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INTERACTION ANALYSIS OF SYSTEMS INVOLVING REFRACTORY COMPOUNDS BY MEANS OF DTA METHOD

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ABSTRACT

Using DTA and other methods, the study on interaction of silicon nitride with nitrides of titanium, vanadium and zirconium carbide was carried out. The typical features of such interactions are the effect of Si_3N_4 dissociation stability and the formation of transient metals' silicides.

INTRODUCTION

One of the promising trends in further development of material science of refractory compounds (ceramics) is to use them in different compositions with refractory metals and other refractory compounds.

Silicon nitride Si_3N_4, being one of the superhard refractory compounds, is widely used now in different branches of industry (1). Dense articles made of Si_3N_4 are usually obtained either using super-high pressures and temperatures (that is disadvantageous), or using MgO, Al_2O_3, Y_2O_3 etc. additives, that activate sintering and decrease considerably temperature and compacting pressure. The character of interaction in these systems is well investigated (2).

However, information about Si_3N_4 interaction with other refractory compounds is very limited. Particularly, interactions of Si_3N_4 with refractory transient metals' nitrides and carbides are almost unknown.

The present paper deals with the results of Si_3N_4 interaction with TiN, VN and ZrC.

MEASURING METHODS

In our experiments, we used HDTA-8 set, in which thermal treatment of starting mixtures and DTA measurements were simultaneously possible in 800-2600 K temperature range in vacuum or inert gas atmosphere (helium, argon, nitrogen) under the pressure

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up to 0.3 MPa. The analysis of HDTA-8 heating chamber design has shown that thermal treatment of specimens in the chamber occurs under environment mass exchange conditions allowing the volatile components leave the reaction area.

Explored specimens were placed into covered crucibles. The weight of every specimen was not more than 0.2 g . Heat contact between specimen and thermocouple junction was realized through the crucible bottom. The recording of thermal curves was carried out in T - ΔT plot. HDTA-8 was calibrated by melting iron and platinum. The accuracy of DTA peak temperature measurements was $\pm$10 K.

Except the DTA method, XRD, metallography, microhardness and weight loss measurements were used.

Starting mixtures were composed by careful mixing of Si_3N_4, TiN, VN and ZrC powders with grain size 5-10 micron in acetone. Mixtures were cold compacted under the pressure of 910 MPa into pellets of 5 mm in diameter and 2 mm height. Heating and cooling were performed in high purity helium atmosphere under the excess pressure of 0.03-0.1 MPa with 80 degrees/minute rate. Crucible with cover of the same material was used as reference body. All specimens were exposed to maximal temperature for 0.3-1 hour.

RESULTS AND DISCUSSION

The system Si_3N_4-TiN. Specimens were thermally treated at 1940 K in helium atmosphere for 20 min . Weight losses after thermal treatment costituted 6-9 wt.%.

On heating thermal curve of sample two endothermic peaks at 1490 and 1570 K were observed (fig.1,a). When samples were heated

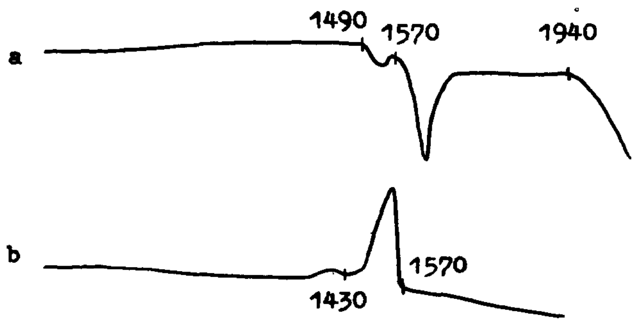

Fig. 1. Thermal curves of specimen Si_3N_4-TiN:
a - heating; b - cooling

above 1940 K, an endothermic peak indicative of Si_3N_4 dissociation start was found. On the cooling curve (fig.1,b) two exothermic peaks at 1570 and 1430 K were found. The presence of thermal peaks testifies to liquid appearance in samples and therefore reaction realization in the system.

XRD analysis showed the presence in specimens of initial ß-Si_3N_4, TiN as well as new phases Ti_5Si_3, $TiSi_2$ and silicon, that appear as a result of heat treatment. No other lines were found on X-ray powder photodraphs. Presence of initial compounds and products of their interaction in specimens testifies to incomplete reaction pass.

The data presented above suggest the following interaction mechanism. At and above 1940 K silicon nitride considerably dissociates when TiN is present. The products of dissociation are silicon and gaseous nitrogen. Nitrogen leaves the reaction area and causes the observed weight losses. Free silicon, being at temperature mentioned above in liquid high-dispersive state, reacts with TiN and forms titanium silicides and gaseous nitrogen. The titanium silicides and excess silicon are in liquid state at 1940 K and crystallize at 1570 and 1430 K when cooled.

The system Si_3N_4-VN. Thermal treatment of specimens was performed at 1900 K in helium atmosphere for 20 min. Weight losses made up to 30 wt.%. On the cooling curve exothermic peaks at 1880, 1580 and 1310 K were found (fig.2). XRD analysis showed the

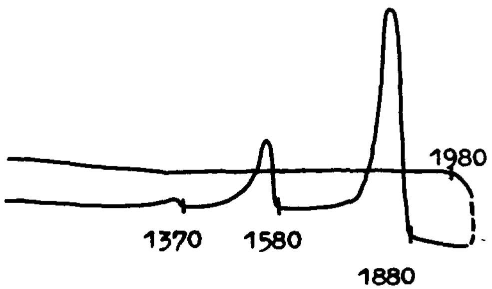

Fig. 2. Thermal curves of specimen Si_3N_4-VN.

presence of VSi_2, silicon, ß-Si_3N_4 and VN-traces in specimens. Three peaks on cooling curve and considerable weight losses testify to the violation of specimens' initial composition towards reduction of nitrogen content.

The system Si_3N_4-ZrC. Thermal treatment of specimens was carried out in helium atmosphere at 1920 K during 1 hour. On the heating curve of specimens two endothermic peaks were found at 1640 and 1770 K (fig.3,a). Two exothermic peaks were found on the cooling curve (fig.3,b). According to the XRD data after thermal treat-

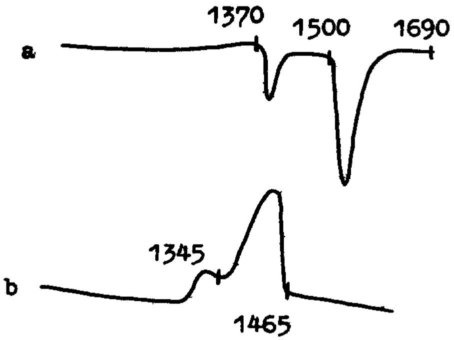

Fig. 3. Thermal curves of specimen Si_3N_4-ZrC:
a - heating; b - cooling

ment specimens contained the following phases: ß-Si_3N_4, ZrC, $ZrSi_2$, ß-SiC, silicon and ZrC_xN_y. Therefore, melting and crystallization peaks on thermal curves can be attributed to $ZrSi_2$ and silicon.

CONCLUSIONS

The basic influence on exchange reaction pass in the systems Si_3N_4-MeN(MeC) renders Si_3N_4 stability. Its dissociation leads to the appearance of silicon and monatomic nitrogen. Silicon interacts with MeN(MeC) and forms the corresponding silicides. Nitrogen either leaves reaction zone as N_2 or forms carbonitrides, as in the case of ZrC_xN_y.

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