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Journal of Nuclear Materials 340 (2005) 171–178

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Electrical conductivity and non-stoichiometry in the $(U,Gd)O_{2\pm x}$ system

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Received 16 July 2004; accepted 10 November 2004

Abstract

The isothermal electrical conductivity and oxygen potential of the $(U,Gd)O_{2\pm x}$ solid solution were measured in various oxygen partial pressure regions at 1200 °C and 1300 °C. The electrical conductivity gradually decreased with decreasing oxygen partial pressure even in the hypo-stoichiometric region. These findings were in contrast to the implication of a hypo-stoichiometry where the electrical conductivity is increased through the formation of oxygen vacancies. The $(U_{1-y}Gd_y)O_{2-y/2}$ was defined as a new stoichiometric composition to determine the relationship between the deviation of the oxygen composition from stoichiometry and oxygen partial pressure. The dependence of the new oxygen deviation, z in $(U_{1-y}Gd_y)O_{2-y/2+z}$, on the oxygen partial pressure corresponds to the dependence of the electrical conductivity, and thus a consistent defect structure model can be deduced from both the dependence curves. It suggests that the defect type is oxygen interstitial even below the oxygen composition of 2.

1. Introduction

Uranium dioxide can accommodate large amounts of excess oxygen atoms, with its cubic symmetry maintained [1–7]. Incorporated and displaced lattice oxygen atoms form defect aggregates called oxygen defect clusters. Various kinds of oxygen defect cluster models have been suggested. Among these, the Willis's $(2O_i^a 2V_O 2O_i^b)$ defect cluster [1,7] and the cuboctahedral cluster [5,8–10] are commonly used for interpreting a defect cluster in the UO_{2+x} system. The oxygen defect structure and its ionization state in the UO_{2+x} system are often deduced from the dependence of the oxygen partial pressure, p_{O_2}, on the oxygen deviation from stoichiometry (x) and /or electrical conductivity (σ) [11–15]. The deviation (x) and the electrical conductivity (σ) have similar correlations with the oxygen partial pressure, i.e., $x \propto p_{O_2}^{1/\alpha}$ and $\sigma \propto p_{O_2}^{1/\beta}$, respectively. The α and β values convey some important information on the defect structure. Thus, the oxygen defect structure can be deduced from the α and β values by applying an appropriate defect model.

A mixture of UO_2 and neutron-absorbing lanthanide oxides (Ln_2O_3), which is in the form of $(U_{1-y}Ln_y)O_2$, is used to control the nuclear fission in nuclear reactors, together with UO_2 fuel [16–19]. A trivalent Ln^{3+} cation substitution leads to changes in the relationship between the oxygen-to-metal (O/M) ratio and oxygen partial pressure. The O/M ratios at all the oxygen partial pressures are decreased by the substitution of the Ln^{3+} cation. In the low oxygen partial pressure region [20,21],

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doi:10.1016/j.jnucmat.2004.11.006

the metal-to-oxygen ratio becomes even smaller than 2.0, i.e. $(U_{1-y}Ln_y)O_{2-x}$, which is not possible for UO_2.

The sub-stoichiometry resulting from the reduction of Pu^{4+} to Pu^{3+} can also be found in the uranium-plutonium mixed oxide (MOX) [22–28]. The defective structure in hypo-stoichiometric $(U_{1-y}Pu_y)O_{2-x}$ is interpreted in terms of a clustering of the Pu^{3+} and oxygen vacancies. The Markin-McIver rule [22] proposed that the oxygen potential depends only on the average valence and not directly on the concentration of plutonium. However, the valence state of the lanthanide cation in $(U_{1-y}Ln_y)O_{2-x}$ system is intrinsic and always fixed at 3+. The oxygen potential depends directly on the substitution amount of the lanthanide cation.

Several researchers have measured the non-stoichiometry and electrical conductivity in the $(U,Ln^{3+})O_{2\pm x}$ system at various oxygen partial pressures and temperatures, and they have suggested various defect models based on those measurements [29–40]. The suggested defect models cover wide ranges of the substituted species, substitution amounts, and measuring temperatures so much so the oxygen defect models in a Ln^{3+} substituted UO_2 are difficult to integrate in a consistent manner. Nevertheless, it has been commonly stated that the defect is related to the oxygen interstitials in the hyper-stoichiometric region and it is related to the oxygen vacancies in the hypo-stoichiometric region. The hyper- and hypo-stoichiometry means the upper and lower deviations from the O/M ratio of 2.0, respectively. Thus the charge concentration should increase as the non-stoichiometry increases, regardless of the types of defects. The electrical conductivity vs. oxygen partial pressure curves of $(U,Ln^{3+})O_{2\pm x}$ should have a parabolic shape with a flat minimum at the O/M ratio of 2.0 as in the $Gd_2(Zr_xTi_{1-y}Ta_y)_2O_7$ system [41].

However, several electrical conductivity measurements of $(U,Ln^{3+})O_{2-x}$ in the hypo-stoichiometric region have shown somewhat opposite results. Matsui et al. found that the electrical conductivity of the hypo-stoichiometric $(U_{1-y}La_y)O_{2-x}$ slightly decreased with decreasing oxygen partial pressure [22]. Ohmichi et al. also found that the isothermal electrical conductivity of hypo-stoichiometric $(U_{1-y}Y_y)O_{2-x}$ decreased with an increase of the oxygen deficiency x [36].

Inconsistency can also be found in the hyper-stoichiometric region. The electrical conductivity is the product of the concentration and mobility of the charge carriers. The concentration of mobile charge carriers is proportional to the oxygen deviation from the stoichiometry, which is determined by the oxygen partial pressure. It is known that the hole mobility for the same type of oxygen defects is almost independent of the change in the oxygen partial pressure [29,40]. This implies that the α and β values in the $x \propto p_{O_2}^{1/\alpha}$ and $\sigma \propto p_{O_2}^{1/\beta}$ equations should be closely interrelated. However, in most cases of the $(U,Ln^{3+})O_{2\pm x}$ system, the two values are quite different from each other, and moreover, relations between them are not clearly explained as yet.

In this study, the electrical conductivity and non-stoichiometry, x, of $(U_{1-y}Gd_y)O_{2\pm x}$ ($y = 0.087, 0.169$) were measured at various oxygen partial pressures at 1200 °C and 1300 °C. A new stoichiometry was proposed to explain in a congruent way the relationship between the electrical conductivity and the non-stoichiometry. The defect structure of $(U,Gd^{3+})O_{2\pm x}$ was deduced from both the electrical conductivity and non-stoichiometry change based on the new stoichiometric oxygen composition.

2. Experimental

Wet ball-milled powders of 6 wt% and 12 wt% Gd_2O_3-doped UO_2 were pressed into cylindrical pellets and sintered in H_2 at 1730 °C for 4 h. The sintered pellets were held at 1650 °C for 20 h in a gas mixture of CO_2 and H_2 ($CO_2/H_2 = 0.3$) for the purpose of chemical homogenization. The annealed sample pellets were cooled to room temperature in 3 vol.% CO_2 containing H_2. The formation of the single-phase solid solution was characterized by X-ray diffraction and EPMA area mapping. For the thermogravimetric studies, 1.5 g of the pellet samples were loaded into a TGA (Shimadzu, TG-50) and the isothermal weight changes according to the variation of the oxygen partial pressure were measured. The oxygen partial pressure was controlled by flowing various CO and CO_2 gas mixtures and monitored by an oxygen sensor. The electrical conductivity was measured by the conventional DC 4-probe method. Two Pt plates were attached to both ends of the cylindrical sample pellet, and two Pt wires in the vicinity of both ends. The constant currents were applied stepwise through the two Pt plates in the range from −40 mA to 40 mA with a 5 mA interval. The corresponding voltage drops between the two inner Pt-wire probes were measured.

3. Results and discussion

3.1. Dependence of the non-stoichiometry and electrical conductivity on the oxygen partial pressure

Fig. 1(a) displays the isothermal O/M ratio changes of $(U_{1-y}Gd_y)O_{2\pm x}$ ($y = 0.087, 0.169$) as a function of the oxygen partial pressure measured at 1200 °C and 1300 °C. As the Gd contents or temperature increase, the O/M ratio shifts to a higher p_{O_2} region, and the p_{O_2} range showing a constant O/M ratio tends to become more narrow. Log$x$ vs. logp_{O_2} is plotted to obtain the value α in the $x \propto p_{O_2}^{1/\alpha}$ relation and are shown in Fig. 1(b). The exponent α is about 1 for the hyper-stoichiom-