INTRODUCTION

Transition metal silicides—such as molybdenum disilicide, MoSi$_2$—are being widely used in fabricating high-temperature heaters and also as structural materials. MoSi$_2$ exhibits high melting point, good oxidation resistance and thermal conductivity but reduced high-temperature strength and toughness that is insufficient for some structural applications of the material. Meanwhile the high-temperature strength of MoSi$_2$ can be markedly (up to 1900–2000°C) improved [1–5] by reinforcement with W, Nb, Ti, etc. yielding composite materials for fabrication of machine parts and deposition of protective coatings. A convenient method for preparation of the above composites seems to be the technology of SHS casting [7–11].

In this communication, we report some results of our systematic studies on the SHS casting of $(Mo,W)Si_2$, $(Mo,Nb)Si_2$, and $(Mo,Ti)Si_2$ silicides and their solid solutions by combining different thermit-like reactive mixtures containing reinforcing W, Nb, and Ti metals and also activating $3CaO_2 + 2Al$ additives.

EXPERIMENTAL

Commercial powders of MoO$_3$, WO$_3$, N$_2$O$_5$, TiO$_2$, CaO$_2$, Al, and Si (all of reagent grade) were used in experiments. Combustion of bulk density green mixtures was carried out either in transparent silica cartridges ($d = 20$ mm, $h = 50$ mm, about 20 g in weight) or in graphite dishes ($d = 40–100$ mm, $h = 50–300$ mm, 100–3000 g) under 50 atm of initial Ar pressure (to suppress melt splashing).

Green mixtures were prepared using different combinations of the following powder mixtures:

- $MoO_3 + 2Al + 2Si \rightarrow MoSi_2 + Al_2O_3 \quad (T_{ad} = 2602 \text{ K})$ (I)
- $WO_3 + 2Al + 2Si \rightarrow WSi_2 + Al_2O_3 \quad (T_{ad} = 2454 \text{ K})$ (II)
- $3TiO_2 + 4Al + 12Si \rightarrow 3TiSi_2 + 2Al_2O_3 \quad (T_{ad} = 1522 \text{ K})$ (III)
- $3Nb_2O_5 + 10Al + 12Si \rightarrow 6NbSi_2 + 5Al_2O_3 \quad (T_{ad} = 2326 \text{ K})$ (IV)
- $3CaO_2 + 2Al \rightarrow Al_2O_3 + 3CaO \quad (T_{ad} = 4249 \text{ K})$ (V)

Mix V was added (in amounts of 5–10 wt %) to various combinations of ‘hot’ mix I with ‘cold’ mixtures II–IV to activate their combustion.

In our experiments we could determine burning velocity $U$ (by video recording), the weight loss caused by material splashing ($\eta_{sp}$), and the fraction of metallic phase in the ingot ($\eta_m$) using the expressions:

$$U = \frac{h}{t},$$

$$\eta_{sp} = \left(\frac{M_0 - M_f}{M_0}\right) \times 100\%,$$

$$\eta_m = \left(\frac{m_{ing}}{M_0}\right) \times 100\%,$$

where $h$ is the sample height (length), $t$ combustion time, $M_0$ mass of green sample, $M_f$ mass of final product, and $m_{ing}$ the mass of metallic ingot (MeSi$_2$).
Our goal was to determine the influence of green composition characterized by parameters $\alpha_i$ ($i = \text{II, III, IV}$) on the characteristics of combustion ($U$, $\eta_m$) and phase segregation in product ($\eta_m$). The $\alpha$ values were defined as:

$$\alpha_{\text{II}} = M_{\text{II}}/(M_1 + M_{\text{II}}),$$
$$\alpha_{\text{III}} = M_{\text{III}}/(M_1 + M_{\text{III}}),$$
$$\alpha_{\text{IV}} = M_{\text{IV}}/(M_1 + M_{\text{IV}}),$$

where $M_i$ is the mass of ‘hot’ mix $i$ and $M_f$ stands for the mass of added ‘cold’ mixtures II, III, and IV.

Combustion products were characterized by XRD (DRON-3) and EDS (Super probe JEOL-733).

**RESULTS AND DISCUSSION**

Control experiments have shown that in our conditions mix IV could not be ignited altogether. Activating mix V yielded the products that upon phase segregation remained in the oxide phase and did not react with target MåSi$_2$ products.

With increasing $\alpha$, burning velocity $U$ was found to decrease (Fig. 1). The effect is most pronounced for mixtures III and IV: combustibility limits are achieved at $\alpha_{\text{III}} = 0.3$ and $\alpha_{\text{IV}} = 0.8$ (Fig. 1, curves 2 and 3'). The former limit could be extended to $\alpha_{\text{III}}$ around 0.6 upon addition of activating additive V (Fig. 1, curve 3'). In all cases, the $\eta_m$ values did not exceed 3%.

Figure 2 presents the extent of phase segregation ($\eta_m$) in an ingot as a function of $\alpha$. With increasing $\alpha$, $\eta_m$ is seen to slightly increase (curve 1), and phase segregation takes place over the entire range of $\alpha$. Upon addition of activating mix V, a decrease in $\eta_m$ was observed due to an increase in the relative amount of the oxide phase. For this reason, in other experiments with II-containing mixtures, activating mix V was not used altogether. Over the entire range of $\alpha$, we obtained single-phase disilicides of Mo and W as well as their solid solutions of varied homogeneity range [10].

With an increase in $\alpha_{\text{III}}$, the $\eta_m$ values gradually decreased and reached their limits at the $\alpha$ values of 0.4 and 0.8, respectively (Fig. 2, curves 2 and 3'). In this case, the addition of mix V (in amounts up to 10%) gave a marked gain in $\eta_m$ and extended the range of phase segregation due to an increase in combustion temperature and melt lifetime (Fig. 2, curve 3'). In this case the readily separable oxide phase of combustion product contained the oxides of Al, Si, and Ca while the metallic phase, the silicides of Mo, W, Nb, and Ti.

Figure 3 shows the diffraction patterns of the Mo$_x$Nb$_y$Si$_z$ materials prepared in the absence (a) and presence (b) of activating additive. Patterns (a) indicate the presence of unreacted Nb and Si, which can be associated with a relatively low combustion temperature. In the presence of activating mix V (Fig. 3b), the above elements have enough time to react and/or form a solution.

Figures 4 and 5 present SEM images and EDS data for Mo–Nb–Si ingots prepared in the absence and presence of activating additive. Those in Fig. 4 exhibit the presence of unreacted Nb and Si while those in Fig. 5, only their trace amounts and the product con-