HOT PRESSING OF OXIDES OF REFRACTORY METALS

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In the manufacture of high-temperature ceramics, refractory oxides constitute the most important class of compounds because they combine a number of attractive properties, such as excellent stability in oxidizing environments, chemical inertness and high oxidation resistance in a wide temperature range, and relatively low thermal and electrical conductivities [1]. These properties are exhibited most fully by dense oxide components, and it is therefore necessary to investigate methods of producing high-density oxide materials.

A number of authors have studied the hot pressing of zirconium dioxide [2-6]. Specimens obtained by hot pressing CaO-stabilized ZrO$_2$ in graphite dies at 1430-2030°C were found to be black in color and had a macrostructure with cracks. When the same material was sintered by hot pressing for 1 h in an oxidizing atmosphere at 1750°C, the resultant specimens were crack-free, uniformly black in color, and virtually non-porous. All other data relating to the hot pressing of oxides of the transition metals are fragmentary and unsystematic.

The object of the present work was to study the sintering, by the method of hot pressing, of powdered oxides of several refractory transition metals, namely, TiO$_2$, ZrO$_2$, V$_2$O$_5$, Nb$_2$O$_5$, and Cr$_2$O$_3$. Hot-pressing experiments were performed using oxide powders of the "pure for analysis" (TiO$_2$, Nb$_2$O$_5$) and "pure" (ZrO$_2$, V$_2$O$_5$, Cr$_2$O$_3$) grades of 2-10-μ mean particle size, made by the Donetsk Chemical Reagents Factory. Their chemical compositions were as follows (in %): ZrO$_2$-97.8 ZrO$_2$, 0.83 SiO$_2$, 0.11 Al$_2$O$_3$, 0.08 TiO$_2$, 0.06 Fe$_2$O$_3$, 0.24 CaO, and 0.1 MgO; V$_2$O$_5$-99.6 V$_2$O$_5$, 0.2 H$_2$SO$_4$, 0.02 SO$_4$, 0.01 Cl, 0.04 Na$_2$O, and 0.01 NH$_4$; Nb$_2$O$_5$-99.3 Nb$_2$O$_5$, 0.02 Ti, 0.05 Si, 0.02 Fe, 0.1 Ta, 0.05 K, 0.05 Na, 0.02 P, 0.05 S, and 0.15 F.

The hot pressing of the oxide powders was performed in a special lever-type press, using graphite dies whose inner surfaces were protected with a coating of the oxide being sintered. The temperature was determined with an OPPIR-017 optical pyrometer. To ensure conditions approximating to the ideal case of isothermal and isobaric sintering, which is essential for the correct interpretation of curves of density plotted against sintering time in hot pressing, the die with powder was heated up to the nominal hot-pressing temperature without load, after which load was rapidly applied to the powder. To follow the changes in density during such sintering, the travel of the upper punch was recorded as a function of time by means of a rheostat and an EPP-09M electronic potentiometer. The oxide sintering temperature was chosen in the range 0.7-0.8 $T_m$ (Table 1), the pressure being 180 kg/cm$^2$. After sintering, the specimens were slowly cooled together with the graphite die. Measurements were made of the density (using hydrostatic weighing) and final dimensions of sintered specimens.

Instantaneous relative density as a function of sintering time was determined from recorded shrinkage curves and from final specimen densities and dimensions, assuming the specimen weight to remain unchanged:

$$\gamma_f \cdot \frac{h_f}{h}$$

where $\gamma_f$ and $h_f$ are the final specimen density and height, and $\gamma$ and $h$ are the corresponding instantaneous values.
Kinetic curves of density vs sintering time for the hot pressing of TiO$_2$, ZrO$_2$, Nb$_2$O$_5$, and Cr$_2$O$_3$ specimens are illustrated in Fig. 1. It follows from these kinetic shrinkage curves that, at a constant holding time, with rise in temperature the rate of densification and density of specimens in hot pressing steadily increase. The densification rates show that raising the temperature increases the fluidity of the materials and accordingly lowers their viscosity. This demonstrates that hot pressing is accompanied by voluminous flow, whose rate sharply falls with decrease in porosity.

Experimental plots of the effect of temperature on the densification rate of the powdered oxides of transition metals show that a rapid initial rise in densification rate is followed by a gradual, almost asymptotic approach to the final density. At all temperatures, densification is characterized by a final density which increases with rise in sintering temperature.

For further investigation, microsections were prepared from some hot-pressed specimens. The procedure employed consisted in rubbing specimens on a smooth steel disk, using first a suspension of boron...