Rheological properties of MoSi$_2$-NbSi$_2$ powders obtained by SHS-method and solid-phase mixture

D D Titov$^1$, P A Miloserdov$^2$, A S Lysenkov$^1$, M G Frolova$^1$, E A Gumennikova$^{1,3}$ and Yu F Kargin$^1$

$^1$Baykov Institute of Metallurgy & Material Science RAS, Moscow, Russia
$^2$Institute of Structural Macrokinetic and Material Science RAS, Chernogolovka, Russia
$^3$Mendeleev University of Chemical Technology of Russia, Moscow, Russia

e-mail: mitytitov@gmail.com

Abstract. (Mo$_{1-x}$Nb$_x$)Si$_2$ powders (0.1≤x≤0.9) were obtained by self-propagating high-temperature synthesis (SHS) in ISMAN RAS. The same mixtures were obtained by commercial powders MoSi$_2$ and NbSi$_2$ solid-phase mixing in a planetary mill. The commercial disilicides were synthesised by magnesium-thermal reaction in Plasmotherm Ltd. During the experiment on powder mixtures deformation an array of data was obtained as a result of loading in a constant-speed regime. A kinetic curves representing the pressure dependence on time was a result of the experiment, then the necessary pressure values were determined in the preliminary cold pressing to provide the selected density of the workpieces, the compressibility modulus and the compressibility factor for each composition were calculated.

1. Introduction
Recently interest has increased in two-component systems based on molybdenum disilicide and niobium disilicide for the production of new generation heating elements and coatings on their basis, which, due to high resistance and good adhesion to high-temperature niobium alloys [1] could increase the products working temperature and their lifespan at 1600°C in oxidising environments [2]. Such materials would increase the thermal efficiency of combustion systems such as jet engines for airplanes, and next-generation ultra-high temperature gas turbine systems in power plants such as the gas turbine combined cycle (GTCC).

The results demonstrated in research [3] that the simultaneous improvement of high-temperature creep strength and room temperature fracture toughness can be first accomplished by the development of unique cross-lamellar microstructure in (Mo$_{0.85}$Nb$_{0.15}$)Si$_2$ composite, which opens a potential avenue for the development of novel ultrahigh-temperature (UHT) materials as alternatives to existing Ni-based superalloys. Koji Hagihara [3] and other researchers [4] shows that (Mo$_{0.85}$Nb$_{0.15}$)Si$_2$ composite is very perspective future contracture material. The initial stage of raw preparation and pressing is no less important than the sintering process.

The most important question in the theory and practice of powders cold pressing consists in establishing the relationship between the applied pressure (P) and the compacts density. The press-density dependence lets it possible to select the required value of P, which provides the given value of
the density (\(\rho\)). A large number of experiments are carried out under conditions of static loading in the regime of constant pressure (\(P = \text{const}\)) [5]. In practice, powder blanks pre-pressing is carried out in special molds on hydraulic presses, which create a constant pressure. However, in this case there are methodological difficulties associated with some uncertainty of such an experiment. This is due to the fact that the compaction process is essentially non-stationary and the compaction degree is continuously changing throughout the time. Therefore, the density corresponding to the preset pressure depends also on the pressing process duration. If \(\rho\) is understood as its maximum value, it is also affected by the dwell time. For different materials, the conditions for obtaining holistic blanks having an optimum density are usually empirically. For various compositions of charge, the corresponding porosity value is 30-50% [6] and it is optimal to obtain a billet blank with a relative density of 60-70% to dilatometric studies. It is important all the compositions have the same relative density when determining the sintering process activation energy [7, 8].

2. Materials and methods of researches

The cast mixture (\(\text{Mo}_{1.8}\text{Nb}_{0.2}\)Si\(_2\)) (where \(0.1 \leq x \leq 0.9\)) was obtained by the SHS method at the Institute of Structural Macrokinetic and Material Science Russian Academy of Sciences (ISMAN RAS) in Chernogolovka Russia [9] and the same mixtures were obtained by solid-phase mixing commercial MoSi\(_2\) and NbSi\(_2\) (Plazmoterm LLC). All powders were characterised by SEM (Supra 50 VP LEO, with microanalysis system INCA Energy + Oxford, Germany), X-ray (Shimadzu XRD-6000, Japan) and granulometric analyses (Fritch, Analysette 22, Germany). The dominant fraction is \(10 \pm 15\) \(\mu\)m particles in both case. Rheological properties were tested on the mechanical testing machine (Instron 5581, Great Britain). The stain velocity was \(1\) mm/min.

The deformation was calculated by the Eq. (1):

\[
\varepsilon = \frac{\Delta h}{h_0}
\]  

(1)

where \(\Delta h\) is the change in the height of the bulk layer over time; \(h_0\) is the initial height of the bulk layer.

The compressibility modulus is numerically equal to the tangent of the linear section slope angle of the diagram strain against deformation, and is calculated by the Eq. (2):

\[
G = \frac{\Delta p'}{\varepsilon^*}
\]  

(2)

where \(\Delta p'\) is the limiting change in the linear section pressure value; \(\varepsilon^*\) is the final value of the linear section deformation.

The compressibility coefficient \((k_c)\) characterises the reversible decrease in the sample height (volume) under the pressure action and is quantitatively determined by Eq. (3):

\[
k_c = \frac{1}{h_0} \frac{\Delta h'}{\Delta p'}
\]  

(3)

where \(\Delta h'\) and \(\Delta p'\) are the limiting values of the height and the linear section pressure variation, \(h_0\) is the initial height of the backfill.

The physical meaning of the compressibility coefficient is characterisation the material ability to compact at the initial (linear) stage, during which the compaction intensity is maximal.

3. Results and discussion

Figure 1 shows stress strain curves for the powder compositions (\(\text{Mo}_{1.8}\text{Nb}_{0.2}\)Si\(_2\)) (where \(0.1 \leq x \leq 0.9\)) obtained by two methods: the SHS method and solid-phase mixing in a planetary mill. The first stage
on the rheological curve is limited to deformation values up to 10-15% and is accompanied by a linear increase in strain and increasing $\varepsilon$, which occurs due to the powder particles movement into the pores.

The second stage corresponds to deformations from 15-20% to 30-35%. In the P-$\varepsilon$ diagram, it corresponds to a very steep nonlinear rise in strain with increasing $\varepsilon$. The particles movement is due to the accommodation (adaptation) of them among themselves and from the other hand due to deformation of their volume [10].

![Figure 1. Diagram strain against deformation: A-SHS and B-solid-phases mixtures powder (Mo$_{1-x}$Nb$_x$)Si$_2$, where 0.1$\leq x$$\leq$0.9](image)

In the third stage, when the stain is increased over a wide range, a small change in the strain occurs. The scaling process is carried out mainly due to the growth of the contact surface during deformation of the particles.

We note that, other things being equal (the main fraction is 10-15 $\mu$m), the powders obtained by SHS method have a narrower divergence of the stress-strain curves of different compositions with respect to the curves for the powders obtained by solid-phase mixing (Fig. 1). Apparently this is due to the uniform distribution of niobium disilicide in molybdenum disilicide. X-ray analysis showed that in SHS synthesis, the crystal lattice deforms from tetragonal to hexagonal with an increase in the concentration of NbSi$_2$ (Table 1). That is, there is basically one hexagonal phase in the SHS powder, and there are simultaneously hexagonal crystals of NbSi$_2$ and tetragonal MoSi$_2$ in the solid-phase mixture, which makes their compatibility difficult when pressed.

| $\text{(Mo}_{1-x}\text{Nb}_x)\text{Si}_2$, $x$ | $a$ [Å] | $c$ [Å] | $V$ [Å$^3$] |
|-----------------|--------|--------|--------|
| MoSi$_2$ [80-0544] | 3.200  | 7.850  | 80.4   |
| 0.1             | -      | -      | -      |
| 0.3             | 4.666  | 6.532  | 123.2  |
| 0.5             | 4.709  | 6.536  | 125.5  |
| 0.7             | 4.749  | 6.557  | 128.1  |
| 0.9             | 4.780  | 6.587  | 130.3  |
| NbSi$_2$        | 4.790  | 6.583  | 130.8  |
Determination of the necessary pressure in the preliminary cold pressing to ensure the selected density of the workpieces is an important task for further dilatometric studies. To compare the sintering processes of different sample compositions, it is required to obtain blanks of the same relative density. We plot the graphs in the "stress-relative density" coordinates (Figure 2).

Table 2. The rheological parameters of SHS powder (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, where 0.1≤x≤0.9

| (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, x | G, MPa (корреляция 0.980) | ε* | k\textsubscript{s}, 10\textsuperscript{6}Па |
|-----------------|-----------------|-----|-----------------|
| 0.1             | 48.0            | 0.0642 | 13.0 |
| 0.3             | 49.8            | 0.0817 | 14.3 |
| 0.5             | 34.4            | 0.0498 | 13.6 |
| 0.7             | 31.7            | 0.0506 | 14.6 |
| 0.9             | 21.8            | 0.0043 | 4.16 |

Table 3. The rheological parameters of solid-phase powder (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, where 0.1≤x≤0.9

| (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, x | G, MPa (корреляция 0.980) | ε* | k\textsubscript{s}, 10\textsuperscript{6}Па |
|-----------------|-----------------|-----|-----------------|
| 0.1             | 17.8            | 0.0234 | 10.7 |
| 0.3             | 35.6            | 0.0657 | 15.1 |
| 0.5             | 32.1            | 0.0551 | 15.3 |
| 0.7             | 59.1            | 0.0831 | 13.1 |
| 0.9             | 76.2            | 0.0890 | 19.0 |

Figure 2. The diagram strain against relative density: A-SHS and B-solid-phases powder (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, where 0.1≤x≤0.9

Analysis of the curves showed a direct relationship between the concentration of niobium disilicide and the relative density of the green body. In case of SHS powder density increases when the concentration of NbSi\textsubscript{2} increased and of solid-phase mixture of two disilicides it decreases. This behaviour can be explained by the difference in the phase composition, which leads to differences in the compaction of powders.

4. Conclusion
A rheological approach was used to study (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2} powder materials, where 0.1≤x≤0.9, obtained by SHS method and solid-phase mixing, based on the study of the kinetics of material deformation in the constant speed mode of the press plunger.
The rheological behaviour of powder materials in the system (Mo\textsubscript{1-x}Nb\textsubscript{x})Si\textsubscript{2}, obtained by SHS method and solid-phase mixing in a planetary mill, is investigated. The numerical characteristics of the materials under investigation have been experimentally obtained: the compressibility modulus G, the final value of the deformation of the linear section of the stress-strain curve $\epsilon^*$, the compressibility coefficient $k_c$, at constant loading rates of 1 mm/s.

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