Kinetics and mechanism of the oxidation of cerium in air at ambient temperature

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ABSTRACT

This paper describes a study of the oxidation of cerium in air at ambient temperature. Specimens were exposed for up to 60 days, during which they were analysed by X-ray diffraction (XRD) at regular intervals. Both XRD and oxide thickness measurements indicate linear oxidation over the duration of this study. Under the conditions employed in this study, the rate of oxide growth has been determined to be 0.1 μm day^{-1}. The oxidation process appears to be assisted by extensive cracking in the oxide layer which acts as a non-protective film for the underlying metal.

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1. Introduction

Cerium (Ce), which is a member of the lanthanide (or "rare earth") group of metals, is a highly complex element: an example of this is the number of crystal structures it can assume, depending on temperature and pressure. At atmospheric pressure, it exhibits four allotropic crystal structures between absolute zero and its melting temperature [1]. At ambient temperature Ce is in the face centred cubic (fcc) gamma phase (γ-Ce), which is stable between approximately −3 °C and 726 °C. When heated it will transform to the body centred cubic (bcc) δ-Ce at 726 °C before melting at 798 °C. When cooled to sub-ambient temperatures it will transform to the double hexagonal close-packed (dcph) β-Ce, which is stable between −228 °C and 2 °C. At even lower temperatures it will transform to α-Ce, the so-called "collapsed fcc" phase, which is stable below −163 °C. Although γ-Ce is the stable allotropic form at ambient temperature, it will transform to α-Ce if it is subjected to pressure. Zukas et al. [2] reported that the pressure required to transform was 8 kbar at 22 °C: this transformation is accompanied by a decrease in volume of 18%.

Another characteristic of Ce is its rapid oxidation. 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 [3]. The rapid oxidation renders it necessary to store Ce in an air-free environment. However, even when stored in a vacuum desiccator, the surfaces of Ce specimens have been seen to tarnish within one

day [4]. One example of the challenges presented by the propensity of Ce to oxidise can be found in metallographic preparation: according to Zukas et al. [2] for best results the final polish during metallographic preparation should be completed in less than two minutes, not more than two minutes should elapse between polishing and etching, and photography should be completed in six to eight minutes.

The oxidation of Ce has been studied since the first half of the last century. One early study by Cubicciotti [5] reported that Ce exhibited parabolic behaviour over the temperature range 30–125 °C. At temperatures above 125 °C he observed that after an initial parabolic stage, the reaction subsequently became linear. In the same year as Loriers [6,7] reported a study of the oxidation of Ce. He used electron diffraction to show that the oxide layer formed on Ce was Ce_2O_3, which is subsequently overlaid with CeO_2. This oxide duplex hypothesis has been confirmed by subsequent studies [8,9] using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). Helms and Spicer [8] subjected Ce to oxygen exposures of up to 500 L (1 Langmuir = 10^{-6} Torr s). Their findings suggested that the oxide initially formed was Ce_2O_3: the experimentally measured energy distribution charts (EDC) showed the oxygen-derived structure was seen to grow monotonically with oxygen exposure with little change in shape consistent with the initial nucleation of Ce_2O_3. The growth of cerium oxide was characteristic of the immediate formation of a semi-protective oxide layer and subsequent diffusion of the oxygen through the layer. Similar conclusions were noted by Platau et al. [9] who used XPS to study the oxidation of Ce when subjected to oxygen exposures of up to 1000 L. In the Ce 3d spectrum a strong peak related to the oxide was

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observed at an exposure of only 2 L. The decrease in growth rate of the Ce 3d, Ce 4p and O 1s peaks with exposure, before final saturation, was attributed to the formation of a protective oxide layer believed to be Ce_2O_3. Using the intensity ratio between the oxide and metal related Ce peaks, the authors estimated the thickness of this oxide to be 7 Å after 100 L exposure. However, this figure was based on a number of assumptions including a flat surface, homogeneous oxide layer and the same value of electron attenuation length in both metal and oxide. The authors acknowledged the need to take into account other factors such as oxide island growth and surface roughness in modelling oxide growth. Similar observations were reported by Praline et al. [10]: for exposures of up to 20 L, a rapid decline in intensity of the metallic Ce 3d peak was observed and growth of features attributable to Ce_2O_3. Continuing O_2 exposure resulted in the appearance of other spectral features which were ascribed to CeO_2. On the basis of these observations the authors concluded that the sequence of oxidation was the formation of a thick layer of Ce_2O_3 which was terminated by a thin layer of CeO_2. Praline et al. [10] estimated a thicker oxide than Platau et al. [9] of 24 Å after an O_2 exposure of 20 L. They attributed the difference between their study and that of Platau et al. [9] to differences in the assignments of metal-derived and oxide-derived features in the spectra.

Strasser et al. [11] used electron energy loss spectroscopy (EELS) in conjunction with Auger electron spectroscopy (AES), work function measurements and electron stimulated desorption (ESD) to study the oxidation of Ce and lanthanum (La) following exposure to oxygen and water. Similar behaviour was observed in both Ce and La at oxygen exposures of up to 100 L. In specimens exposed to O_2, EELS spectra showed the low energy interband transition peak at 3 eV to shift to lower loss energies before disappearing at O_2 exposures of 3–4 L. This was attributed to depletion of the metal conduction band caused by electron transfer into O 2p dominated oxide valence bands. The most significant difference between Ce and La was the emergence at high O_2 doses (>100 L) of a peak at 4.5 eV, indicative of the presence of CeO_2. This feature was not seen in the spectra for La.

It should be noted that the oxidation of a metal in air can differ significantly from that observed in pure O_2 owing to the active role played by water vapour, which can result in hydroxide-rich outermost layers of the oxide [12]. Barr [13] has investigated the oxidation in air of a wide range of metals, including Ce. Using the terminology originally employed by Sun [14] to classify oxide glasses and later adopted by Fehlner and Mott [15] for use in an oxidation context, Barr categorised the metals into two groups, which he termed "network modifiers" and "network formers". The network modifiers passivate by forming an oxide film of low or intermediate oxidation state, which is terminated by a film of the metal in its highest (common) oxidation state [13]. In contrast, the network formers, in most cases, exhibit only one oxidation state. According to this classification, Ce is a network modifier. In addition to the presence of surface hydroxide, the effect of moisture has also been seen to cause a significant change to the oxidation behaviour. Greene and Hodge [16] compared the oxidation of Ce in dry and moist air at 100 °C: weight gain measurements showed that the presence of moisture caused the oxidation behaviour (parabolic in dry air) to become linear. This was attributed to the presence of the water vapour, which caused the formation of the hydroxide, which offered less protection to the metal. In EELS, AES and ESD of Ce and La exposed to water, Strasser et al. [11] found that the spectra exhibited similar features to those of Ce and La exposed to oxygen; however, an additional feature was seen at 11 eV, which was ascribed to surface hydroxyl species. This conclusion was supported by ESD observations, which found that the yield of the dominant desorbing ion (H^+) in H_2O dosed surfaces exceeded that from O_2 dosed surfaces by a factor of between 50 and 100. Furthermore, a reduction in the work function of 1.6 eV following H_2O exposure was also consistent with the formation of a surface OH species.

Koel et al. [17] used XPS to study the interaction between Ce and heavy water (D_2O). At 27 °C, exposure to D_2O resulted in features characteristic of both oxide and hydroxide, the latter being in the form of Ce_2O_3. Such features were not seen by the same authors in another XPS study of Ce exposed to O_2 [10]. In another study, Barr [18] used XPS to examine the passivation layer in Ce foil and found the near-surface region to be a mixed oxide-hydroxide CeO_2. In regions closer to the metal a mixed oxide-hydroxide Ce_2O_3 was seen, while the regions adjacent to the metal were only Ce_2O_3.

Recent years have seen an increasing level of interest in Ce and other rare earth elements for use in electronic components and "green" technologies [19]. However, it is important to understand the properties of any material before it can be used in new applications. The mechanical properties of Ce and a Ce-La alloy were the subject of a recent study [20] which used nanoindentation and ultrasonic velocity measurements to measure their hardness and elastic modulus. The effect of the surface oxide layer on the hardness and elastic modulus was concluded to be negligible [20]; however, an understanding of the kinetics of the oxidation process would benefit future studies of Ce. Although the previous oxidation studies of Ce (discussed above) have elucidated the sequence of oxide formation, the kinetics and mechanisms of oxide growth on Ce have been less widely reported. For this reason, the present study was carried out in order to obtain a better understanding of the oxidation of cerium in air under ambient conditions.

2. Materials and methods

The cerium (99.9% purity) was supplied by Goodfellow Metals (Huntingdon, U.K.) and was in the form of a 12 mm diameter rod. Specimens were cut from the rod into discs approximately 2 mm in thickness using a precision slitting saw in the presence of lapping oil. Initial work focused on detailed microstructural characterisation of the metal. Specimens were cold mounted in epoxy resin for metallographic examination and prepared by grinding using progressively finer silicon carbide (SiC) abrasive in lapping oil (Buehler AutoMet), the final stage being 4000 grit SiC before being cleaned in ethanol. This was followed by a chemical polishing procedure which was employed in order to reveal the grain structure of the metal. For this a solution of 60 vol.% nitric acid/40 vol.% isopropanol was used and was followed by washing of the specimen in ethanol. Examination by optical microscopy was performed immediately after metallographic preparation.

X-ray diffraction (XRD) was performed on free-standing Ce specimens using a Bruker D8 powder X-ray diffractometer. Prior to analysis the specimens were prepared using the same procedure as the metallographic specimens. 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 2θ = 20–90° at a rate of 0.025° s^{-1}, each scan taking approximately 50 min to complete. The specimen was also subjected to extended scans over the range 2θ = 20–150° at a rate of 0.017° s^{-1}, in order to determine the lattice parameter of both the alloy and the oxide layer.

The oxidation behaviour was studied by exposing free-standing specimens to the open laboratory atmosphere for a period of up to 60 days. The specimens were prepared in the same way as for metallographic examination, the final stage being 4000 grit SiC; both sides of the specimen were prepared in this way. Unlike the metallographic preparation, the chemical polish was not performed in this case. During this time the specimens were regularly subjected to XRD analysis in order to monitor the growth of the oxide species that had formed on the surface. The relative humidity and