PHYSICOCHEMICAL AND STRUCTURAL INVESTIGATIONS OF MATERIALS

PHYSICOCHEMICAL INVESTIGATION OF THE REACTION OF COMPONENTS OF THE Si−Al−O−N−Ti SYSTEM IN THE Si₃N₄−Al₂O₃−AlN−SiO₂−TiN−TiO₂ REGION

II. SUBSYSTEMS Si₃N₄−AlN, TiN−AlN, Al₂O₃−AlN

V. G. Khoruzhaya, P. S. Martsenyuk, K. A. Meleshevich, and T. Ya. Velikanova

UDC 546.173:546.28:546.3:669.018.85

The reaction of components of the Si−Al−O−N−Ti system in its elements Si₃N₄−AlN, TiN−AlN, and Al₂O₃−AlN was investigated by differential thermal and x-ray diffraction analysis. It was established that upon hot pressing mixtures of Si₃N₄ and AlN (up to ~1950°C) free silicon is formed by the decomposition of Si₃N₄, which reacts with oxygen present as an impurity to form SiO. When TiN reacts with AlN a phase with the spinel structure (Al₂₃O₂₇N₅), which can form only in the presence of excess oxygen, appears in addition to the initial components. Spinel is also produced by the reaction of Al₂O₃ with AlN. In this case a eutectic between Al₂₃O₂₇N₅ and Al₂O₃ is observed.

Keywords: composite, sialon, eutectic, spinel.

INTRODUCTION

There is considerable interest in the development of new tool materials based on sialons and the more complex systems including them. This explains the intense and diversified investigation of these at the present time. It is predicted that additions of solid refractory compounds such as nitrides, carbides, or borides will improve the properties of sialons. The processes which occur upon sintering the components of complex systems such as Si−Al−O−N−Ti in the composition range of practical interest for the development of tool materials is studied in the present work. In addition to x-ray diffraction (XRD) analysis, differential thermal analysis (DTA) of the initial mixtures was used as a basic method in the study. As is known, observed thermal effects can be used as indicators of reactions occurring in the mixtures in accordance with the phase equilibrium diagram of the component system.

Phase polyhedration of a multicomponent system in which compounds of variable composition exist (in the given case titanium nitride), as with any process of dividing a complex system into simpler subsystems is used merely for convenience in studying the complex system. It is recognized that there is no singular method for carrying out such a subdivision. In studying phase formation in the reaction of TiN with sialons (TiN−Si₃N₄−Al₂O₃) the object of investigation is a portion of the Si₃N₄−Al₂O₃−AlN−SiO₂−TiN−TiO₂ system, which can be represented as the two mutual systems Si₃N₄−Al₂O₃−AlN−SiO₂ and TiN−Al₂O₃−AlN−TiO₂. As was pointed out in [1], the elements of the latter are pseudoternary and pseudobinary systems. These are geometrically represented by the faces and edges of the five-sided polyhedron Si₃N₄−Al₂O₃−AlN−SiO₂−TiN−TiO₂ shown in Fig. 1. The physicochemical reactions
in the complex system are conveniently investigated by beginning with the simpler bounding systems. Therefore, in [1] we considered the processes of phase formation in the pseudobinary systems Si$_3$N$_4$ - TiN, Si$_3$N$_4$ - Al$_2$O$_3$, and TiN - Al$_2$O$_3$. In the present work, based on data in the literature and our own investigations we have considered phase formation and component reactions in the bounding pseudobinary systems which include AlN: Si$_3$N$_4$ - AlN, TiN - AlN, and Al$_2$O$_3$ - AlN. Published data for all three ternary systems, sections of which are the binaries under consideration, give a sufficiently clear picture of the phase relationships in them. This simplifies discussion of the differential thermal analysis results obtained in the process of sintering the mixtures, and enables us to evaluate the applicability of the proposed approach.

**LITERATURE DATA**

The calculated isothermal section of the Si – Al – N system at 1027°C (Fig. 2) [2] indicates the presence of a two-phase region AlN + Si$_3$N$_4$. Noticeable ranges of solid solutions based on these compounds were not found. The Si$_3$N$_4$ - AlN polythermal section [3] shows the phase composition at various temperatures. A two-phase equilibrium Si$_3$N$_4$ + AlN exists up to 1839.6°C (Fig. 3).

It follows from the structure of the isothermal sections of the Ti – Al – N system at 1300 and 1000°C (Figs. 4, 5), and also from the metastable phase diagram of its TiN – AlN section (Fig. 6), that at temperatures, at least, above 1000°C their is a stable equilibrium between the phases based on TiN and AlN.

In the quasibinary system Al$_2$O$_3$ – AlN a ternary intermediate phase Al$_{23}$O$_{27}$N$_5$ with the spinel structure and a homogeneity range extending from 27 to 40 mole% AlN forms at temperatures below 2050°C (Fig. 7). The lattice parameter of this phase over the homogeneity range varies from $a = 0.7951$ nm to $a = 0.7938$ nm. The phase melts congruently at 2165°C. It forms a eutectic with the phase based on Al$_2$O$_3$ at 1850°C and 78 mole% Al$_2$O$_3$. A series of polytypes are observed in the region of AlN-rich compositions in the system above 1920°C. Equilibriums with a gas phase are observed above 2225°C.

**METHODS OF INVESTIGATION**

The methods of x-ray diffraction and differential thermal analysis were used to investigate the reaction of components in the Si$_3$N$_4$ – Al$_2$O$_3$ – AlN – SiO$_2$ – TiN – TiO$_2$ system. DTA was carried out in a protective atmosphere of helium in hafnium oxide crucibles; the heating and cooling rates were approximately 30 deg/min. A thermal effect from a phase transformation in the crucible material is not specified in the thermograms. Sintering occurred in several stages (heating – cooling); the maximum temperature chosen in each stage was that most useful from the viewpoint of