

APPLICATION OF HIGH-TEMPERATURE THERMAL METHODS TO THE INVESTIGATION OF REFRACTORY AND RELATED MATERIALS

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ABSTRACT

Selected high-temperature thermal methods are discussed and investigated refractory materials are reviewed on the basis of conference contributions.

INTRODUCTION

High-temperature thermal methods have been used for the study of refractory compounds. Mo, Nb, V and Cr alloy systems were prepared and their melting diagrams were constructed. For the investigation of phase relationships in the system $\text{Sm}_2\text{O}_3\text{--HfO}_2$, a thermal device made of tungsten was used up to 2600°C. By means of an HDTA-8 apparatus under vacuum or an inert gas atmosphere, $\text{Si}_3\text{N}_4\text{--TiN}$, $\text{Si}_3\text{N}_4\text{--VN}$ and $\text{Si}_3\text{N}_4\text{--ZrC}$ systems were investigated, and in an atmosphere of air Si_3N_4 powders were studied by continuous TG, DTA and DTG-TG. Silicon nitride synthesized under high pressure possesses a higher resistance to oxidation in an air atmosphere. Oxidation of $\text{TiC}_{1-x}\text{N}_x$ ($x = 0\text{--}1$) ceramic material was examined by means of a potentiometric sensor for evolved gas analysis (EGA) with addition TG and DTA methods. A complex thermal analysis method was used to study the oxidation processes of diamond powders.

DISCUSSION

DTA apparatus equipped with photocells has been used to study the melting diagrams of the systems Mo-(Nb, V, Cr), V-(Nb, Cr) and Mo-V-(Nb, Cr) and the metastable diagram of the chromium-carbon system [1]. The use of photocells as temperature elements permitted the DTA of alloys of refractory materials up to 3000 K. By the DTA method

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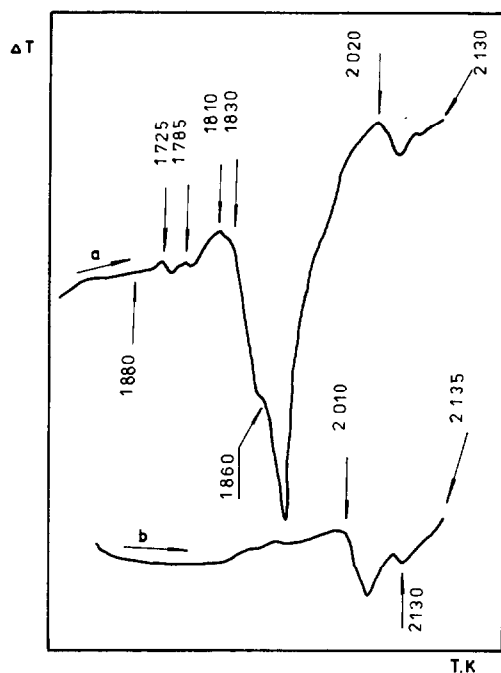


Fig. 1. DTA curves of the chromium-graphite mixture. (a) Heating, (b) cooling.

complete melting diagrams of binary and ternary systems were constructed. Liquidus curves for most of the systems studied and the melting diagram of the Mo-V-Cr system have been determined for the first time.

Endothermic effects below the stable equilibrium solidus temperature of the chromium-carbon system have been observed. Figure 1 shows DTA heating curves for a mixture of chromium and graphite powders. The effects at 1830, 1860 and 2020 K on the heating curve belong to the stable Cr-C equilibrium diagram and those at 1680, 1725, 1785 and 1810 K are due to metastable eutectics. The second heating curve features only the effects of the stable equilibrium solidus (2010 K) and liquidus (2130 K). From the thermal effects obtained the phase diagram of the system Cr-C was constructed.

DTA was also applied to the investigation of high-temperature polymorphic transitions of pure lanthanide oxides and to determine their melting temperatures [2].

A thermocouple wire was the basis of a DTA device working in a controlled gaseous environment up to 2600°C. A thermal device made of tungsten was used with WRe 20-W thermocouples. Thermal curves were recorded with a Khurnakov pyrometer. TA was carried out in a solar furnace of capacity 1.5 kW using a pyrometric system working in the wavelength range 0.65–2.0 μm as a temperature transducer. The effective-

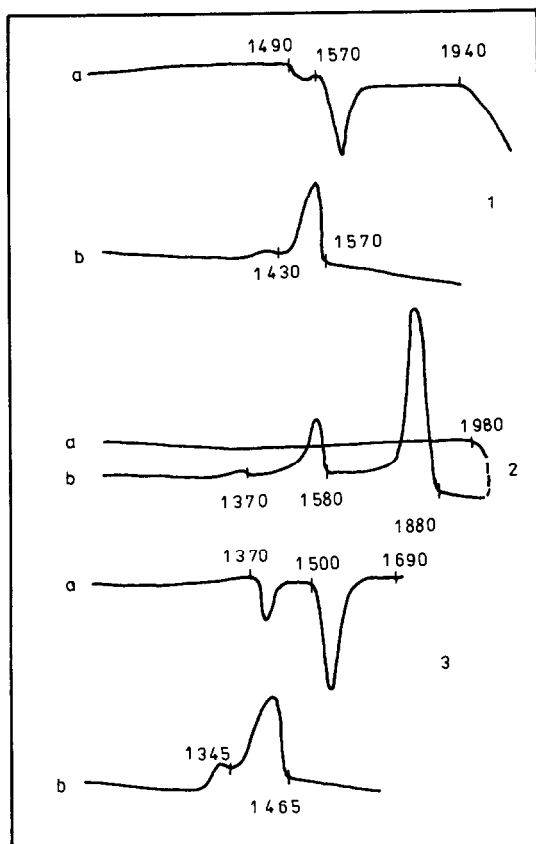


Fig. 2. DTA curves for the (1) Si_3N_4 -TiN, (2) Si_3N_4 -VN and (3) Si_3N_4 -ZrC mixtures. (a) Heating, (b) cooling.

ness of the application of DTA and TA to phase relationships in systems formed of the highly refractory oxides Sm_2O_3 , HfO_2 was demonstrated.

For the study of the interaction of silicon nitride with nitrides of titanium, vanadium and zirconium carbide, a thermal method was used [3]. Thermal treatment of starting mixtures and DTA measurements on an HDTA-8 apparatus were simultaneously possible in the temperature range 800–2600 K under vacuum or in an inert gas atmosphere. The HDTA-8 apparatus was calibrated by melting iron and platinum. In addition to the DTA method, X-ray, metallography, microhardness and weight loss measurements were used. By means of these methods, for the system Si_3N_4 -TiN it was determined that above 1940 K Si_3N_4 dissociates when TiN is present (Fig. 2), giving silicon and gaseous nitrogen. The free silicon reacts with TiN and forms titanium silicides, and gaseous nitrogen leaves the reaction area. The titanium silicides and excess of silicon are in the liquid state at 1940 K and crystallize at 1570 and 1430 K, respectively, when cooled.

Thermal treatment of specimens of the system $\text{Si}_3\text{N}_4\text{-VN}$ was performed at temperatures up to 1900 K. Exothermic peaks at 1880, 1580 and 1370 K were found on the cooling curve. By X-ray analysis, VSi_2 , silicon, $\beta\text{-Si}_3\text{N}_4$ and traces of VN were identified. On the heating curve of specimens of the system $\text{Si}_3\text{N}_4\text{-ZrC}$ up to 1920 K, two endothermic peaks were found (Fig. 2). Two exothermic peaks were found on the cooling curve. The phases $\beta\text{-Si}_3\text{N}_4$, ZrC, ZrSi_2 , $\beta\text{-SiC}$, silicon and ZrC_xN_y were identified.

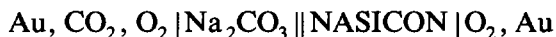
It was stated that dissociation in the systems $\text{Si}_3\text{N}_4\text{-MN}$ (MC) leads to the appearance of silicon and monatomic nitrogen. Silicon interacts with MN (MC) and forms the corresponding silicides. Nitrogen either leaves reaction zone as N_2 or forms carbonitrides, as in the case of ZrC_xN_y .

The resistance of Si_3N_4 to scaling after preparation at high pressures was studied by continuous TG, DTA and DTG-TG [4]. Derivatographic studies of Si_3N_4 powders showed that in an atmosphere of air significant polymorphic transformations occurred in silica formed from free silicon at 473–523 K, and adsorption-desorption processes also occurred. The low adsorption activity of the powders under study can be explained by the properties of the fine crystalline structure of silicon nitride. The presence of silicon atoms can be explained by the fact that each of the fourth hybrid sp^3 orbits of the Si atom is overlapped by a hybrid sp^2 orbit of the N atom.

The oxidation isotherms for high-pressure samples are located much lower than those for hot-pressed samples. Samples synthesized at 7000 MPa do not suffer any oxidation at temperatures up to 1473 K. The DTA results confirmed that the silicon nitride after high-pressure action is inert to oxidation up to 1773 K. On the oxidation thermogram for Si_3N_4 the DTG-TG curves are straight lines; the small exothermic peak on the DTA curve in the range 813–1103 K is related to the formation of extremely thin β -quartz and α -cristobalite films and the endothermic peak at 1593–1710 K is related to the formation of fibrous silica.

It was concluded that silicon nitride synthesized under high pressures possesses a higher resistance to oxidation in an air atmosphere. It was shown that the improvement in thermal stability is related to the nature of fibrous silicon dioxide formed on the surfaces of oxidized samples.

Maruyama [5] studied the oxidation of $\text{TiC}_{1-x}\text{N}_x$ ($x = 0\text{-}1$) ceramic powder by complex thermal methods and EGA using a newly developed potentiometric CO_2 sensor. The sensor is composed of Na_2CO_3 and NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$), which are both sodium ion conductors, and is based on the following electrochemical cell:



The electromotive force is expressed by the Nernst equation:

$$E = E_0 - (2.303RT/2F) \log(a_{\text{Na}_2\text{O}} P_{\text{CO}_2} / 1.01 \times 10^5)$$

where E_0 is a constant, R the gas constant, T the absolute temperature, F

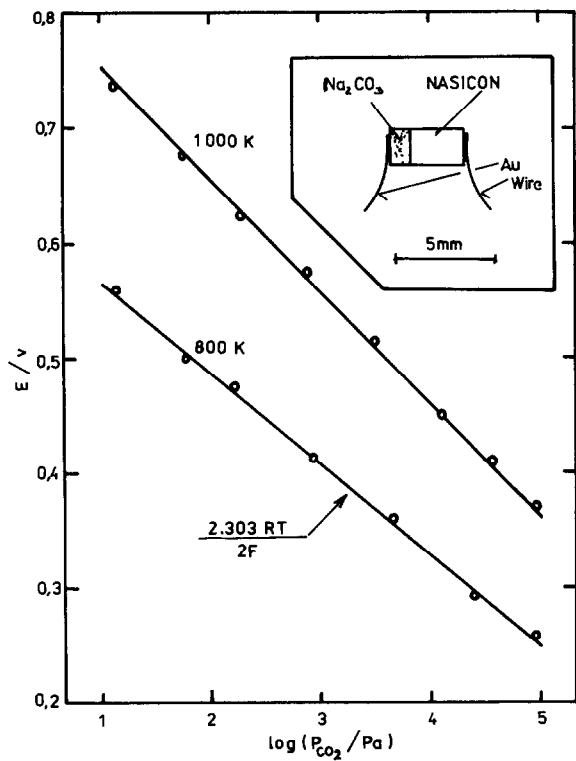


Fig. 3. Partial pressure of CO_2 vs. e.m.f.

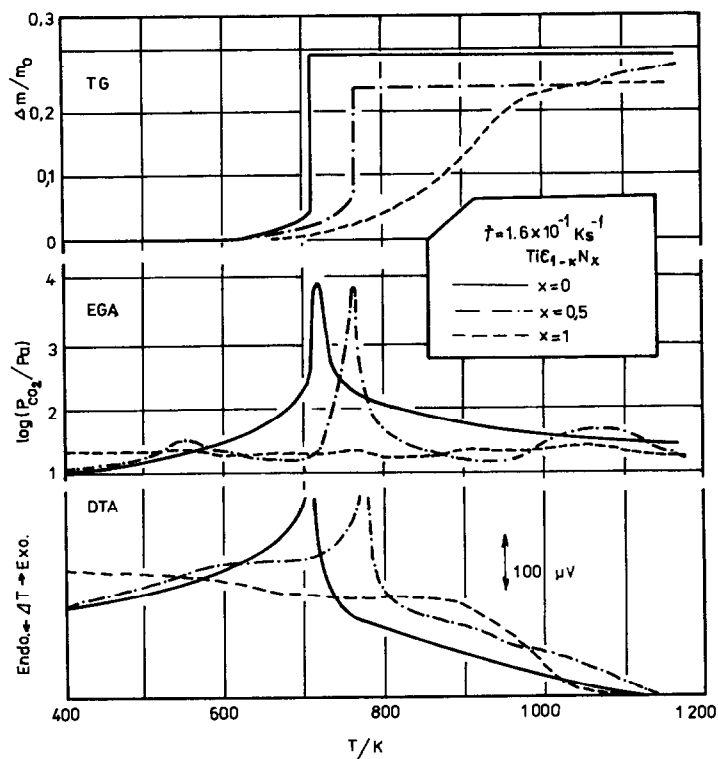


Fig. 4. TG, EGA and DTA curves using the CO_2 sensor.

the Faraday constant, $a_{\text{Na}_2\text{O}}$ the activity of Na_2O in NASICON and P_{CO_2} the partial pressure of CO_2 in pascals. With a fixed activity of Na_2O in NASICON, the partial pressure of CO_2 can be calculated from the measured e.m.f. Figure 3 shows the typical e.m.f. characteristics of the sensor.

Figure 4 shows typical TG, DTA and EGA curves at a heating rate of $1.6 \times 10^{-1} \text{ K s}^{-1}$. The CO_2 sensor was held at 900 K. It can be seen that the CO_2 sensor is more sensitive than TG. Explosive oxidation is observed at 710 K, with a decrease in the heating rate. Samples with higher carbon concentrations explode at lower temperatures and heating rates. The DTA curves showed that the heat evolved decreased with increase in x . The sample with $x = 1$ yielded small amounts of anatase and rutile, then the anatase was transformed into rutile until the oxidation was complete. The explosive oxidation yielded only rutile.

The oxidation can be described by the equation



and the value of P_{CO_2} can be calculated from the observed curve and the flow-rate of oxygen. The calculated and observed values are compared in Fig. 5 for the early stage of oxidation. In first case ($x = 0$) oxidation proceeds mainly through the described reaction; when $x = 0.5$ there is a

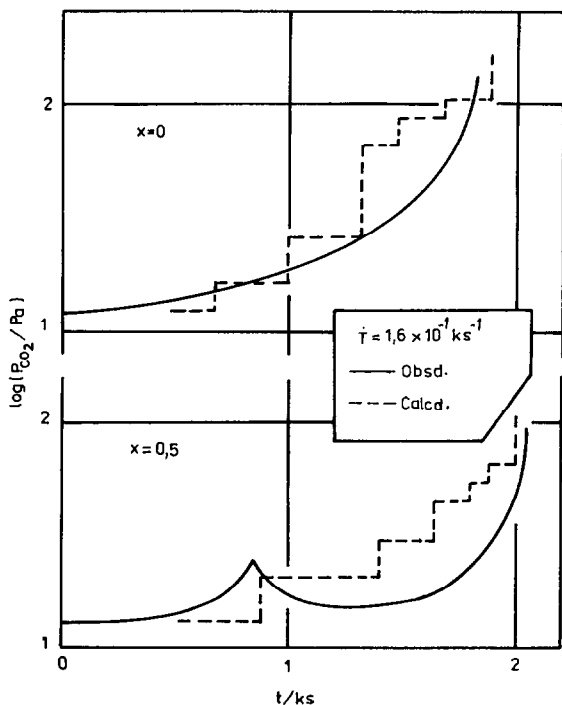


Fig. 5. Calculated and observed values of partial pressure of CO_2 .

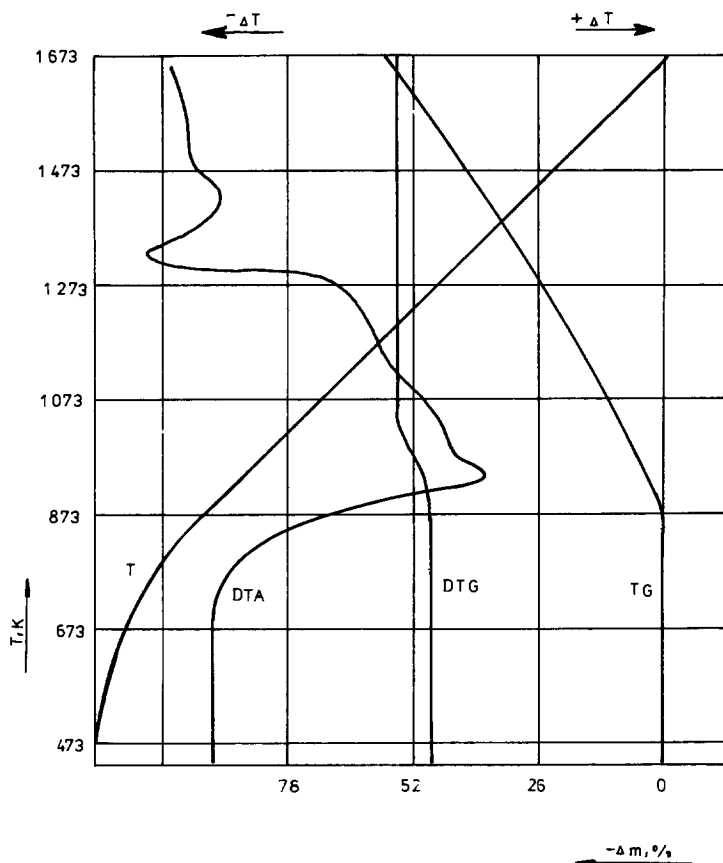


Fig. 6. Typical thermogram curves of synthetic diamond powder.

significant difference between the calculated and observed values. This can be explained by the dissolution of oxygen in interstitial sites.

Complex thermal analysis was also applied to study the oxidation processes of diamond powders [6]. DTA-DTG-TG was carried out on an MTB 10-8 thermal microanalyser (Setaram, France).

A typical thermogram for the oxidation of one type of synthetic diamond powder is shown in Fig. 6. The studies were carried out at atmospheric pressure in air. The thermal analysis results show that diamond oxidation which follows a multi-stage mechanism. Variations in the mechanism are determined by the crystal quality, the impurity content and changes in the composition of the reaction mixture.

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