minute is less than 1 % of the indentation depth.

Figure 9 shows a typical graph of change in indentation depth with time at maximum load from one of the indentations made in a Ce-5La specimen. In the final portion of the dwell time (60 – 120 s) the depth increase is 64 nm, which is 0.75 % of the indentation depth after 60 s at maximum load, and therefore satisfies the criterion proposed by Chudoba and Richter [32]. Moreover, examination of the initial portion of the unloading curves (such as that shown in Figure 8) revealed no discernible non-linearity. Therefore, on this basis, the effect of creep on the elastic modulus values can be regarded as negligible.

Initial analysis of the nanoindentation data revealed that the hardness values (determined using the Oliver and Pharr method [25]) were between 25% and 38% higher than the corresponding micro-hardness values. A similar discrepancy was seen for the nanoindentation elastic modulus values when they were compared with the moduli determined from the ultrasonic velocity measurements. Such discrepancies have been reported in other studies, such as that of Qian *et al.* [33] who found that nanoindentation hardness can be 10-30 % higher than the micro-hardness values. This was attributed to differences in the contact area between the two techniques. The nanoindentation hardness uses the projected contact area at peak load (A_c) instead of the residual projected area (A_r) used in the micro-hardness test [33]. One of the sources of error associated with the Oliver and Pharr [25] analysis method is that it cannot account for pile-up around the indenter which effectively means that, for very ductile materials, the true contact depth is measured from a position above the original surface of the material [34]. Such under-estimates in contact area are particularly acute for soft materials. Indeed, use of the Oliver and Pharr method can underestimate the contact area by as much as 60 % for materials in which the ratio of residual depth to depth at maximum load (h_f / h_{max}) > 0.7 [35]. In a study of single-crystal nickel, Bull [34] reported that the values of both hardness and elastic modulus obtained using the Oliver and Pharr method were significantly higher than the values determined by other methods. For the alloys in the present

study, h_f / h_{max} is between 0.92 and 0.94: therefore, errors introduced by the Oliver and Pharr method of analysis are likely to have contributed to the discrepancies in the present study.

Figure 10 shows a two-dimensional surface profile of a residual Berkovich indent in the Ce-5La alloy; a line profile through the indent is also included in the figure. It shows the extent of the pile-up around the indent to be approximately 1 μm . Although pile-up can be generated by both Vickers and Berkovich indenters, it is not taken into account in the determination of micro-hardness as the dimensions are measured from the corners of the residual indents. Surface displacement such as pile-up tends to occur along the indent sides, declining to negligible levels at the corners of the indent owing to geometrical constraint imposed at the sharp edge of the indenter [36]. Therefore, the presence of pile-up could exert an influence on nanoindentation measurements but not on micro-hardness.

Another method of obtaining the hardness is the Oliver two-slope method, which is based on determining the slopes of the loading and unloading curves. This enables both the hardness and the contact modulus to be calculated [37].

The hardness is calculated using the following equation:

$$H = \frac{1}{C_o P} \left(\frac{S_u S_l}{2S_u - \epsilon S_l} \right)^2 \quad (3)$$

Where S_l and S_u are the slopes of the loading and unloading curves respectively and ϵ is a constant that depends on the indenter geometry (0.75 for a Berkovich indenter). P is the load and C_o is a coefficient obtained during the determination of the indenter area function (in the present study the value of C_o was 21.151). S_l and S_u were acquired from the final 10 % and initial 10 % of the loading and unloading curves respectively. The results (listed in Table 3) show better agreement with the values obtained from the micro-hardness measurements when expressed in units of GPa. The mean hardness values were 0.28 GPa (Ce-3La), 0.30 GPa (Ce-5La) and 0.28 GPa (Ce-10La).

The contact modulus (E_r) was also determined using the two-slope method, the expression for which is given below:

$$E_r = \frac{1}{2\gamma\beta P} \sqrt{\frac{\pi}{C_o}} \left(\frac{S_u^2 S_l}{2S_u - \varepsilon S_l} \right) \quad (4)$$

Where β is an indenter geometry shape factor (1.034 in this study) and γ is a constant that accounts for deviations from the ideal Sneddon flat punch behaviour [37]; in this study a value of 1.06 [34] was used. The E_r values are also listed in Table 3. They show that the mean E_r values were 38 GPa (Ce-3La), 39 GPa (Ce-5La) and 39 GPa (Ce-10La). These values are similar to those reported in the previous study. Although they are still higher than the values determined from the ultrasonic velocity measurements, higher moduli have been reported in other studies [38]. This is partly a consequence of the more localised nature of the nanoindentation test, which renders it more sensitive to microstructural variations (e.g. grain size or variations in alloy content).

4.0 Discussion

4.1 Comparison of Ce-La with Pu-Ga properties

Figure 7 showed that at a load of 1 kg, the mean hardness of the Ce-La alloys ranged from 20.7 HV_{1.0} (Ce-3La) to 24.5 HV_{1.0} (Ce-10La). These figures enable a comparison to be made with Pu-Ga alloys reported in other studies [39-41].

The alloying of Pu with elements such as Ga enable the fcc δ -Pu phase – only stable at between 310 °C and 452 °C in unalloyed Pu – to be retained to ambient temperature. The minimum Ga content required is approximately 0.3 wt.% Ga, provided that the Ga is evenly distributed, and at ambient temperature the δ -Pu phase field extends to approximately 2.4 wt.% [42]. Within the region of δ -Pu stability, Miller and White [26] have shown that Ga serves to confer solution hardening of the δ -Pu phase with an approximately straight-line increase in hardness

with Ga content. However, it should be noted that hardness is also affected by other factors such as grain size, impurity content, processing history (e.g. heat treatment time and temperature) and Ga homogeneity [39].

The hardness values of the Ce-La alloys are close to those of homogenized Pu-Ga alloys in the Ga-lean part of the δ -Pu phase field: the mean hardness of a Pu-0.32 wt.% Ga alloy was 23.3 ± 1.7 HV_{1.0} [40], while for Pu-0.64 wt.% Ga the corresponding value was 34.9 ± 1.1 HV_{1.0} [39]. Also plotted in Figure 7 are the data of Hays [41] who measured the micro-hardness of Pu-0.78 wt.% Ga at loads of between 15 g and 500 g; like the Ce-La alloys, they show an increasing hardness as the load decreases. Regarding the elastic moduli of Ce-La and Pu-Ga alloys, Chung *et al.* [43] have reported the elastic modulus of Pu-0.6 wt. % Ga, which was determined from tensile tests, to be approximately 40 GPa. Therefore, for both hardness and elastic modulus, the Ce-La alloys exhibit reasonable agreement with Pu-Ga.

In Figure 5 it could be seen that La appeared to exert a modest degree of solid solution hardening. Given the similarities between Ce-La and Pu-Ga in other respects [2,5,6,20], it is instructive to compare the role of La with that of Ga in the solid solution hardening of Ce and Pu alloys respectively. In the case of Pu-Ga alloys, Miller and White [26] showed that within the region of delta-phase stability, the hardness of Pu-Ga alloys increased approximately linearly with Ga content by approximately 4.75 HV / at.% Ga. In contrast, the corresponding figure for Ce-La is 0.47 HV / at.% La. This difference between the two alloys is attributed to the differences in atomic radii of solute and solvent, as well as the changes in lattice parameter resulting from solute additions, both of which are known to affect the degree of solid solution hardening [44] by introducing local stress fields in the lattice and impeding the motion of dislocations. The extent of solid solution hardening in Ce-La appears to be close to that of another δ -Pu alloy (Pu-Ce), in which the additions of Ce to Pu resulted in a much lower degree of solid solution hardening (0.53 HV / at.%) than for Pu-Ga [26]. Miller and White [45] attributed this difference to less distortion of the δ -Pu lattice caused by the presence of Ce than that caused by the presence of Ga. The difference in atomic radii between δ -Pu and α -Ce is approximately 4 %, which is close to that of Ce and La (2.8 %).

4.2 *Effect of oxidation on nanoindentation measurements*

Owing to its reactive nature, Ce oxidises readily, especially in the presence of water. Indeed, Ce is one of the most reactive of the lanthanide elements: only europium (Eu) has been observed to corrode more rapidly in air at 25 °C [46]. Previous work by the authors included nanoindentation measurements on a specimen of bulk cerium oxide (CeO₂). The mean hardness, measured using a maximum load of 500 mN, was found to be 6.40 ± 0.43 GPa [16], which is more than twenty-five times the hardness values of the Ce-La alloys.

Other work by one of the authors [19] on the oxidation of Ce in air at ambient temperature has shown that the oxidation of Ce proceeds in a linear manner. This was demonstrated by XRD and corroborated by direct measurements of the oxide thickness from transverse sections of oxidised specimens. The rate of oxide growth was determined to be approximately $0.1 \mu\text{m day}^{-1}$. In another study [18] the oxidation of a Ce-5La alloy was found to behave in a similar manner, although the rate of oxide growth was slightly higher at approximately $0.2 \mu\text{m day}^{-1}$. The presence of such an oxide layer may result in higher hardness and elastic modulus values at low loads, such as can be seen in Figure 7.

In order to ascertain the extent of any oxidation and the potential effects on the nanoindentation behaviour, Ce-La specimens were analysed by EDS using the XPP method devised by Pouchou and Pichoir [47-49]. This method has been used to measure the thickness of thin films, for example hydrogen-containing amorphous carbon (a-C:H) films on silicon substrates [50]. In another study Poulter and Lang [51] used EDS to determine the thickness of air-grown uranium dioxide (UO₂) on depleted uranium metal. They found the oxide thickness to vary between 34 nm and 92 nm. The film thickness is determined from the intensity of a characteristic X-ray line from one element in the film after comparison with the intensity of the same X-ray line from a bulk standard [49]. In the present case the X-ray line in question was O K α (0.523 keV). A tantalum pentoxide (Ta₂O₅) film grown by anodic oxidation on a Ta foil substrate (and certified by the Institute for Reference Materials and Measurements (IRMM)) was used as a standard: the Ta₂O₅ thickness was 30 nm. A specimen of each of the Ce-La alloys was prepared using the same procedure as

that employed for the specimens used in metallography, micro-hardness and nanoindentation. The accelerating voltage was 10 kV and the probe current was 6 nA, while the density of the oxide layer was assumed to be 7.21 g cm^{-3} . The oxide thickness was calculated from the EDS data using the Thin Film ID software (Oxford Instruments, High Wycombe, U.K.). The calculated thickness of the Ta_2O_5 layer was to an accuracy of 5 nm.

The depth of analysis under the conditions used in the EDS oxide thickness measurements was calculated using WinCasino 2 (Universite de Sherbrooke, Sherbrooke, Quebec, Canada), which is a Monte Carlo simulation of electron trajectories in solids. Figure 11 shows a graph of Intensity as a function of mass thickness ($\Phi(\rho z)$) vs. depth, which shows the calculated depth of emission of the O $\text{K}\alpha$ X-rays in a CeO_2 layer on a Ce-10La alloy; for comparison, the corresponding graph for both bulk CeO_2 is also shown. It can be seen that the full depth of emission is approximately 350 nm while the oxide-metal interface is located close to the region of maximum X-ray intensity which enhances the accuracy of the calculated oxide thickness values. The O $\text{K}\alpha$ signal is therefore taken from the underlying metal as well as the full thickness of the oxide layer.

The oxide thickness values determined from the EDS measurements showed that La content appeared to influence the oxide growth with the thickest layers being present on the Ce-10La alloy. The mean oxide thickness values were $41 \pm 5.3 \text{ nm}$ (Ce-3La), $75 \pm 17.6 \text{ nm}$ (Ce-5La) and $86 \pm 9.6 \text{ nm}$ (Ce-10La).

In the indentation of an oxidised metal, which is an example of a coated system, the hardness is a composite response of both the coating and the substrate. The composite hardness (H_c) is dependent on the relative indentation depth (z), which is defined as the ratio of the indentation depth (δ) to the coating thickness (t). In cases where $z < 0.1$, H_c is generally considered to be independent of the substrate, although it has been demonstrated that this “rule of thumb”, which has no theoretical basis, is too simplistic in many cases [52]. As z increases there is a transition in behaviour as the substrate exerts a greater influence; for a hard coating on a softer substrate, indentation depths approximately equal to the coating thickness H_c has been observed to reduce asymptotically to a near-substrate value of hardness [53].

Although the exact depth at which a coating ceases to influence the substrate properties depends on the coating thickness, as well as the properties of coating and substrate, a number of studies have shown that this is when z is between 1 and 10 [53-55]. In the present study, the smallest depths of indentation were approximately 3 μm : at such a depth, z is between 35 (Ce-10La) and 74 (Ce-3La). Therefore, under these conditions, the influence of the oxide layer on the hardness and elastic modulus can be regarded as negligible.

Instead of the influence of the surface oxide, a more likely explanation for the increase in hardness at the lowest loads is that of the indentation size effect (ISE), which is the observation, commonly seen in many materials, that the hardness undergoes a significant increase with decreasing load or depth [56-59]. The ISE has been suggested to arise from the increased contribution of geometrically necessary dislocations at small indentation depths over that of the statistically stored dislocations [57]. Its magnitude can be dependent on the microstructure: large grain polycrystals will exhibit an ISE if the impressions at different loads are localised inside one grain [57]. Such behaviour in the present study is believed to be, in part, a consequence of the large grain sizes of the alloys. The average diagonals of the indents made at a load of 25 g. were approximately 38-42 μm . The indent diagonals at 100 g. load were 84-88 μm : as can be seen from Figure 1, these values compare with mean grain sizes of more than 100 μm . It is only at loads of 200 g. or more that the indent diagonal exceeds that of the average grain size.

The oxide thickness values on the Ce-La alloys are comparable to those measured in studies of Pu-Ga alloys. Like Ce, the oxophilic nature of Pu causes it to be covered by an oxide layer under ambient conditions, although the rate of oxidation can be significantly reduced when Pu is alloyed with Ga and Al [60]. In the case of Pu, the oxide layer has usually been described as being in the form of a trivalent sesquioxide (Pu_2O_3) which is overlaid with a tetravalent PuO_2 oxide layer [61,62]. Owing to the radioactive and toxic nature of Pu, hardness tests, like many other processes involving Pu, are usually carried out in gloveboxes containing inert atmospheres [63]. However, even in this environment ($\text{O}_2 \sim 1\%$, $\text{H}_2\text{O} < 5 \text{ ppm}$), an oxide layer is still found to form on the surface, although recent studies have concluded that its character is closer to that of an amorphous PuO_2 -like film [64].

Larson and Cash [65] used ellipsometry to determine oxide thickness and thereby study the kinetics of Pu-1.0 wt.% Ga oxidation in 5.0×10^{-2} Torr at temperatures of between 28 and 90 °C. They found that after 1 hour at 28 °C the oxide thickness was 20 nm, which had grown to approximately 29 nm after 7 hours. In another study, Pugmire *et al.* [66] also used ellipsometry to measure the oxide thickness of a Pu-Ga alloy in dry air. They found that an oxide film of 23 nm in thickness had formed after 12 minutes, which had grown to 27 nm after 1 hour. Continued exposure to this atmosphere resulted in further growth to a thickness of 85 nm after 60 days. It should be noted that Pu oxidation is highly dependent on environmental conditions and can be accelerated by the presence of trace amounts of contaminant gases such as water vapour [64]. Nevertheless, assuming an oxide thickness of 30 nm in a typical glovebox environment, it is possible to assess whether the oxide might influence the hardness values.

A study by Wheeler *et al.* [40] of a Pu-0.32 wt.% Ga alloy recorded a mean hardness of 23.3 HV_{1.0}, the indent diagonal of which was approximately 280 µm. The corresponding indent diagonal is approximately 280 µm, making the maximum depth – one seventh of the diagonal for a Vickers indenter [67] – of such an indent approximately 40 µm. Therefore, the relative indentation depth (z) in this case is 1333. At smaller indentation depths, the data of Hays [41], who used loads of between 15 and 500 gf., can be used to estimate the indentation depths. The indentation diagonals can be obtained from the Vickers hardness (HV) data using the following equation:

$$HV = 1.8544 (P / d^2) \quad (5)$$

Where P is the load and d is the indent diagonal. For a Pu-0.78 wt.% Ga at a load of 15 gf., the measured hardness was 43 HV_{0.015}, the corresponding diagonal of which is 25 µm and an indentation depth of 3.6 µm. At a load of 500 gf., the hardness was 36 HV_{0.5}, the diagonal was 160 µm, which gives an indentation depth of 23 µm. Over this range of loads, the relative indentation depth varies between 120 (15 gf.) and 767 (500 gf.). Therefore, under these conditions, an oxide thickness of 30 nm would not be sufficient to exert a significant influence on the hardness.

5.0 Conclusions

The structural similarities between Ce-La alloys containing between 3 and 10 wt.% La with δ -phase Pu-Ga alloys have been found to be replicated in their hardness and elastic modulus values. Micro-hardness and nanoindentation measurements have shown that the hardness values of the Ce-La alloys in this study are similar to homogenized Pu-Ga alloys in the Ga-lean part of the δ -Pu phase field.

The use of the Oliver and Pharr analysis method for determining the hardness and elastic modulus of a range of Ce-La alloys resulted in significant discrepancies between the values and those recorded in micro-hardness measurements. This was attributed to errors associated with the Oliver and Pharr method, which does not account for the presence of pile-up around the indenter.

The Oliver two-slope method appears to offer a more suitable means of determining the hardness and elastic modulus of the alloys used in this study. The nanoindentation hardness values exhibited good agreement with the micro-hardness values obtained under the same load.

The oxide thicknesses of the as-prepared alloys have been determined using EDS and the mean values have been found to vary between 41 nm (Ce-3La) and 86 nm (Ce-10La). A comparison of these values with the nanoindentation depths (greater than 3 μm in all measurements) indicates that the influence of the oxide layer on the hardness and elastic modulus can be regarded as negligible.

CRedit authorship contribution statement

D.W. Wheeler: Conceptualization, Methodology, Data curation, Writing – original draft. **J. Zekonyte:** Investigation, Writing – review and editing. **R.J.K. Wood:** Writing – review and editing.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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	Ce-3La	Ce-5La	Ce-10La
Mean grain size (μm)	111 ± 34	143 ± 53	126 ± 51
Range of grain sizes (μm)	47 – 193	64 – 227	47 – 217
Mean aspect ratio	1.51 ± 0.49	1.87 ± 0.75	1.55 ± 0.41

Table 1: Summary of the grain size measurements of the Ce-La alloys.

	Ce-3La	Ce-5La	Ce-10La
Density (g cm^{-3})	6.72	6.70	6.68
Longitudinal velocity (m s^{-1})	2217 ± 9	2293 ± 19	2354 ± 42
Elastic modulus (GPa)	28 ± 0.2	30 ± 0.4	31 ± 1.0

Table 2: Results of the density measurements, the measured longitudinal wave velocities and the corresponding elastic moduli.

	Ce-3La	Ce-5La	Ce-10La
Vickers micro-hardness (GPa)	0.24 ± 0.01	0.25 ± 0.01	0.27 ± 0.02
Nanoindentation hardness (Oliver two-slope method) (GPa)	0.28 ± 0.03	0.30 ± 0.04	0.28 ± 0.04
E_r (Oliver two-slope method) (GPa)	38 ± 2.1	39 ± 2.4	39 ± 2.4
E (Calculated from Oliver two-slope E_r values using Equation 2) (GPa)	37 ± 1.9	38 ± 2.2	37 ± 2.2

Table 3: Results of Vickers micro-hardness, together with nanoindentation hardness results determined by the Oliver two-slope method. The load used in the micro-hardness measurements was 50 g. (491 mN) while for the nanoindentation measurements it was 500 mN.

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Figure 1

Fig. 1: Optical micrograph showing the microstructure of the central region of the Ce-3La alloy.

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Figure 9

Fig. 9: Graph showing the change in indentation depth with time at maximum load for Ce-5La.

Figure 10

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Declaration of competing interest

The authors declare that they have no known conflicts of interest that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

D.W. Wheeler: Conceptualization, Methodology, Data curation, Writing – original draft. **J. Zekonyte:** Investigation, Writing – review and editing. **R.J.K. Wood:** Writing – review and editing.