Die Werkstoffanstrengung im elastisch-plastischen Bereich kann beschrieben werden, indem man in den Lösungen (10) und (15) die elastische Querzahl ν durch die elastisch-plastische Querzahl ν_{ep} gemäß Gl. (22) ersetzt. Die Ergebnisse lauten dann:

\[ \sigma^a = \frac{\nu}{2} \left( 1 - \frac{1}{1 - 2\nu} \frac{E}{T} \right) \sigma_{ij} \]  
(23a)

bzw.

\[ \sigma^e = \frac{\nu}{2} \sigma_{ij} \sigma_{ij} - (1 - 2\nu) \left( \frac{J_2}{\nu} - \frac{J_1}{\nu} \right) \frac{E}{T} \]  
(23b)

und

\[ \frac{d\sigma^e}{d\varepsilon} = \frac{\nu}{2} \sigma_{ij} \sigma_{ij} - (1 - 2\nu) \left( \frac{J_2}{\nu} - \frac{J_1}{\nu} \right) \frac{E}{T} \]  
\[ + \frac{J_2}{3\nu} \left( 1 - \frac{1}{1 - 2\nu} \frac{E}{T} \right) \]  
(24)

die für \( T = 0 \) (idealplastischer Werkstoff) in die entsprechenden Beziehungen der Mises'schen Theorie übergehen und für \( T = E \) (elastischer Bereich) mit den Ergebnissen gemäß Gl. (10) und Gl. (15) identisch sind. In Gl. (23b) kann noch eine kürzere Schreibweise benutzt werden, wenn man berücksichtigt, daß

\[ J_2' = \frac{1}{2} \sigma_{ij} \sigma_{ij} = \frac{1}{2} \left( \sigma_{ij} \sigma_{ij} - \sigma_{kk}^2 \right) \]  
(25)

gilt, so daß damit

\[ J_2' - \frac{1}{2} J_1^2 = \frac{1}{2} \left( \sigma_{ij} \sigma_{ij} - \sigma_{kk}^2 \right) = J_2 \]  
(26)

wird. Somit kann Gl. (23b) auch in der Form

\[ \sigma^e = 3 J_2' - (1 - 2\nu) \left( \frac{E}{T} \right) J_2 \]  
(27)

geschrieben werden. Darin ist \( J_2' \) die zweite Invariante des Spannungstensors \( \sigma_{ij} \). Für den elastischen Bereich \( (T = E) \) geht Gl. (27) wegen des Zusammenhangs (26) über in:

\[ \sigma^e = J_2' + 2(1 + \nu) \frac{E}{T} J_2 \]  
(28)

während für idealplastischen Werkstoff \( (T = 0) \) wieder der Mises'sche Ansatz anfällt.

Zusammenfassung

Im Gegensatz zur Mises'schen Theorie wird im vorliegenden Aufsatz zur Beurteilung der Werkstoffanstrengung das elastische Potential zu Grunde gelegt. Das führt auf die Hypothese von der elastischen Formänderungsarbeit, die auf Beltrami zurückzuführen ist und nur für den elastischen Bereich gültig ist. Für \( \nu = \frac{1}{2} \) erfolgt ein zwangloser Übergang zur Mises'schen Theorie. Durch Einführung einer elastisch-plastischen Querzahl ν_{ep} kann die Hypothese von der elastischen Formänderungsarbeit auf den elastisch-plastischen Bereich erweitert werden, wie in der Untersuchung gezeigt wird.

Non-Congruent Vaporization of Some Rare Earth Oxides

G. Trevisan and R. Depaus

(Z. Naturforsch. 28a, 37—45 [1973]; received 6 October 1972)

The vaporization of lanthanum and yttrium oxides has been studied at temperatures as high as 1 900 and 2 200 °C respectively, by means of high temperature mass spectrometry. Emphasis has been placed on the study of the phenomenon on first heating (transient stage). Both monoxide and atomic oxygen partial pressures were recorded and found to be time-dependent in the transient stage and in the case of the lanthanum oxide also dependent on the initial water content of the sample. Variations of the metal to oxygen ratio in the solid and the possible vaporization reactions are discussed.

1. Introduction

Extensive and systematic investigations of the vaporization processes of rare earth oxides have been carried out in the past years 1, 2, 3, 4. From mass-spectrometric measurements, the thermodynamic behavior of nuclear materials, IAEA Vienna, p. 417 [1962].

ponents of the vapour phase over these oxides in the temperature range 2 000–2 400 °C have been found to be the monoxide, atomic oxygen and minor quantities of the metal, so that the vaporization process might be attributed to the simultaneous occurrence of the following reactions

\[
\text{Me}_2\text{O}_3 (c) \rightarrow 2 \text{MeO} (g) + \text{O} (g), \quad (1)
\]
\[
\text{MeO} (g) \rightarrow \text{Me} (g) + \text{O} (g). \quad (2)
\]

The relative weight of reaction (2) has been found to be nearly negligible in this temperature range and relevant only in the case of the heaviest rare earths.

In the specific cases of the lanthanum and yttrium oxides the absolute equilibrium partial pressures and the related thermodynamic data have been calculated by means of weight loss experiments, assuming that only reaction (1) occurs.

Some authors have observed that an isothermal vaporization process can be subdivided into two stages characterized by varying values of the vaporization rate (transient stage) and constant values of this rate (steady state). Furthermore, at the end of the experiment the oxide is always darker in colour.

They tentatively explained these findings by supposing that during the transient stage the oxide vaporizes incongruently and oxygen is eliminated in excess of the stoichiometric rate, the sample thus turning to a slightly defective dark solid, which however, evaporates congruently in the steady state.

White and Ackermann report that after a typical experiment the formulas of the dark oxides were respectively \(\text{La}_2\text{O}_2.975 \pm 0.015\) and \(\text{Y}_2\text{O}_2.996\).

This paper represents a contribution to the study of the transient stage and deals with the results of isothermal vapour pressure measurements carried out with a high temperature mass-spectrometer.

2. Experimental

**Materials**

**Lanthanum oxide**

The lanthanum sesquioxide was obtained from Alfa Inorganics. The purity was reported to be 99.99 %. Two samples, A and B, were prepared, having respectively a high and a low hydroxide content at the time of their introduction into the furnace of the mass spectrometer. Both samples were first baked out at 1 000 °C in air to eliminate hydroxide and carbonate impurities. Sample A was then cooled in air during its loading into the Knudsen cell (10–15 minutes) which was introduced into the furnace of the spectrometer and outgassed overnight at 1 000 °C under vacuum. Sample B was cooled under vacuum, exposed to air during the loading of the cell and then treated as A.

**Yttrium oxide**

The yttrium sesquioxide was obtained from Alfa Inorganics. The samples were first heat-treated in air at 1 000 °C overnight and then outgassed at 1 200 °C under vacuum in the furnace of the spectrometer as in the case of the lanthanum oxide. The samples underwent a final outgassing at 1 700 °C for about two hours before the vaporization experiment was begun.

**Apparatus and procedure**

The Knudsen vaporization experiments were carried out at temperatures as high as 1 927 °C for the lanthanum oxide and 2 183 °C for the yttrium oxide in the high temperature furnace of a Nuclide Associates mass spectrometer type 90 HT following the technique described by Inghram and Drowart.

The Knudsen cells and liners which were made from tungsten, were first baked out at 2 200 °C in order to avoid any possible variation of the hole size as a consequence of recrystallization of the tungsten during the experiment. Knife edged holes of about 1 mm diameter and samples of about 0.5 g were used throughout. At the experimental temperature the samples sinter and take the form of small cylinders. The ratio of the area of the sample to that of the Knudsen hole was never lower than 100.

The temperature was measured by means of an automatic optical pyrometer (Pyro Photomatic) sighting a pyrometric hole of \(\oplus 1 \times 5 \text{ mm}\) which was drilled in the Knudsen cell 1 mm below the bottom of the sample. The pyrometer was calibrated directly at the melting point of alumina, taken as 2 051 ± 6 °C.

The melting point of alumina was detected by monitoring the \(\text{Al}^+\) ion current and recording the melting plateau.

The absolute pressures were obtained from the ion currents by means of a silver calibration, according to the relationship

\[
p_x = \frac{I_x T_x P_{AB} \gamma_x \sigma_x}{I_{AB} T_{AB} \gamma_x \sigma_x} \quad (3)
\]

where \(I_x\) are the ion currents, \(\gamma_x\) the gains of the electron multiplier, \(\sigma_x\) the cross sections for the electron,
The temperatures in °K at which the species i is evaporated and $P_i$ the partial pressures.

The electron multiplier gains were obtained by direct comparison of the Faraday cup and electron multiplier currents. The vaporization experiments were carried out at an electron energy of 25 eV for the lanthanum oxide and 45 eV for the yttrium oxide. The cross sections were obtained from published data and experimental ionization efficiency curves according to:

$$\left( \frac{\sigma_i}{\sigma_j} \right)_E = \frac{(l_i)_{\text{max}}}{(l_j)_{E}} \frac{(l_i)_E}{(l_i)_{\text{max}}} \left( \frac{\sigma_i}{\sigma_j} \right)_{\text{max}}$$

where $E$ = electron energy in eV.

The $(\sigma_{LaO}/\sigma_{La})_{\text{max}}$ ratio has been taken as 0.60 and the $(\sigma_{YO}/\sigma_{Y})_{\text{max}}$ one as 0.68.

The background does not interfere seriously at the mass numbers of the gaseous species coming from the vaporization reaction, except in the case of atomic oxygen.

In this case the oxygen ion current $I_{o}$ was measured by making use of a movable shutter which can separate the ion source from the Knudsen cell furnace chamber, so that:

$$I_{o} = (I_{o}) \text{ sh. on} - (I_{o}) \text{ sh. off} .$$

To make sure that $I_{o}$ refers only to the oxygen evolved in the Knudsen cell, and not to oxygen present in the furnace, the cell was brought out of alignment with the ion source chamber by means of a micrometric device and the oxygen ion current $(I_{o})'$ measured, keeping the shutter in its open position. $(I_{o})'$ was found to be equal to $(I_{o})$ sh. off.

Possible interactions with the container have been also taken into account, monitoring the tungsten containing species in the vapor phase as well as analyzing the total tungsten content of the specimen after the vaporization experiment. The interaction has been found to be not negligible, and will be treated more extensively in the following chapter.

Four isothermal vaporization experiments (A, B, C and D) were carried out with four different samples. A and B were lanthanum oxide samples and were vaporized at 1 927 °C. Sample A had a high initial hydroxide content and sample B a low one. Sample C was yttrium oxide pre-dried as described before and sample D the sintered cylinder as obtained from the experiment C, heated in air at 1 500 °C until its white...
colour was restored. Both C and D were vaporized at 2183 °C. The ion currents of monoxides and oxygen were plotted as functions of time (Figure 1). The zero of the time scale was chosen as the time at which the samples reached the experimental temperature starting from the final outgassing temperature. The time needed for this step was of the order of 10 minutes.

All the physical parameters considered in this paper are derived from ion current vs. time curves (see Figure 1), obtained from the experimental data by best fit treatment. From the ion currents the partial pressures were derived by means of the silver calibration (see above). From the partial pressures, the vaporization rates \( W \) and the fraction vaporized (defined as the ratio of the vaporized quantity to the initial weight of the sample) \( F_t \) were obtained by using Knudsen’s equation:

\[
Z_i = P_i (2 \pi M_i R T)^{-\frac{1}{2}}
\]

\[
Z_i = \frac{1}{s} \cdot \frac{dN_i}{dt},
\]

where

\( s \) = area of the Knudsen hole, \( N_j = \) number of models evaporating at any instant and the other symbols have their usual meaning.

By combining (6) and (7) and integrating to obtain the total number of moles evaporated at the time \( t \):

\[
(N_i)_t = \frac{s}{(2 \pi M_i R T)^{\frac{1}{2}}} \int_0^t - P_i dt
\]

both the total effusion rate \( (W) \) and the fraction vaporized \( (F_t) \) can in principle be calculated at any time according to:

\[
W = \sum W_i = \sum Z_i M_i = (2 \pi R T)^{\frac{1}{2}} \sum \frac{V_i M_i}{P_i},
\]

\[
F_t = \frac{\sum (N_i)_t M_i}{g_{MO} g_{O}}
\]

where \( g_{MO} \) is the initial weight of the sample in grams.

In order to give a quantitative description of the vaporization during the transient stage we write formally the following reactions:

\[
\xi La_2O_3 (c) + \frac{\xi}{2} La = (2\xi) + (\xi - \frac{\xi}{2}) LaO (g) + (\xi - \frac{\xi}{2}) O (g), \tag{11}
\]

\[
\xi Y_2O_3 (c) = (2\xi) + (\xi - \frac{\xi}{2}) YO (g) + \frac{\xi}{2} Y_1 + (\xi + \frac{\xi}{2}) O (g) \tag{12}
\]

where \( La_i \) and \( Y_i \) mean interstitial atoms in the oxide lattice and \( \xi \) and \( \xi \) are the stoichiometric coefficients. We define a parameter \( R \) as the ratio of the stoichiometric coefficients of MO to O in reactions (11) or (12)

\[
R = \frac{Z_{MO}}{Z_O} = \frac{(2\xi + \xi)}{(\xi + \xi)} = \frac{P_{MO}/P_O}{V_{MO}/V_{MO}}.
\]

The parameter \( R \) thus describes the tendency of the oxide to deviate from stoichiometry during the transient stage: if \( R \) approaches its steady state value from lower values, the solid will become oxygen deficient, and if \( R \) approaches the steady state starting from higher values, the solid will become metal deficient.

**Experimental results and discussion**

In agreement with published data \(^2\,^3\) we found that the gaseous phases in equilibrium with lanthanum and yttrium oxides were composed of the respective monoxides, atomic oxygen and minor quantities of atomic metal.

The \( P_{LaO}/P_{La} \) ratio at 1927 °C and the \( P_{YO}/P_{Y} \) one at 2183 °C were found to be about 13 and 26 respectively throughout the whole isothermal vaporization experiment. In agreement with published data \(^2\,^3\,^4\) we also found that the white lanthanum and yttrium sesquioxides turn dark grey under vacuum at temperatures of the order of 1900 °C.

Possible reactions of the lanthanum and yttrium oxides with the tungsten container were carefully checked, by monitoring the tungsten containing vapour species in the gaseous phase and analyzing the samples after the experiments.

The only tungsten containing vapour species observed were \( WO_2, WO \) and \( WO_3 \) in order of abundance. It was observed that the pressure of these species is directly proportional to the atomic oxygen partial pressures. In the case of the lanthanum oxide at 1927 °C at the steady state, a pressure of \( 3.8 \times 10^{-9} \) atm was measured for the species \( WO_2 \), the ratio being \( P_{WO} : P_{WO_3} = 1 : 0.46 : 0.13 \).

For the yttrium oxide at 2183 °C it was observed that these species are only detectable during the initial phase of the vaporization and become undetectable at the steady state.

The chemical analysis of the samples after a typical vaporization experiment are given in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tungsten content weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>lanthanum oxide</td>
<td>0.116</td>
</tr>
<tr>
<td>yttrium oxide</td>
<td>6.8</td>
</tr>
</tbody>
</table>

It must be pointed out here that at the end of the experiment the sintered cylinders both of lanthanum and yttrium oxide look black, but that in the case of the yttrium oxide the lateral wall of the liner appeared to be covered by a layer of a red compound. Both red compound and black cylinder were separat-
ely analyzed: the cylinder was found to contain some less tungsten than the red compound (5.96 weight %). For our purposes however we have neglected this small difference and have considered that the composition of the black cylinder and of the red compound be approximately the same.

The red compound has been also analyzed by means of X-ray diffraction: the X-ray data could not be referred to any structure reported by the ASTM system; even though similarities were found with the patterns of certain \( Y_2O_3 - WO_3 \) solid solutions.

The samples of lanthanum and yttrium oxide resulting from the vaporization experiments were re-heated in air or oxygen at 1200-1500 °C for periods of the order of days until a constant weight had been achieved and checked for colour and weight variations. The lanthanum oxide on being held at 1500 °C for 7 days did not change its colour nor showed any tendency to increase its weight. On the other hand the yttrium oxide after a heating at 1200 °C lasting 64 hrs became white in colour and increased its weight by 0.62 ± 0.1 %, which in terms of stoichiometric coefficients corresponds to a variation between \( Y_2O_3 \) and \( Y_2O_2.915 \cdot 0.15 \).

From the above data, we see that in the case of both lanthanum and yttrium oxides on first heating a non-congruent vaporization takes place.

Figure 2 presents the partial pressures of the monoxides and of the atomic oxygens as functions of the fraction vaporized for the samples A, B, C and D. It is evident from these plots that, in agreement with the cited data, the partial pressures of the involved species are time dependent on the first heating. It appears also that the partial pressures of the monoxides (and atomic metals) on one side and those of the atomic oxygen on the other, approach their steady states following opposite paths. In agreement with the equilibrium constants for the reaction (11) and (12)
\[ K = \frac{P_{MO} P_{O}}{a_{MgO}} \]

where \( a_{MgO} \approx 1 \) is assumed.

After the transient period the partial pressures do not show any tendency to further changes in the time considered.

As far as the \( P_{MO}/P_M \) ratios are concerned, it must be pointed out here that in the case of the lanthanum oxide, it is much lower and in the case of the yttrium oxide somewhat higher than those reported by White and Ames. The high value of \( P_{La} \) cannot be explained however in terms of fragmentation of the LaO molecule. Indeed experimental ionization efficiency curves as well as the cited sources show that the ion \( La^+ \) does not originate from the fragmentation of the LaO molecule.

From the plots in Fig. 2 the influence of the hydroxide content on the form of the pressure isotherm for the case of the lanthanum oxide is also apparent.

In particular, we see that the isotherms of lanthanum monoxide become smoother and reach their steady state value more slowly as the initial content of hydroxide is reduced. On the other hand, the isotherm of the atomic oxygen shows the opposite trend, i.e. when the initial content of hydroxide is reduced, the curve is steeper and the equilibrium value is reached faster.

A more comprehensive picture of the phenomenon of the transient stage of vaporization can be drawn in terms of parameter \( R \).

As also demonstrated in separate experiments, the parameter \( R \) (see Fig. 3) approaches the steady state value in a time, which is inversely proportional to the temperature, directly to the initial weight of the sample and in the case of the lanthanum oxide depends on the initial state of hydration of the sample.

From plots in Fig. 3 it appears that at the steady state the parameter \( R \) has a value of about 2.3 for the lanthanum oxide and 2.8 for the yttrium oxide. Taking into account the uncertainty relevant to the procedures adopted, these values appear as very near to 2, which is the value of \( R \) in the stoichiometric reaction (1). The problem of the determination of the accuracy and reliability of the partial pressures obtained employing the theoretical cross sections is still a matter of
We have kept a pragmatic attitude to this problem and have approached it as follows. In Table 2 the transient stage a compositional shift takes place that causes the solid to reach a metal to oxygen ratio difference of Eq. (8), assuming that the starting composition calculated via Eq. (8) and that obtained by means of reoxidation. From the plots in Fig. 2 it is also evident that the composition of the yttrium oxide during the transient stage is more oxygen deficient than that reported by Ackermann 4 for the same oxide at 2 300 ± 200 °C, but still within the stability limits given by the other as an overall proof on the reliability of the methods adopted.

Table 2. Comparison of the weighed (G) and calculated (G') weight losses on vaporization and of the experimental (W) and literature vaporization rates (W'). Sample B is lanthanum oxide and sample C is yttrium oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. °C</th>
<th>G g</th>
<th>G' g</th>
<th>W g cm⁻² sec⁻¹ × 10⁵</th>
<th>W' g cm⁻² sec⁻¹ × 10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1927</td>
<td>0.035</td>
<td>0.017</td>
<td>2.1</td>
<td>3.9</td>
</tr>
<tr>
<td>C</td>
<td>2183</td>
<td>0.013</td>
<td>0.008</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Therefore we have taken the satisfactory agreement between G and G' on one side and between W and W' on the other as an overall proof on the reliability of the methods adopted.

The experimental vaporization rates (W) are compared with the ones reported in the literature (W').

From these plots it is also evident that, in the case of lanthanum oxide the parameter R approaches its steady state value from higher values and that the higher the initial hydroxide content of the lanthanum oxide is, the higher is the starting value of R.

Therefore in the case of the lanthanum oxide during the transient stage the non-congruent vaporization results in a monoxide overloss and its extent is directly proportional to the initial hydroxide content of the sample.

Thus, if the starting composition of the oxide were stoichiometric, the overloss of monoxide should give rise, after the vaporization experiment, to a hyper-stoichiometric solid of the type La₂O₃ + y.

In the case of the yttrium oxide we observe that the parameter R approaches its steady state value from lower values, therefore indicating that the transient stage produces an oxygen deficient oxide. The exploitation of Eq. (8), assuming that the starting composi-

Fig. 4. Vaporization rate ($W$) vs. fraction vaporized ($F_t$) for samples A, B, C, D.

Different from the stoichiometric one. The term $(M/O)_{exp}^{-\left(M/O\right)_{theor}}$ is usually positive and directly proportional to the temperature. As required by the different exponents of the $P_{MO}$ and $P_O$ terms in the equilibrium constant (15), the curves $P_{MO}$ vs. $F_t$ and $P_O$ vs. $F_t$ are not symmetric. After the transient stage however, the vaporization occurs congruently, or at least according to a reaction of the type (11) or (12) where $\xi$ is very near to one and $\zeta$ very near to zero. An analysis of the published data 10, 11 shows that also the thorium and zirconium oxides undergo the transient stage of vaporization. Reportedly their monoxide partial pressures increase during a time interval that is inversely proportional to the temperature. No data are reported on the oxygen partial pressures. We therefore suggest here that the majority of the refractory oxides might behave during the transient according to the yttrium oxide pattern.


The behaviour of the lanthanum oxide however is clearly in contradiction with this picture. In fact the trend of the parameter $R$ and the vaporization rate during the transient appear to be opposed to those of the yttrium oxide.

Thus, applying to the lanthanum oxide the adopted reasoning, we should be forced to the absurd conclusion that the lanthanum oxide becomes hyper-stoichiometric as a consequence of the initial non-congruent vaporization.

To tentatively explain our findings, we have related this deviation from the general trend to the hygroscopicity which is a property which makes lanthanum differ from the cited oxides.

We would guess that the solid, at time zero on our scale, contains lanthanum interstitials in excess of the equilibrium concentration at 1927 °C and would relate this initial excess to a reaction of the type

$$xLa(OH)_3 + La_2O_3 \rightarrow La_2O + 1.5 O_3 + 1.5 H_2O + 1.5 H_2O$$

which might occur during the outgassing of the sample in the mass spectrometer furnace at 1000 °C.

Acknowledgements

Acknowledgements are due to Prof. S. Pizzini of the Electrochemical dept. of the Milan University, Italy, for encouraging discussions.

Thanks are also due to Dr. G. Pellfgrini (C. C. R. Petten) and to members of the staff of the Analytical chemistry dept. of the C. E. N. Mol, Belgium for the analytical support offered to this work.

Verzögerte Fluoreszenz von Mischkristallen aus Benzophenon und aromatischen Kohlenwasserstoffen

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Delayed Fluorescence of Benzophenone-Aromatic Hydrocarbon Mixed Crystals

The earlier observation of delayed fluorescence in mixed crystals of aromatic hydrocarbons in benzophenone is studied by time-resolved spectroscopy using methyl-coronene, pentaphene, anthanthrene and 1,8,9-peri-naphtho-xanthene besides naphthalene as guests. Host-guest triplet annihilation is identified as the mechanism of delayed fluorescence. Naphthalene as an additional guest component acts as trap for the triplet excitation of the host and further increases the delay of fluorescence emission.

Einleitung
