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16. Some Material Properties of Cerium Sesquioxide

By

Toshiyuki SATA and Masahiro YOSHIMURA

(Research Laboratory of Engineering Materials,

Tokyo Institute of Technology, Ōokayama, Meguro-ku, Tokyo)

1. Introduction

Since rare earth elements are generally stable in a trivalent state in normal conditions, their oxides exist as forms of sesquioxide (Ln_2O_3) in air. However, cerium usually exists in a quadrivalent state in air, namely in the form of CeO_2 as oxide. In this reason, the studies of the material properties of cerium oxides have been mainly carried out for CeO_2 instead of Ce_2O_3 . Few properties of cerium sesquioxide have been discussed, i.e. the electrical conductivity, the chemical stability, and the melting point were reported by E. Friedrich et al.¹⁾ in 1927, and the resistivity²⁾ and the thermal expansion³⁾ were studied by M. Föex in 1944 and 1946, respectively. In these studies, however, the considerations for the experimental devices and conditions seem to be insufficient, and it is probable that Ce_2O_3 have changed into the intermediate phase.

Ce_2O_3 is prepared from CeO_2 by reduction with H_2 , CO, etc. and is golden or mustard yellow in color. Its crystal system is hexagonal La_2O_3 -type: $a=3.889 \text{ \AA}$, $c=6.054 \text{ \AA}$ ⁴⁾. It is well known that La_2O_3 structure is related with CaF_2 structure of CeO_2 and that several intermediate phases^{4), 5)} which are represented by CeO_{2-x} exist in the composition range between Ce_2O_3 and CeO_2 .

In this work, the stability, the melting point, the thermal expansion coefficient, the electrical conductivity and the magnetic susceptibility have been studied for powdered sample and sintered bodies of Ce_2O_3 , as a part of the investigations of the sub-oxides or lower oxides for engineering materials.

2. Experimental

2.1 Preparation of Ce_2O_3 specimen

The starting material was high purity CeO_2 powder (99.95%) obtained from Lindsay Chemical Corp., Chicago. The observed magnetic suscepti-

bility ($0.14 \times 10^{-6} \text{ emu/g}$) of this CeO_2 was in agreement with the literature value⁶⁾ of carefully purified CeO_2 especially not to contain 3d elements. The spectroscopic analysis was also undertaken. The lattice constant of this CeO_2 was $a=5.410 \text{ \AA}$, which agrees with the literature value⁷⁾.

CeO_2 powder was pressed with some methanol at 1 t/cm^2 into a round pellet ($10 \text{ mm} \phi \times 3 \text{ mm}$). The pellet was hanged using a molybdenum wire in a high alumina tube of a SiC electric furnace and heated in an atmosphere of flowing dry hydrogen (0.2 l/min). By keeping for 2~10 hours at 1400°C , the reduction into Ce_2O_3 was accomplished.

(a)

(b)

(a) Sintered for 4 hours at 1400°C .

(b) Sintered for 2 hours at 1700°C .

Fig. 1. Microphotographs of the surface of the Ce_2O_3 specimen.

After the treatments, the samples were dropped into an iced acceptor for quenching. When they were slowly cooled, Ce_2O_3 changed into the intermediate phase by some oxidation. The lattice constants of Ce_2O_3 obtained in this treatment were determined to be $a=3.892 \text{ \AA}$, $c=6.064 \text{ \AA}$. The reduction process from CeO_2 to Ce_2O_3 and the behaviors of the intermediate phases are described in another report⁷⁾.

For the measurements of the thermal expansion and the electric conductivity, CeO_2 powder was hydrostatically pressed into a bar form at 3 t/cm^2 and was sintered in an atmosphere of hydrogen as described above in order to obtain Ce_2O_3 bar specimen ($4 \times 4 \times 25 \text{ mm}^3$). The sintered density was found to be 88% of theoretical.

A microphotograph of the polished surface of the sintered specimen is shown in Figure 1(a). A microphotograph of the specimen sintered for 2 hours at 1700°C is also shown in Figure 1(b) for references, though the reduction did not proceed furthermore (<1.50 of O/Ce atomic ratio) at temperatures above 1400°C .

2.2 Stability

Ce_2O_3 powder and sintered pellets were heated in air in a platinum crucible in order to observe their oxidation behaviors. Weight increasings were also determined by means of thermogravimetric analysis (TGA). The reactivities of Ce_2O_3 with water, acids and alkaline solutions were studied.

2.3 Melting point

A small piece of Ce_2O_3 which was hanged by a tungsten wire in a tungsten tube heater was heated in an atmosphere of flowing dry hydrogen. The melting behavior of the test piece was observed through a window on the shell of the furnace. Temperatures were measured with a W-5% Re-W-26% Re thermocouple situated near by the test piece. The thermocouple was calibrated with the melting points of Au, Pd, Pt, Rh and Ir metals using the same method as above. The details of this method and the tungsten furnace used here were previously reported by one of the authors⁸⁾.

2.4 Thermal expansion

A horizontal dilatometer with a dialgauge (0.001 mm) was used for measurements where the sample holder and the extension rod were made from high purity alumina of Degussa Co., Germany. The experiments were carried out in temperatures between a room temperature and 1400°C with heating and cooling rates of about 4°C/min. in an atmosphere of flowing hydrogen (0.2 l/min.). The thermal expansion coefficients were calculated from the thermal expansion curve obtained. For comparison, measurements for CeO_2 specimen sintered for 2 hours at 1500°C in air were carried out in air.

2.5 Electrical conductivity

Both ends of a bar specimen were coated with platinum paste for platinum electrodes contact and two platinum wires were wrapped tightly around the bar as potential probes. The a.c. bridge of 1000 cps (Yokogawa Electric Work Co., Tokyo, Type BV-Z-13A) was mainly used for measurements. Four probes or two probes d.c. methods were also attempted. The differences of measurements between a.c. and d.c. method were negligible small. A complete description of the SiC furnace and electrodes assembly is shown in Figure 2. The atmosphere was chiefly dry hydrogen, though argon, vacuum and air were also employed in a lower temperature range. The composition of the samples was found to be $\text{Ce}_2\text{O}_{3.042}$ by means of the perfect oxidation method to CeO_2 .

Fig. 2. Arrangements and electrodes assembly for the electrical conductivity measurement.

2.6 Magnetic susceptibility

A torsion type magnetobalance (Shimadzu Seisakusho Ltd., Kyoto, Type MB-II) was used for measurements. The block diagram is shown in Figure 3. A guaranteed reagent of copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which was purified with a procedure of two times recrystallization, was employed as the standard material.

The magnetic susceptibility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is known to be $5.84 \times 10^{-6} \text{ emu/g}$ at 293°K . The experimental conditions were as follows:

Temperature range $77^\circ \sim 300^\circ\text{K}$
Field strength 10,500 Oersted

Fig. 3. Block diagram of the magnetobalance.

Heating rate 1.5°C/min

Atmosphere dry H₂ at 200 mmHg

The composition of sample was found to be Ce₂O_{3.047}.

3. Results and Discussions

3.1 Stability

Ce₂O₃ was very unstable in air and the oxidation of Ce₂O₃ occurred even at a room temperature. When a pellet was warmed in air, its surfaces changed from mustard to white in color and swelled up above ca. 100°C. The oxidation reaction was remarkably exothermic, so it was often observed that Ce₂O₃ ignited spontaneously on exposure to the atmosphere. The weight increasing curves of Ce₂O₃ powder and pellet with the oxidation to CeO₂ were shown in Figure 4, where the formations of the intermediate phases in this oxidation process were not observed.

Fig. 4. Weight increasing curves of Ce₂O₃ with the oxidation into CeO₂ in air.

When a following heterogeneous reaction is considered,

Free energy change of this reaction is given by

$$\Delta G_h = -RT \ln K_h \quad (2)$$

where K_h is the equilibrium constant and equal to square root of oxygen partial pressure ($P_{\text{O}_2}^{1/2}$).

From the first law of the thermodynamics, the following equation is known:

$$\Delta G_h = \Delta H_h - T \Delta S_h \quad (3)$$

By F.A. Kuznetsov and his coworker⁹⁾, $H_{298.2^\circ\text{K}}$ of CeO₂ and Ce₂O₃ were given to be -260.18 kcal/mole and -434.93 kcal/mole, respectively, and $\bar{C}_p$ of CeO₂ and Ce₂O₃ to be $15.03 + 2.513 T \times 10^{-3}$ cal/mole°K and $25.17 + 6.327 T \times 10^{-3}$ cal/mole°K, respectively. Using these values, the equilibrium oxygen pressures ($P_{\text{O}_2}^{1/2}$) of Ce₂O₃ were calculated to be 1.3×10^{-58} atm at 298°K and 9.0×10^{-13} atm at 1000°K, respectively. By comparison, the observed values of $P_{\text{O}_2}^{1/2}$ was obtained to be 5.1×10^{-15} atm at 1000°K by D.J.M. Bevan⁹⁾. On the basis of

above discussions, it is obviously understood that the oxidation of Ce₂O₃ can not be prevented in an ordinary atmosphere as argon, vacuum to say nothing of air.

Ce₂O₃ did not dissolve in alkaline solutions but very slowly in acids and reacted with water in the same manner as La₂O₃ and produced white material which gradually changed into CeO₂ in several days or dehydration process. Details of this hydrated material was not studied in this work.

3.2 Melting point

The obtained values of the melting point of Ce₂O₃ are shown in Table 1. Although a piece of CeO₂ pellet was used in No. 3 experiment, it would be reduced into Ce₂O₃ in hydrogen. The quenched samples after melting were easily separated from a tungsten wire by crashing and was confirmed to be Ce₂O₃ by X-ray diffraction analysis.

Table 1. Melting point of Ce₂O₃.

No.	e.m.f. (mV)	Melting point (°C)
1	36.30	2220
2	36.12	2202
3	36.13	2203
4	36.10	2200

In addition, a test piece sublimated completely in vacuum (10^{-5} mmHg) at temperatures above ca. 1900°C. CeO₂ sample also showed the similar vaporization in vacuum. Since $P_{\text{O}_2}^{1/2}$ is about 10^{-8} mmHg in this vacuum, both CeO₂ and Ce₂O₃ sample would change into the intermediate phase, CeO_{2-x}. Friedrich obtained 1690°C for the melting point of Ce₂O₃ in nitrogen¹⁾. But this value seems to be too low because the oxidation of Ce₂O₃ to CeO_{2-x} can not be prevented in nitrogen even if it was purified. The melting point values of rare earth oxides reported by various authors are summarized in Table 2.

Table 2. Melting points of Ln₂O₃.

Ln ₂ O ₃	Temperature (°C)	Environment	References
La ₂ O ₃	2210±20	H ₂	10
	2307	Air	11
	2304±2	A	8
Ce ₂ O ₃	2210±10	H ₂	This work
	1690	N ₂	1
Pr ₂ O ₃	2200	—	12
Nd ₂ O ₃	2272±20	He	10
Sm ₂ O ₃	2300±50	He, H ₂ , Vac.	13
	2350±50	Air	14

The value, 2210±10°C, obtained in this study is reasonable in comparison with the values of other oxides. It is interesting for engineering materials that rare earth sesquioxides have generally high melting points of above 2200°C and are stable up to the melting point.

3.3 Thermal expansion coefficient

A thermal expansion curve was represented by the following linear equation:

$$(l_2 - l_1)/l_1 = \bar{\alpha}(t_2 - t_1) \quad (4)$$

where l_1 and l_2 are lengths of the specimen at

(a) Ce_2O_3 specimen in hydrogen.
(b) CeO_2 specimen in air.

Fig. 5. Thermal expansion curves and linear expansion coefficients (α).

temperatures of t_1 and t_2 , respectively. $\bar{\alpha}$ is the average value of the linear expansion coefficients between t_1 and t_2 . The expansion curves and the calculated linear expansion coefficients for Ce_2O_3 and CeO_2 are shown in Figure 5(a) and 5(b), respectively. Both Ce_2O_3 and CeO_2 showed continuous expansion in all over the temperatures.

The calculated expansion coefficients are given as follows:

for Ce_2O_3 $\alpha = 12.0 \times 10^{-6} \text{deg}^{-1}$ at a room temperature

$\alpha = 14.8 \times 10^{-6} \text{deg}^{-1}$ at 1350°C

for CeO_2 $\alpha = 10.0 \times 10^{-6} \text{deg}^{-1}$ at a room temperature

$\alpha = 13.5 \times 10^{-6} \text{deg}^{-1}$ at 1100°C

Since an anomalous expansion owing to the formation of CeO_{2-x} from Ce_2O_3 was observed between 600°C and 1050°C , no data was expressed in Figure 5(a) in this temperature range.

The values of the expansion coefficients for Ce_2O_3 has not been published previously, but the values for La_2O_3 and Nd_2O_3 which have a similar structure to Ce_2O_3 have been reported. Those values and the results of this work are tabulated in Table 3, and are compared with each other. The values of the volume expansion coefficient (β) were calculated from the values of α by following relations:

Table 3. Volume thermal expansion coefficients (β) of rare earth oxides.

Oxides	β (deg $^{-1}$)	Temp. range ($^\circ\text{C}$)	Method	Reference
La_2O_3	35.9	R.T.-1000	Dilatometer	(15)
	37.9*	R.T.-1100	Dilatometer	(16)
Ce_2O_3	40.5	R.T.-1400	Dilatometer	This work
Pr_2O_3	—	—	—	—
Nd_2O_3	34.2	R.T.-1050	Dilatometer	(15)
	36.9*	R.T.-1150	Dilatometer	(16)
CeO_2	36.3	R.T.-1000	Dilatometer	(17)
	35.6	R.T.-625	High-temp. X-ray	(18)
	37.5	R.T.-1000	Dilatometer	(3)
	36.0	R.T.-1100	Dilatometer	This work

* Single crystal sample

for a sintered specimen $\beta = 3\alpha$(5)

for a single crystal $\beta = 2\alpha_a + \alpha_c$(6)

Here α_a and α_c are the linear expansion coefficients along the a -axis and c -axis, respectively.

The value for CeO_2 was in good agreement with the published values. But the value for Ce_2O_3 was greater than the expected value in ca. 11%. It is supposed that the sample body was oxidizing into CeO_{2-x} of which molar volume is greater than those of both Ce_2O_3 and CeO_2 (max. 8%) at the surface during the experiments.

3.4 Electrical conductivity

The relation of the logarithm of the electrical conductivity ($\log \sigma$) versus the reciprocal absolute temperature ($1/T$) was shown by a straight line with a break at about 950°C (Figure 6). In a low temperature range, the conductivity at any temperature was found to be a similar value in any atmosphere except for air.

The electrical conductivity was represented in a following relation:

$$\sigma = \sigma_0 \exp(-E/kT) \dots \dots \dots (7)$$

where E is the activation energy for the electrical conduction. The following values were obtained

Fig. 6. The logarithm of electrical conductivity ($\log \sigma$) vs. reciprocal absolute temperature ($1/T$).

from the results in the low temperature range :

$$\sigma_{300^\circ\text{K}} = 7.7 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}, \quad E = 0.40 \text{ eV}$$

For the high temperature range,

$$\sigma_{1673^\circ\text{K}} = 8.0 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}, \quad E = 0.95 \text{ eV}$$

Since an anomalous conduction derived from the formation of CeO_{2-x} from Ce_2O_3 appeared in the temperature range of $150^\circ \sim 1050^\circ\text{C}$, no result was represented in Figure 6 as the conduction of Ce_2O_3 . It is supposed from these results that the conduction mechanisms are different between the low temperature range and the high temperature range.

The electrical conductivities of a series of the rare earth oxides were studied by W. Noddack and H. Walsh¹⁹⁾ and N.P. Bogoroditskii²⁰⁾ in air, i.e. CeO_2 was employed as a cerium oxide. Only M. Föex²¹⁾ studied the conductivity of Ce_2O_3 in cooling process in hydrogen. He, however, did not observe the break at about 950°C . In most rare earth oxides, the break in the relation of $\log \sigma$ vs. $1/T$ was observed between 700°C and 1000°C , but its reasons have not been explained yet²¹⁾.

Noddack and Bogoroditskii concluded that the conduction in the rare earth oxides were purely electronic, i.e. up to 99.7% by the latter. These workers, however, did not consider the variations in the sample composition of nonstoichiometric oxides (Pr_6O_{11} , Tb_4O_7 , etc.) of which compositions could be varied by P_{O_2} and temperatures. On the other hand, in studies on the conduction of CeO_2 - La_2O_3 solid solutions which remained in a fluorite-type structure having much oxygen vacancies, T. Takahashi and coworker²²⁾ indicated that the conduction was predominated by oxygen ions moving through the vacancies and found the activation energy for this mechanism to be about 1 eV. As described above, the conduction of the rare earth oxides was affected with the stoichiometry and P_{O_2} . A study on the conductivity of near-stoichiometric CeO_2 as a function of P_{O_2} was undertaken by E.H. Greener et al.²³⁾. They found that CeO_2 was n -type semiconductor, and assumed that the conduction in CeO_2 was dominated by the electrons trapped at oxygen vacancies.

In addition, several studies of praseodimium oxides, PrO_y ($1.5 \leq y \leq 2.0$), which exists in two valence states (Pr^{3+} , Pr^{4+}), were published recently. J.C. Conwell et al.²⁴⁾, who studied the conduction and Seebeck coefficients of PrO_y , found that PrO_y was n -type for $2.000 \geq y \geq 1.725$, p -type for $1.725 > y \geq 1.500$, and indicated that the conduction was understood by a sort of the hopping-type mechanism with electron transfer. On the other hand, L. Eyring et al.²⁵⁾ considered the contributions of ionic conduction in the range of y value slightly greater than 1.50 at temperatures below 600°C .

As described above, the conduction mechanisms of the rare earth oxides have not been completely understood and the conclusions appeared to be partly inconsistent with each other. In general, however, it is well known that the mixed valent oxides, PrO_y , CeO_{2-x} , Tb_4O_7 , etc., have greater conductivity and smaller activation energy (0.3~0.6 eV) than those of the stoichiometric oxides.

On the basis of above discussion, the results of this study may be considered qualitatively as follows; the conduction of Ce_2O_3 in the low temperature range appears to be electronic one of hopping-type by Ce^{4+} ions formed in the sample ($\text{Ce}_2\text{O}_{3.042}$). The activation energy for this mechanism was found to be 0.40 eV. In the high temperature range, the intrinsic conduction of Ce_2O_3 appeared with the activation energy, 0.95 eV, which was comparable with the values of other stable rare earth oxides.

In addition, the ionic contributions should be considered for oxides which have much oxygen vacancies, i.e. PrO_y , $(\text{Ce}, \text{La}) \text{O}_{2-x}$, etc. It is reported that oxygen ions can move reasonably fast in those oxides²⁶⁾. The mobility of ions, however, is thought to be smaller than that of electrons, so it is most probable that electrons are dominant for the conduction in these oxides.

If the conduction in Ce_2O_3 was represented by the hopping-type mechanism ($\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$), the following relation was crudely expected :

$$\sigma \propto [\text{Ce}^{3+}][\text{Ce}^{4+}] \dots\dots\dots (8)$$

Indeed, it was observed that CeO_{2-x} showed an extremely higher conductivity than both CeO_2 and Ce_2O_3 .

3.5 Magnetic susceptibility

The relations of the molar magnetization (M) versus the field strength (H) are shown in Figure 7. They were represented by a straight line passing through the origin at each temperature, namely the following equation was satisfied.

$$M = \chi_m \times H \dots\dots\dots (9)$$

where χ_m is the molar magnetic susceptibility. As shown in Figure 8, the relation of $1/\chi_m$ versus T

Fig. 7. Magnetization (M) vs. field strength (H)

Fig. 8. Reciprocal molar susceptibility ($1/\chi_m$) vs. temperature (T).

was linear in all over the temperature range studied following the Curie-Weiss law,

$$\chi_m = C/(T - \theta_p) \quad (10)$$

where C is the Curie-Weiss constant, θ_p is the paramagnetic Curie temperature. From Figure 7 and 8, it is well understood that Ce_2O_3 behaves paramagnetically in all over the temperatures studied, and following values were obtained:

$$\chi_{m293^\circ\text{K}} = 3.90 \times 10^{-3} \text{ emu/mole},$$

$$\theta_p = -90^\circ\text{K}, \quad C = 0.728$$

The effective magnetic moment (μ_{eff}) was calculated from the following relation,

$$\mu_{\text{eff}} = \sqrt{3kC/N\mu_B} = 2.83\sqrt{C} \quad (11)$$

and was found to be $\mu_{\text{eff}} = 2.44$ Bohr Magnetons.

The electron structure of Ce^{3+} ion is shown in $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4f^1 5s^2 5p^6$. Ce^{3+} ion is characterized in having one unpaired electron $4f^1$, and $5s^2 5p^6$ electrons in outer shell shield the effects of the crystalline field for $4f^1$ electron. In other words, Ce^{3+} ion is regarded as a free ion at temperatures except for low temperatures. The results of this investigation are consistent with the above arguments. The theoretical effective magnetic moment for Ce^{3+} ion was calculated to be 2.56 B.M. by Van Vleck and A. Frank²⁶⁾. The experimentally determined value, 2.44 B.M., was in good agreement with the literature values²⁷⁾ obtained for Ce^{3+} aqueous solutions. No prior studies on the magnetic susceptibility for Ce_2O_3 are found, but the susceptibility for Pr^{4+} oxides, isoelectronic with Ce^{3+} , were measured as follows:

$$\text{for } \text{PrO}_{2.007}^{28)} \quad \mu_{\text{eff}} = 2.51 \text{ B.M.} \quad \theta_p = -90.1^\circ\text{K}$$

$$\text{for } \text{PrO}_{2.00}^{29)} \quad \mu_{\text{eff}} = 2.47 \text{ B.M.} \quad \theta_p = -105^\circ\text{K}$$

These values are in good agreement with the results of this investigation. The negative θ_p values indicates that the interaction of $4f^1-4f^1$ is antiferromagnetic and an antiparallel ordering should occur below 77°K .

4. Conclusion and summary

There are few previous studies on the properties of Ce_2O_3 , which was obtained from CeO_2 by the reduction with hydrogen at 1400°C . Powdered or sintered samples were used for experiments. The results obtained were as follows.

(1) It was recognized that Ce_2O_3 was very unstable and was slowly oxidizing to CeO_2 in air even at a room temperature. The oxidation process was so exothermic that a spontaneous ignition was often observed. It was also observed that Ce_2O_3 changed into CeO_{2-x} in ordinary atmospheres, i.e. vacuum, argon, nitrogen, hydrogen, etc, at temperatures between several hundreds and one thousand degrees in centigrade. The compositions of CeO_{2-x} were varied by P_{O_2} and temperatures. Ce_2O_3 hardly dissolved in acids and alkalis but reacted with water.

(2) The melting point of Ce_2O_3 was found to be $2210 \pm 10^\circ\text{C}$, which is comparable with the values of other rare earth oxides. Ce_2O_3 was stable in hydrogen up to the melting point without decomposition. On the other hand, CeO_{2-x} seemed to be unstable.

(3) The thermal expansions Ce_2O_3 and CeO_2 were studied between a room temperature and 1400°C , and were found to be linear without a discontinuity induced by the crystal transformations. Experimentally determined linear expansion coefficients were as follows:

$$\text{for } \text{Ce}_2\text{O}_3 \quad \alpha_{RT} = 12.0 \times 10^{-6} \text{ deg}^{-1}$$

$$\alpha_{1350^\circ\text{C}} = 14.8 \times 10^{-6} \text{ deg}^{-1}$$

$$\text{for } \text{CeO}_2 \quad \alpha_{RT} = 10.0 \times 10^{-6} \text{ deg}^{-1}$$

$$\alpha_{1100^\circ\text{C}} = 13.5 \times 10^{-6} \text{ deg}^{-1}.$$

(4) The electrical conductivity of Ce_2O_3 was measured from a room temperature to 1400°C . The relation of $\log \sigma$ vs. $1/T$ was shown by a straight line with a break at about 950°C . The following results were obtained:

$$\sigma_{300^\circ\text{K}} = 7.7 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1} \quad E = 0.40 \text{ eV}$$

$$\sigma_{1673^\circ\text{K}} = 8.0 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \quad E = 0.95 \text{ eV}$$

It is assumed that the conduction mechanism in the low temperature range was similar to that of mixed valent oxides, i.e. PrO_y , Tb_4O_7 , CeO_{2-x} , etc. Namely, a sort of the hopping-type conduction mechanism with formation of Ce^{4+} ion is supposed. The intrinsic conduction of Ce_2O_3 , of which mechanism is similar to that of other stable rare earth oxides, was presented in the high temperature range.

(5) The magnetic susceptibility of Ce_2O_3 was studied between 77°K and 300°K . M vs. H were shown by straight lines passing through the origin at each temperature. In addition, $1/\chi$ vs. T was represented by a straight line, so the Curie-Weiss law was confirmed to follow. The results obtained are as follows:

$$\theta_p = -90^\circ\text{K} \quad \mu_{\text{eff}} = 2.44 \text{ B.M.}$$

These are comparable with the theoretical or experimental values in literatures.

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三 二 酸 化 セ リ ウ ム の 材 料 物 性

佐 多 敏 之・吉 村 昌 弘

(東京工業大学工業材料研究所)

三二酸化セリウム (Ce_2O_3) の材料物性は、従来ほとんど検討されていなかった。 Ce_2O_3 は二酸化セリウム (CeO_2) を水素中 1400°C 以上で還元して得られる。このようにして得た焼結体および粉末を用いて測定を行ない、以下の結果を得た。

(1) Ce_2O_3 は極めて酸化しやすく、空気中では室温でも酸化の進行が認められ、加熱した場合は約 60°C 以上で急激に酸化し CeO_2 になった。また通常の真空中、アルゴン中、水素中でも数 100°C から 1000°C の温度では、いくらか酸化して中間相 (CeO_{2-x}) を生成した。アルカリには不溶、酸にはゆっくり溶け、水と反応して水和物をつくることが観察された。

(2) Ce_2O_3 の小片を水素気流中、タングステン炉で融点を測定し、 $2210 \pm 10^\circ\text{C}$ の値を得た。 Ce_2O_3 は水素中で融点まで安定に存在したが、中間相は不安定であった。

(3) 熱膨張の測定から、線膨張係数として、 Ce_2O_3 に対しては室温で $12.0 \times 10^{-6} \text{deg}^{-1}$ 、1350°C で $14.8 \times 10^{-6} \text{deg}^{-1}$ が、 CeO_2 に対しては室温で $10.0 \times 10^{-6} \text{deg}^{-1}$ 、1100°C で $13.5 \times 10^{-6} \text{deg}^{-1}$ が得られた。

(4) 電気伝導度の対数 $\log \sigma$ と温度 T との関係は、約 950°C にクニックを持つ直線で表わされる。 $\sigma_{300^\circ\text{K}} = 7.7 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ 、 $\sigma_{1673^\circ\text{K}} = 8.0 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ で活性化エネルギーは高温域で 0.95 eV、低温域で 0.40 eV で、低温域では、 Ce^{4+} の混入による一種のホッピング型電導が現われたものとみなされる。

(5) 77°K から 300°K の間で、 Ce_2O_3 の磁化 (M) と磁場 (H) の関係および、 $1/x$ と T の関係はいずれも直線的で常磁性的挙動を示した。 $\theta_p = -90^\circ\text{K}$ 、 $\mu_{\text{eff}} = 2.44 \text{ B.M.}$ は理論値と良く一致した。

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