The sintering process difference of MoSi$_2$, NbSi$_2$ and (Mo$_{1-x}$,Nb$_x$)Si$_2$ solid solution

D D Titov$^1$, P A Miloserdov$^2$, M G Frolova$^1$, A S Lysenkov$^1$, Yu F Kargin$^1$, N V Petrakova$^1$ and A A Ashmarin$^1$

$^1$Baykov Institute of Metallurgy and Materials Science RAS, Moscow, Russia
$^2$Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka, Russia

e-mail: mitytitov@gmail.com

Abstract. The dilatometric sintering process experimental results of pure niobium disilicides, molybdenum disilicides, 50wt.%MoSi$_2$ + 50wt.%NbSi$_2$ solid-phases mixtures and (Mo$_{1-x}$,Nb$_x$)Si$_2$ were presented. Both MoSi$_2$ and NbSi$_2$ were synthesised by magnesium-thermal synthesis (Plasmotherm LLC). The solid solution (Mo$_{1-x}$,Nb$_x$)Si$_2$ were synthesised by self-propagating high-temperature synthesis (SHS) (ISMAN RAS). The shrinkage curves analysis of MoSi$_2$ and NbSi$_2$ showed the similar shrinkage curve relief. The pure MoSi$_2$ relative shrinkage is greater than NbSi$_2$ under the same conditions at 1900°C in Ar atmosphere. The two disilicides mixture shrinkage curve shifted $T_{onset}$ to a higher temperature region relatively pure disilicides. The (Mo$_{1-x}$,Nb$_x$)Si$_2$ solid solution had a completely different shrinkage curve, it was characterised by a pick at 305°C and a double kink in the sintering process corresponded to the passage of two successive sintering processes. The solid solution shrinkage curve was different both NbSi$_2$ and MoSi$_2$ and there was (Mo$_{1-x}$,Nb$_x$)Si$_2$ phase transition at 305°C.

1. Introduction

There is a great demand for the development of a new super-high-temperature structural material as an alternative to Ni-based superalloys that can be applied above 1400°C without cooling. Such materials will increase the thermal efficiency of combustion systems, for example for jet engines of aircraft, and an ultra-high-temperature gas turbine of the next generation in power plants. Transition metal disilicides are potential constructional materials suitable for this purpose. Molybdenum and niobium disilicide meet these requirements, they have a high melting point ($T_{MoSi2} = 2020°C$ and $T_{NbSi2} = 1950°C$), low density (6.26 and 5.7 g/cm$^3$, respectively), oxidation-resistant in air above 1000°C and have a high electrical conductivity (21.6 $μΩm*cm$). Molybdenum and niobium disilicides form various crystals: MoSi$_2$ - tetragonal syngony, C11b space group, cell parameters a = 0.3206 nm, c = 0.7846 nm [1] and NbSi$_2$ - hexagonal system, C40 space group, cell parameters a = 0.4787 nm, c = 0.6587 nm [2]. Molybdenum disilicide undergoes transformation in the interval 1850-1900°C [3]. The low-temperature form of $α$-MoSi$_2$ has a body-centered tetragonal structure. High-temperature $β$-MoSi$_2$ crystallises into a hexagonal structure [4, 5]. However, the strength and thermal stability of high-temperature materials play a crucial role in the high-temperature environment. Importantly, keeping the balance of mechanical properties and thermal stability is still a big challenge. Therefore, it is necessary to explore new method to improve the overall performance of high-temperature material. Pan et al [6] find that the compression strength of NbSi$_2$ with alloying element of Re is up to 15.3%
in comparison to perfect NbSi$_2$. Importantly, alloying elements at Si site result in brittle-to-ductile transition for NbSi$_2$. The NbSi$_2$ heat capacity with alloying elements is slightly larger than that pure NbSi$_2$.

Nakano et al. [7] found that two different mechanisms could control the so-called yield stress anomaly behaviour in C40-(Nb,X)Si$_2$ at temperatures below and above approximately 1200°C.

The results demonstrated in research [8] 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 [8] and other researchers [6] 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.

Despite the active study of materials based on NbSi$_2$, up to the present time in the literature there is insufficient information on the process of sintering of niobium disilicide and its comparison with the process of sintering molybdenum disilicide. Information on the sintering mechanism and the corresponding parameters are useful in optimising the manufacturing processes of the required parts with controlled compaction and microstructure.

2. Materials and methods of research

The cast mixture (Mo$_{1-x}$,Nb$_x$)Si$_2$ (where 0.1≤x≤0.9) was obtained by the SHS method at the Institute of Structural Macrokinetics and Materials 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) with high temperature prefix (Shimadzu HA-1001, Japan) and granulometric analyses (Fritch, Analysette 22, Germany). The dilatometric analysis was performed on DIL 402C (Netzsch, German) 10°C/min heating rate up to 1900°C at Ar atmosphere [10, 11].

![Figure 1. SEM images of 1 – 50 wt.% MoSi$_2$ + 50 wt.% NbSi$_2$ solid-phases mixtures powder and 2 – (Mo$_{0.5}$,Nb$_{0.5}$)Si$_2$ SHS power.](image)

X-ray confirmed the NbSi$_2$ phase predominance ≥95% and MoSi$_2$ ≥99% with traces of Nb$_5$Si$_3$ ≤5%, and Mo$_5$Si$_3$ ≤0.5%, respectively. (Mo$_{0.5}$,Nb$_{0.5}$)Si$_2$ SHS power had a distorted hexagonal structure parameters (a = 4.709 Å, c = 6.536 Å) and Al$_2$O$_3$ traces.

3. Results and discussion
The niobium and molybdenum disilicides synthesised by magnesium-thermal analysis (Plasmotherm LLC), 50wt.% MoSi\textsubscript{2}+50wt.% NbSi\textsubscript{2} solid-phases mixtures and (Mo\textsubscript{0.5}Nb\textsubscript{0.5})Si\textsubscript{2} SHS power (ISMAN RAS) sintering process experimental results of the dilatometric analyses are presented (figure 2).

It is presented that the niobium disilicide at the initial stage expands up to 2%, while MoSi\textsubscript{2} expands only 1%, on the MoSi\textsubscript{2} and NbSi\textsubscript{2} shrinkage curves (figure 2). Then the process of sintering the sample starts, the MoSi\textsubscript{2} and NbSi\textsubscript{2} sintering point of the onset (T\textsubscript{onset}) is 1541°C and 1823°C respectively. The sample shrinkage is 13.68% and 22.85% at 1900°C, respectively MoSi\textsubscript{2} and NbSi\textsubscript{2}.

The 50wt.% MoSi\textsubscript{2} and 50wt.% NbSi\textsubscript{2} solid-phase mixture behaves in a similar manner as single disilicide. The shrinkage is 12.84% at 1900°C, T\textsubscript{onset}=1618°C.

The (Mo\textsubscript{0.5}Nb\textsubscript{0.5})Si\textsubscript{2} cast mixture behaviour during sintering is clearly different. During the sintering, a phase transition was observed at 305°C (figure 3), which is fixed only for the SHS powder. The sintering process begins at T\textsubscript{onset}=1555°C. The shrinkage value is 17.69% at 1900°C. The solid solution starts sintering at lower temperature than the two disilicides mixture. Two minimums corresponding to the two-stage sintering process of a solid solution were observed on the shrinkage rate curve (figure 3). This behaviour indicates the formation of an intermediate compound different from MoSi\textsubscript{2} and NbSi\textsubscript{2}.

**Figure 2.** The shrinkage of 1 – MoSi\textsubscript{2}, 2 – NbSi\textsubscript{2}, 3 – (Mo\textsubscript{0.5}Nb\textsubscript{0.5})Si\textsubscript{2} SHS and 4 – 50 wt.% MoSi\textsubscript{2} + 50 wt.% NbSi\textsubscript{2} solid-phases mixtures.

**Figure 3.** The shrinkage range of 1 – MoSi\textsubscript{2}, 2 – NbSi\textsubscript{2}, 3 – (Mo\textsubscript{0.5}Nb\textsubscript{0.5})Si\textsubscript{2} SHS and 4 – 50 wt.% MoSi\textsubscript{2} + 50 wt.% NbSi\textsubscript{2} solid-phases mixtures.

There is difference in sintering process due to the niobium disilicide uniform distribution in molybdenum disilicide. X-ray analysis showed that in SHS synthesis powders the crystal lattice deforms from tetragonal to hexagonal when the concentration of NbSi\textsubscript{2} increase (table 1). 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.

Table 1. The cell parameters in (Mo$_{1-x}$Nb$_x$)Si$_2$ system, where 0.1≤x≤0.9, obtained by the SHS method.

| (Mo$_{1-x}$Nb$_x$)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     |

X-ray with a prefix for high-temperature studies confirmed that phase changes and lattice rearrangement occur in the region of 300°C. It was found that the lattice parameters do not return to the initial values after heating to 320°C and then cooling to room temperature. We cannot explain this effect at this stage. Therefore, in this paper we give only the experimental values (table 2).

Table 2. (Mo$_{0.5}$Nb$_{0.5}$)Si$_2$ SHS lattice parameters dependence on temperature up to 320°C.

| Temperature, °C | a [Å]  | c [Å]  | V [Å$^3$] |
|-----------------|--------|--------|-----------|
| 22°C            | 4.709  | 6.536  | 125.5     |
| 280°C           | 4.716  | 6.528  | 125.7     |
| 290°C           | 4.719  | 6.547  | 126.3     |
| 300°C           | 4.719  | 6.548  | 126.3     |
| 310°C           | 4.722  | 6.549  | 126.5     |
| 320°C           | 4.717  | 6.548  | 126.2     |
| 280°C           | 4.715  | 6.547  | 126.0     |
| 22°C            | 4.708  | 6.528  | 125.3     |

It can be seen (table 2), the lattice volume increases abruptly at 290°C and reaches a maximum value at 310°C. These results are well correlated with dilatometric shrinkage curves.

4. Conclusions

The pure MoSi$_2$, NbSi$_2$ and (Mo$_{1-x}$Nb$_x$)Si$_2$ solid solution, obtained by SHS method and solid-phase mixing, were studied up to 1900°C in Argon atmosphere by dilatometric analysis.

It is shown that the continuous shrinkage curve of molybdenum disilicide and niobium has a similar relief. The two disilicides mixture shrinkage curve shifted T$_{onset}$ to a higher temperature region. The (Mo$_{1-x}$Nb$_x$)Si$_2$ solid solution had a completely different shrinkage curve, it was characterised by a pick at 305°C and a double kink in the sintering process corresponded to the passage of two successive sintering processes.

The x-ray analysis confirmed the change in lattice parameters in the temperature range from 280° to 320°C.

Acknowledgements
The reported study was funded by RFBR project No18-38-00327.

The methodical part of the work (X-ray and SEM) was carried out according to the state task № 007-00129-18-00.

The authors are grateful to Plasmotherm LLC and ISMAN RAS for providing the initial materials and for a fruitful discussion.

5. Reference

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