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TA METHOD APPLIKATION TO THE HIGHEST REFRACTORY OXIDE SYSTEMS INVESTIGATION

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ABSTRACT

DTA method application to the controlled gaseous environment up to the temperature of 2600°C and TA method application in air using solar heating up to the 3000°C are considered. Phase trans formations in the highest refractory systems based on the lanthanide oxides: zirconium, hafnium, yttrium oxides as well as IIA subgroupe element oxides have studied by these methods.

INTRODUCTION

TA method has succeeded in phase equilibration investigation in salt and metal systems. The study of oxide systems with the mel ting temperature above 2000°C using DTA method has not yet found a sufficient development. It is due to the deficiences of the har dware, to the compatibility problem of the test material and container to the atmosphere reaction. The oxide TA systems radiation heating provides the measurements in air and in different gaseous environments. Since heating occures only for the sake of radiation the test object contamination should be excluded.

MEASURING METHOD

The idea of string thermocouple by J.A. Kocherghinsky [1] is used in this investigation. It lies in the base of DTA devise design working in the controlled gaseous environment up to the 2600°C. Thermodevise made of tungstem is used with the thermocoup les WRe 20-W, differentially connected. Termal curves record was performed by N.S. Khurnakov pyrometer, providing a low noise level The devise calibration was done according to the fine metal and oxides melting points. Phase transformation temperatures in the oxide systems were defined during heating, cooling curves were read with the aim of quality picture obtaining owing to the oxide increased tendency to supercooling.

Oxide systems TA is carried out on the solar furnace the capacity of which is 1,5 kW using the pyrometric systems working in the wave length range from 0,65 to 2,0μm as a temperature transducer. The temperature determination method according to the rotaling blade [2] and according to partially melted sample surfase [3] was used for the oxide TA carring out. In both cases the cooling curves are recorded after the radiant flux is cut off. Aluminium, yttrium, zirconium, hafnium oxides as well aslanthanide and scandium oxides were used as reference material in the temperature range 2000–2900°C.

EXPERIMENT RESULTS

DTA method application has allowed to investigate high temperature polymorphic transitions of the lanthanide pure oxides and to determine their melting temperatures. More precise melting tem peratures and rare earth oxides polymorphic transformations are summarised in Table.

Oxide	Melting temp. °C	Transf. temp. H→X,°C	Transf. melt. A→H,°C	Transf. melt. B→H,°C	Transf. melt. B→A,°C	Transf. melt. C→H,°C	Transf. melt. C→B,°C
La_2O_3	2310	2100	2030				
Ce_2O_3	2240	2170	2120				
Pr_2O_3	2280	2130	2030				
Nd_2O_3	2300	2180	2060				
Sm_2O_3	2310	2225	2070		1870		
Gd_2O_3	2410	2370	2200	2170	2170		
Tb_2O_3	2400	2370	2175	2175	2160		
Dy_2O_3	2400	2385	2190	2200	2190		1980
Y_2O_3	2440		2390			2390	
Ho_2O_3	2400			2200			2190
Er_2O_3	2420					2320	
Tm_2O_3	2410					2350	
Yb_2O_3	2450					2380	
Lu_2O_3	2510						
Sc_2O_3	2470						

HfO_2 influence on the high temperature polymophic transitions of the lanthanide oxides was studied. At HfO_2 introducing the polymorphic transition temperatures of the lanthanide oxides may re duce (X⇄H), (H⇄A) and increase (C⇄B). The phase field boundares for the given forms are determined by DTA data which allowed to define eutectoid range in the investigated systems.

It was found out that HfO_2 maximum permissible solubility in polymorphic forms X, H, A and B reduces and in C-form encreases with the lanthanide atomic number growth.

Eutectic melting temperature is raised with the lanthanide atomic number growth. It correlates with the pure oxide melting temperature increase[4] .

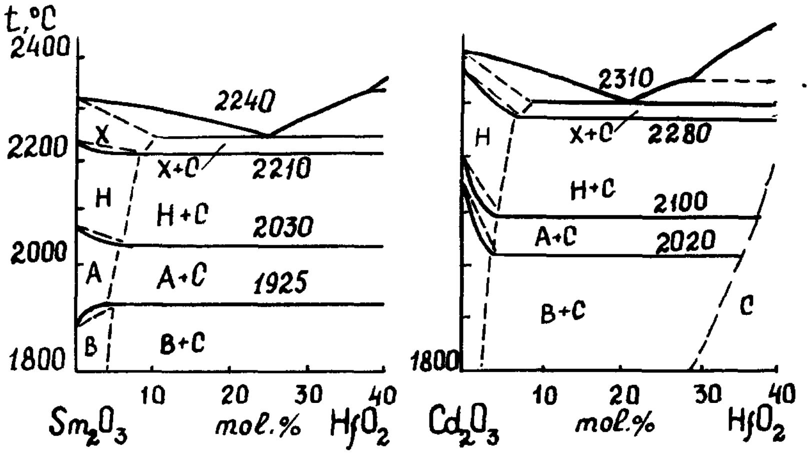

Fig. 1. Phase diagram elements of the lanthanide oxides-hafnium oxide.

High temperature polimorphism ZrO_2 and HfO_2 was analysed and the regularity of rare earth oxide influence on the Hfo_2 phase transformation temperature change was studied. It was found out that HfO_2 mon.⇄tetr. transformation ~~in to cubic form~~ occures at 1830± 20°C, the transformation in to cubic form occures at 2530± 50°C. ZrO_2 tetr.⇄cub. transformation occures at 2330± 30°C.

Lanthanide oxides reduce mon.⇄tetr. transition temperature from 1830 to 1750-1780°C along the lanthanide row. Rare earth oxides effect the best cubical modification HfO_2, extending it concentration and temperature.

At the highest refractory systems study (HfO_2-CaO, HfO_2-MgO) eutectic and eutectoid points references (DTA) were established and systems liquidus (TA) was determined[5, 6].

Melting temperature of the congruently melting composition $CaHfO_3$ equal to 2590± 30°C was defined and for the first time it was found out this composition to undergo some reverse polymorphic transformation rhomb.⇄cub. modification[7] at 2000± 10°C.

The analogous transformation temperature of the $CaZrO_3$ composition was 2000 ± 10°C as well, melting temperarure was 2510 ± 30°C.

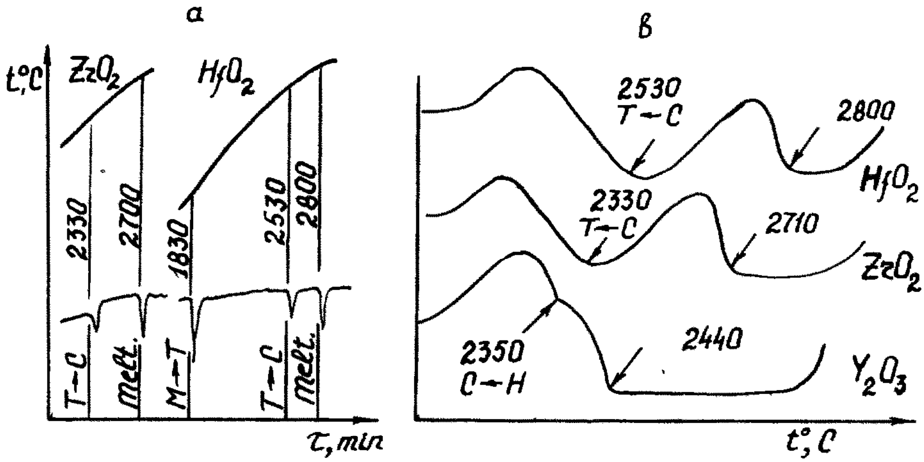

Fig.2(a), (b). DTA curves ZrO_2 and HfO_2 and TA curves HfO_2, ZrO_2 and Y_2O_3.

The analogous transformation temperature of the $CaZrO_3$ composition was 2000 ± 10°C as well, melting temperature was 2510 ± 30°C.

Phase diagrams of the oxide systems formed by HfO_2 with the rare earth oxides [8] were studied using the above mentioned methods.

CONCLUSION

In this paper we have shown the effectiveness of DTA and TA application to the phase relations in the systems formed of the high refractory oxides.

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