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STUDIES ON MECHANISM OF HIGH-TEMPERATURE OXIDATION OF MOLYBDENUM, TUNGSTEN, AND ZIRCONIUM DISILICIDES BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

High-temperature oxidation (200-1600°C) of molybdenum, tungsten, and zirconium disilicides in air and in a pure oxygen atmosphere at a pressure of 740 Torr was investigated by differential thermal analysis and isothermal thermogravimetry. The composition and structure of oxide phases were determined by petrography and X-ray diffraction. It was found that on ZrSi2 samples protective silicate films were formed.

INTRODUCTION

The oxidation of disilicides is a complex multistage process associated with the formation of silicide phases with a lower silicon content, metal oxides, silicon oxides SiO_2 and SiO as well as silicate phases of $MeSiO_4$ and Me_2SiO_2 types. From known metal disilicides, $MoSi_2$, WSi_2, and $ZrSi_2$ are the most resistant to high-temperature oxidation. These compounds and materials based on them are widely used as heating elements in high-temperature furnaces which operate in ambient air at the temperatures up to 1500-1600°C.

The data on the mechanism of protective action of surface films formed on these materials at high temperatures are scarce, in particular a possible formation of amorphous silicate phases or double compounds of mixed oxides has not been elucidated. The combination of traditional methods for studying surface phases with differential thermal analysis provides wide opportunities in this respect.

EXPERIMENTAL

The oxidation kinetics of powders and compacts from molybdenum, tungsten, and zirconium disilicides were studied on a Du Pont 1090 thermal analyzer. The investigations were performed both under isothermal conditions and under programmed heating conditions with a rate of 20°/min. The solid products of the reaction were

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investigated by X-ray diffraction and petrography. The powders of molybdenum, tungsten, and zirconium disilicides with an average particle size of 8.3 μm were produced by self-propagated high-temperature synthesis. Compacted $ZrSi_2$ and $MoSi_2$ samples with porosity of not more than 5% were obtained by hot pressing.

RESULTS AND DISCUSSION

From the DTA results presented in Fig.1 one can see that the oxidation of WSi_2 powder in air starts at 500°C and is completed above 1100°C. By this moment the initial disilicide is fully transformed into WO_3 and SiO_2. The weight gain of the sample is 45.3% which coincides practically with the value of theoretical transformation of 46.6% (with the account of ideal stoichiometry of compounds). On the DTA-curve, besides the main peak (T_{max}=910°C) corresponding to the WO_3 formation, the exothermal peak at 825°C is also observed. It has been established that at the primary oxide film (α-WO_3)-disilicide interface the interaction of WSi_2 with WO_3 occurs leading to the formation of γ-phase ($WO_{2.75}$). The fact of formation of intermediate tungsten oxide is confirmed by thermodynamic calculations as well as by X-ray diffraction results (in the temperature range of 600-900°C).

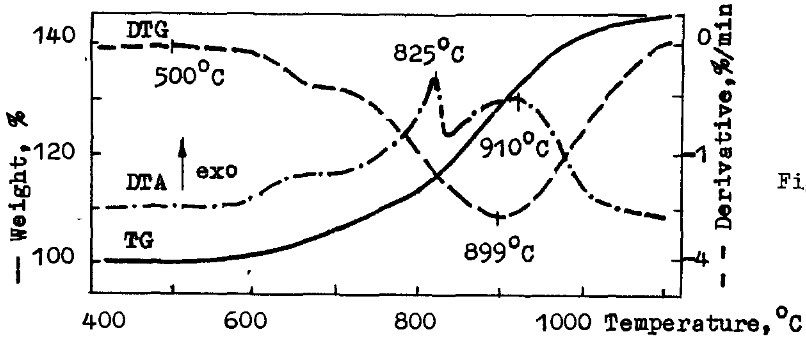

Fig. 1

The kinetic curves obtained in the temperature range of 700-1200°C (Fig.2) are indicative of high $ZrSi_2$ resistance to oxidation. At the temperatures below 800°C the reaction rate is very low and increases considerably only at 900°C. Further temperature increase does not accelerate the process markedly which is in good agreement with the DTA results (Fig.4). The exothermal peak at 895°C on the DTA-curve corresponds to the formation of zirconium dioxide. And $ZrSi_2$ is preferably oxidized along the grain bounda-

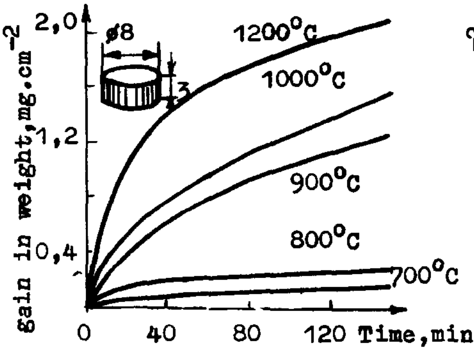

Fig. 2

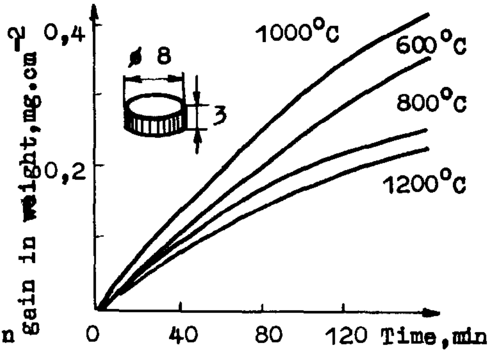

Fig. 3

ries (according to petrography and X-ray diffraction results). The oxide film formed consists of SiO_2 and monoclinic ZrO_2 (refractive indices $n_p \sim 2.12$, $n_q \sim 2.15$). At the temperatures above 1200°C zirconium silicate $ZrSiO_4$ is formed due to the interaction of ZrO_2 with SiO_2. The peak (T_{max}=1375°C) on the DTA-curve (Fig.4) corresponds to this process. A thin film preferably consisting of $ZrSiO_4$ (refractive indices $n_p \sim 1.91$, $n_q \sim 1.95$) is a reliable protective barrier for further oxidation of the material at higher temperatures.

As opposed to WSi_2 and $ZrSi_2$, in the $MoSi_2$-O_2 system at high

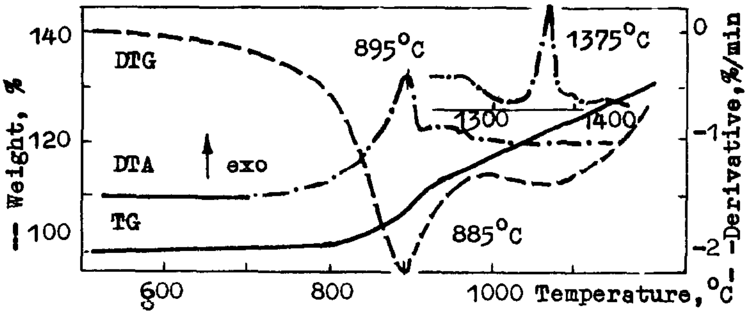

Fig. 4

temperatures the reactions can proceed with the formation of solid and volatile products. As can be seen in Fig.3, in the range of 600-800°C the process obeys the parabolic law, at 1000°C and 1100°C in the initial period it obeys the linear law changing into the parabolic one with the growth of the thickness of protective glassy film (SiO_2). The differences in oxidation laws are determined by a different composition of the phases formed and MoO_3 volatility. The exothermal peak at 485°C on the DTA-curve corres-

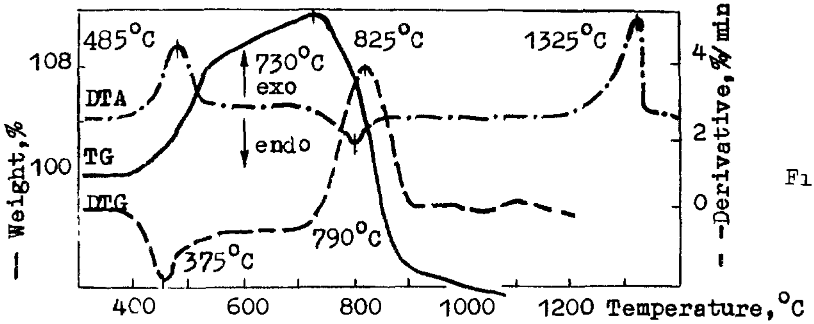

Fig. 5

ponds to the MoO_3 formation (Fig.5), the endothermal peak at 790°C is indicative of its vaporization. A lower rate of $MoSi_2$ weight gain in the temperature range of 550-700°C is also associated with MoO_3 vaporization. At 730°C (TG-curve) the vaporization rate of this oxide is equal to the rate of its formation. Above 700°C on the TG-curve only weight loss is observed, and in the oxidation products at 900°C α-quartz and small amount of molybdenum suboxide Mo_3O are detected by X-ray analysis.

With temperature increase due to preferable silicon oxidation, the Mo_5Si_3 layer is formed under the α-quartz film. The analysis of elementary composition of oxide films during this period has demonstrated that after the formation of continuous Mo_5Si_3 layer the main oxidation product is amorphous SiO_2 enriched with metal ions. The local increase of molybdenum concentration in SiO_2 results, apparently, in the formation of molybdenum silicate $m{\cdot}MoO_3{\cdot}nSiO_2$ ensuring the retardation of oxygen diffusion. A distinct exothermal peak at 1375°C on the DTA-curve corresponds to the formation of molybdenum silicate (Fig.5).

CONCLUSIONS

It has been established that the oxide film on disilicides has high protective properties due to the formation of glassy silica as well as zirconium and molybdenum silicates. The silicate phases having high heat resistance ensure the protection of these materials in air over the temperature range of 1100-1700°C.