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Tailoring the microstructure of molybdenum disilicide matrix composites with Nb additions

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Abstract

The effect of Nb addition on the microstructure of $MoSi_2$ alloy was studied. Two kind of composition designations were adopted to get different microstructures. In the first group, the compositions are designed as $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–$x$Nb ($x=0.05$, 0.1 and 0.4375). In this group, a composite containing $MoSi_2$ and Nb_5Si_3 as well as Nb_5Si_3C is formed. The volume fraction of Nb_5Si_3 and Nb_5Si_3C phases increase with Nb addition and become the predominant matrix phase when Nb addition is 43.75%. In the second group, the compositions are designed as $(Mo_{1-x}, Nb_x)Si_2$. A composite containing $MoSi_2$ and $NbSi_2$ as well as a small amount of Nb_5Si_3 is formed.

Keywords: Composites; Microstructure; $MoSi_2$; Nb addition; Silicides

1. Introduction

Molybdenum disilicide has been receiving more and more attentions for its outstanding corrosion and oxidation resistance and is now widely used as heating elements. It has also been considered for structural applications.[1,2] But two main drawbacks of this material are that it has low room temperature toughness and insufficient high temperature creep resistance. Incorporating metal reinforcements such as Nb and W was proved to be an effective way to improve the mechanical properties.[3,4] However, a general understanding of the Nb addition on the microstructure of molybdenum disilicide is still lacking in the literature. In this research we try to obtain two kinds of microstructures in the $MoSi_2$ matrix with Nb addition. The first is $MoSi_2$–Nb_5Si_3 and the second is the $MoSi_2$–$NbSi_2$ microstructure. Both of the two kinds of microstructure have been suggested to be beneficial for better mechanical properties.

2. Experimental procedure

Two group samples with different composition designations were made in this research. In the first group, Nb powders was added directly to $MoSi_2$ powders and the compositions are designed as $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–$x$Nb ($x=0.05$, 0.1 and 0.4375). The maximum Nb content $x=0.4375$ was chosen upon the suggestion that a single phase $(Nb,Mo)_5Si_3$ will form with this composition. Since Mo:Si ratio in this group was designed to be 1:2 samples of this group will be made from mixture of $MoSi_2$ powders and Nb powders. And for simplicity, samples of this group will be called 5Nb, 10Nb and 43.75Nb samples. In the second group, Mo, Nb and Si elemental powders were mixed to make the alloys and the compositions are designed as $(Mo_{1-x}, Nb_x)Si_2$ ($x=0.05$, 0.10, 0.20). The maximum Nb content $x=0.2$ was chosen because some report indicate that 20% Nb addition will change the alloy into single phase $(Nb_{0.20}, Mo_{0.80})Si_2$ with a C40 crystal structure.[5] Compositions of the samples are listed in Table 1

Commercial $MoSi_2$ powders (99.9% purity, 2–20 μm particle size) and Nb powders (99.9% purity, 20 μm particle size) were used to make the first group samples; Mo (99.9% purity 3 μm particle size), Si (99.9% purity, 74 μm particle size) and Nb powders (99.9% purity, 20 μm particle size) were used to make the second group alloys. These powders were dry mixed in plastic bottles for at least 2 h. After that the powders were cold pressed under 50 MPa pressure. The compacts have a size of Φ20 mm×6 mm. Sintering was performed with a Pulse-

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Table 1
Compositions of the samples

Group I $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–xNb	$Mo_{0.317}Si_{0.633}$ –0.05Nb	$Mo_{0.3}Si_{0.6}$ –0.1Nb	$Mo_{0.1425}Si_{0.285}$ –0.4375Nb
Group II $(Mo_{1-x}, Nb_x)Si_2$	$(Mo_{0.95},Nb_{0.05})Si_2$	$(Mo_{0.90}, Nb_{0.10})Si_2$	$(Mo_{0.80}, Nb_{0.20})Si_2$

Discharge-Sintering machine at 1500 °C for 30 min under a pressure of 56 MPa. The time for heating to 1500 °C was generally 60 min and cooling to about 720 °C took about 15 min. After sintering, the samples were polished to make a mirror surface for XRD test and SEM examination. A solution containing one part HNO_3, one part HCl and three parts water was used to etch the sample for further microstructure revealing.

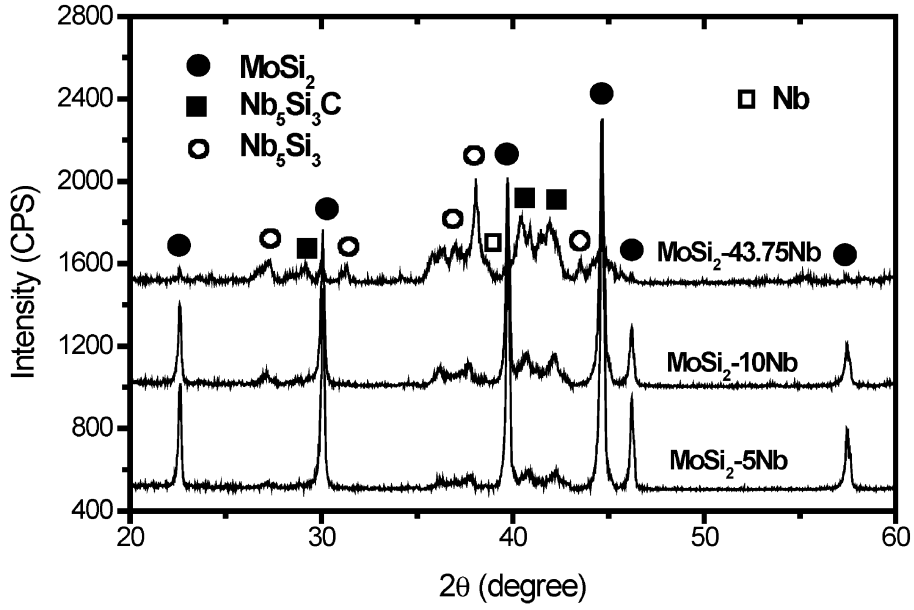

Fig. 1. X-ray diffraction spectrums of $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–$x$Nb ($x = 0.05$, 0.1 and 0.4375) samples.

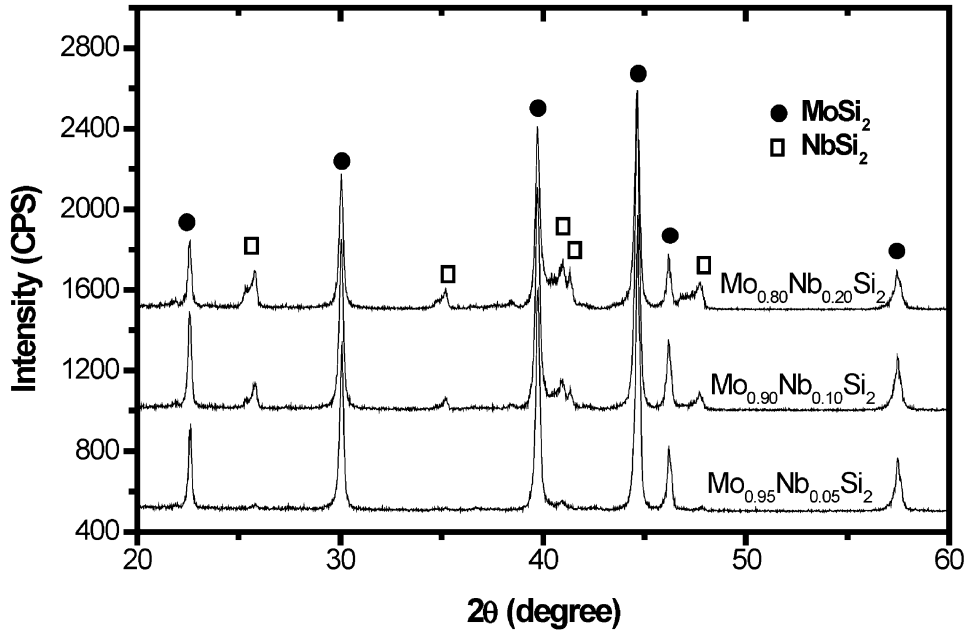

Fig. 2. X-ray diffraction spectrums of $(Mo_{1-x},Nb_x)Si_2$ ($x = 0.05$, 0.10, 0.20) samples.

3. Results and discussion

3.1. XRD examination

The XRD spectrums of the first group samples are shown in Fig. 1. Four phases are identified in these samples. They are: the $MoSi_2$ phase with a $C11_b$ crystal structure; tetragonal Nb_5Si_3 phase and carbon stabilized Nb_5Si_3C phase; Nb metal phase which has weak intensity. For the existence of $Nb_5Si_{3C,}$ it is believed that the carbon comes from the graphite die. In a study on the manufacture of Nb_5Si_3–Nb composites Nb_5Si_3C was also found.[6] In this group, it shows that the relative intensities of Nb_5Si_3 and Nb5Si3C phases from the 5Nb and 10Nb alloys increase with the increasing of Nb addition. The peaks of the $MoSi_2$ phase are predominant. However, in the 43.75Nb alloy, peaks from Nb_5Si_3 and Nb_5Si_3C are predominant while the peaks from $MoSi_2$ phase become very weak. These results suggest that with up to 43.75% Nb addition most $MoSi_2$ and Nb metal have reacted to form Nb_5Si_3 or Nb_5Si_3C phases. Only very few $MoSi_2$ and Nb metal phases are remained.

The XRD spectrums of the second group samples are shown in Fig. 2. Two phases are identified in these samples. They are: the $MoSi_2$ phase with a $C11_b$ crystal structure; $NbSi_2$ phase with a C40 crystal structure. Peaks from Nb and Nb_5Si_3 or Nb_5Si_3C are not observed. The intensities of the peaks from $NbSi_2$ phase increase along with the increasing of Nb addition. Appearance of $NbSi_2$ phase is not out of expectation but the relative intensities is too low. We have expected a predominant $NbSi_2$ phase microstructure in the sample with a composition of $(Mo_{0.8}, Nb_{0.2})Si_2$. A single $NbSi_2$ (C40) phase structure has been reported in sample with this composition.[5] The discrepancy between this research and former report might arise

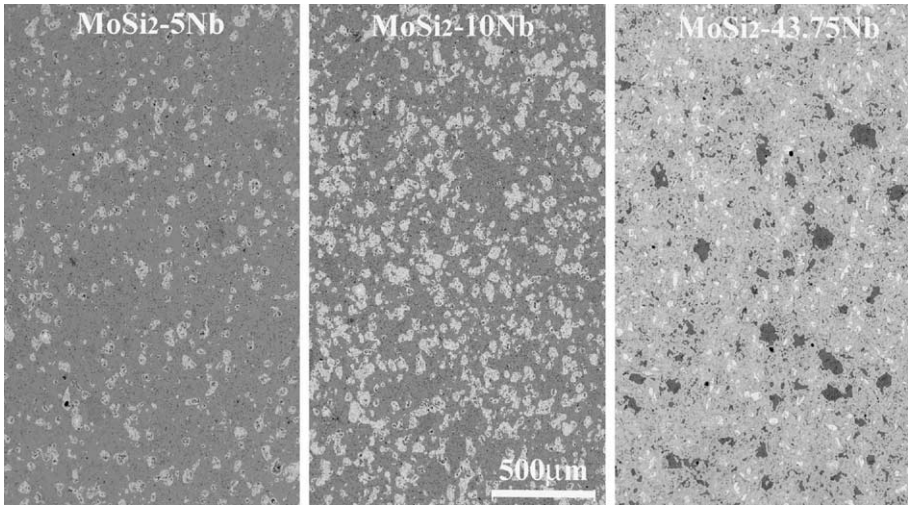

Fig. 3. SEM micrograph of $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–$x$Nb ($x = 0.05$, 0.1 and 0.4375) samples.

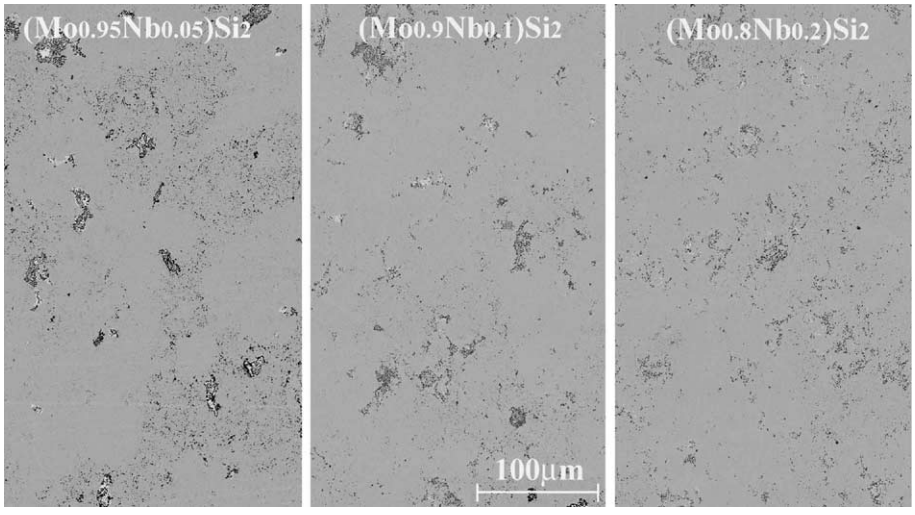

Fig. 4. SEM micrograph of $(Mo_{1-x},Nb_x)Si_2$ ($x = 0.05$, 0.10, 0.20) samples.

from the difference in sample preparation. In the earlier report sample was made through arc melting while in this research sample was made by powder metallurgy. It is quite possible that current sample is not in equilibrium state. This will be discussed in more detail later upon the data from SEM and EDAX examinations.

3.2. SEM examination

The microstructures of the first group samples are presented in Fig. 3. Under the back scattering electron (BSE) detecting mode in SEM, phases are clearly revealed. The matrix is the $MoSi_2$ phase and the bright phases in 5Nb and 10Nb alloys are Nb_5Si_3 or Nb_5Si_3C phases. It is not possible to identify these two phases under SEM. There are some very bright phases the center of the Nb_5Si_3 or Nb_5Si_3C phases in 5Nb and 10Nb alloys. These are Nb phases. The Nb phase volume fraction is very few in the 5Nb and 10Nb alloys but some high in the 43.75Nb alloy. These phases can easily be identified by EDAX composition analysis except the Nb_5Si_3C phase because EDAX could not detect carbon. In addition, there exist some dark areas that are believed to be amorphous silica or cavities. These observations are in agreement with that of XRD examinations. Similar agreement is also found for the second group samples. The SEM micrographs are shown in Fig. 4. $MoSi_2$ and $NbSi_2$ phases can be detected by EDAX. Bright phases in these samples are

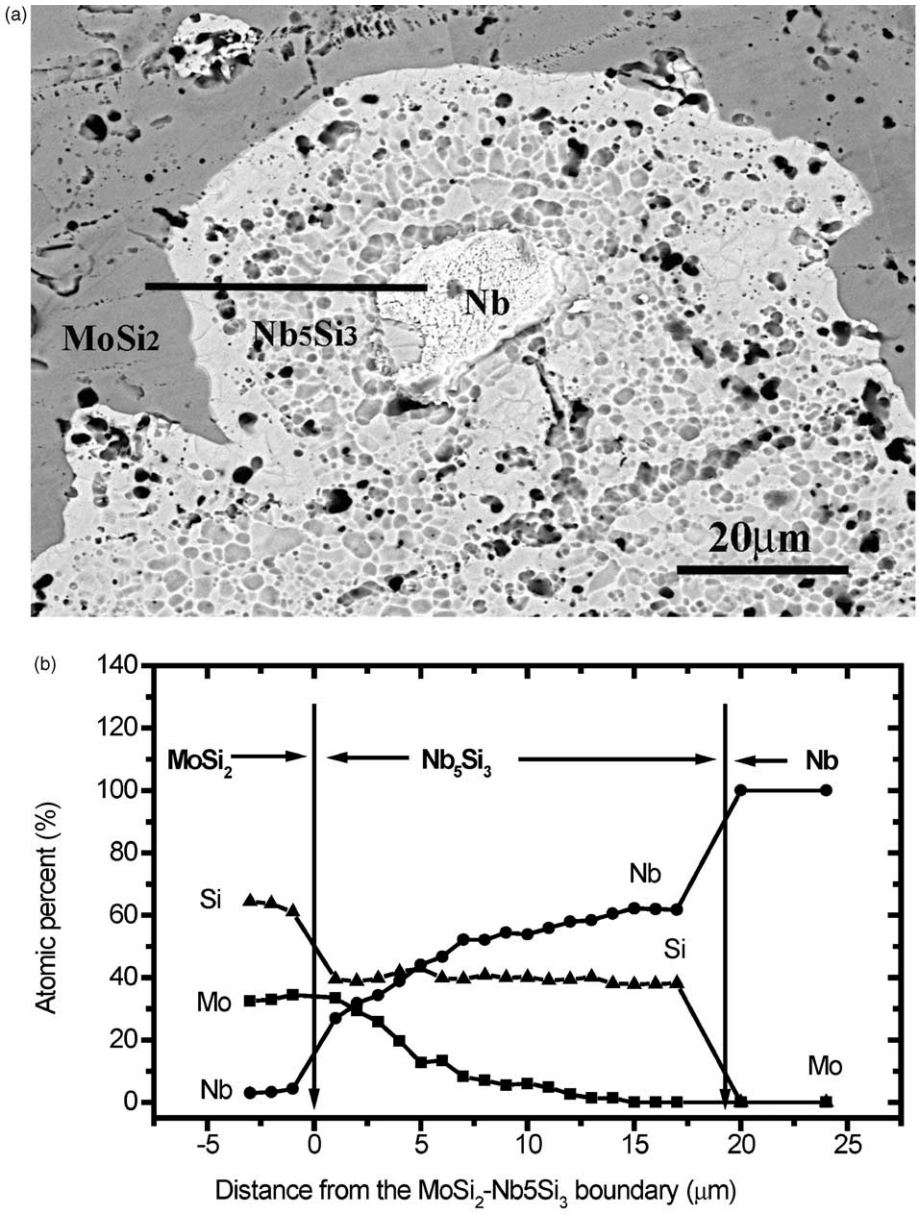

Fig. 5. (a) SEM micrograph of $MoSi_2$–10Nb sample. (b) Composition profile from marked bar in (a).

found to be Nb_5Si_3 or Nb_5Si_3C phases containing some Mo. These bright phases do not result in any peaks in Fig. 2 presumably because of its very low volume fractions.

After etching, the microstructures can be revealed more clearly. Fig. 5(a) shows the SEM micrograph of $MoSi_2$–10Nb sample and Fig. 5(b) shows the composition profile from marked bar in Fig. 5(a). Similar composition distribution was found in all the three samples of the first group. From Fig. 5(a) and (b) it is clear that Nb particle has reacted with the $MoSi_2$ phase and this process produced Nb_5Si_3 or Nb_5Si_3C phases. Furthermore, the Nb content distribution in Nb_5Si_3 or Nb_5Si_3C is not uniform. It shows a diffusion direction from the center to the boundary of the Nb_5Si_3 or Nb_5Si_3C phase. This phenomenon has been reported in Nb–$MoSi_2$ diffusion couple and $MoSi_2$–Nb ribbon composites.[7,8] In this research Nb particles are distributed in the $MoSi_2$ matrix. After sintering at high temperatures the Nb particles react with matrix and formed Nb_5Si_3 or Nb_5Si_3C phases. These Nb_5Si_3 or Nb_5Si_3C phase are believed to have better high temperature strength due to its more complex crystal structure. A composite of $MoSi_2$–Nb_5Si_3 can be expected to have better mechanical properties. Through this experiment it is evident that a composite that contain $MoSi_2$ and Nb_5Si_3 or Nb_5Si_3C can be made simply by adding Nb powders to $MoSi_2$ powders. And the volume fractions of the two phases can be adjusted in the range from 0 to 100%.

The results of EDAX examination on the phases in the samples of the second group suggest that the Nb phase has completely reacted with Mo and Si elements.

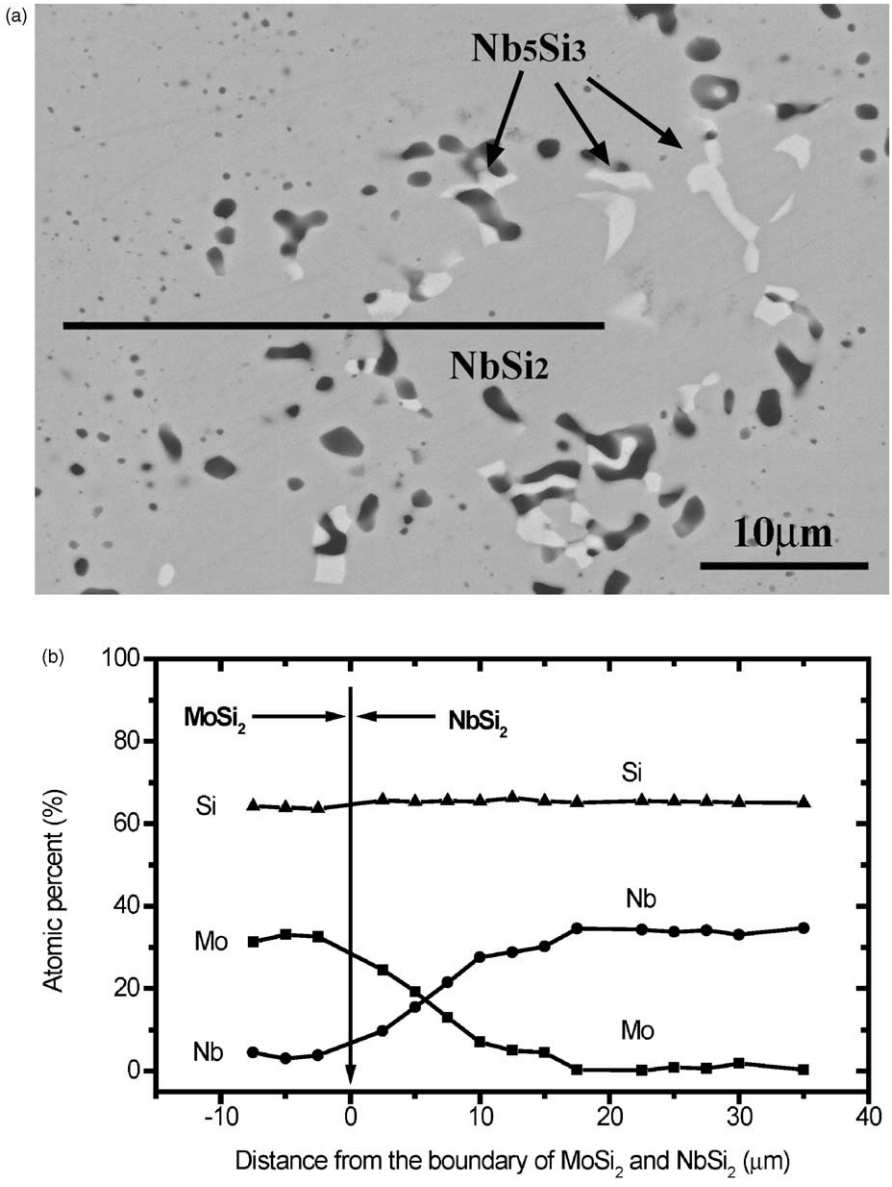

Fig. 6. (a) SEM micrograph of $(Mo_{0.8},Nb_{0.2})Si_2$ sample. (b) Composition profile from marked bar in (a).

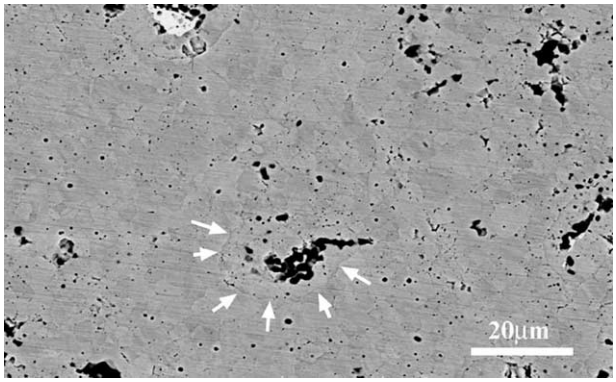

Fig. 7. SEM micrograph of $(Mo_{0.8},Nb_{0.2})Si_2$ sample. The boundary of $NbSi_2$ and $MoSi_2$ is indicated with arrows.

No pure Nb phase was found in this group. But the Nb distribution is not uniform either. There are some Nb_5Si_3 phases near the original Nb powders positions. $NbSi_2$ phases exist around these Nb_5Si_3 phases. This is shown in Fig. 6(a) and (b). Since $MoSi_2$ and $NbSi_2$ have different crystal structures, the two phases should have a boundary. This boundary is clearly revealed by etching as shown in Fig. 7. Detailed EDAX examination revealed that the Nb:Mo atomic ratio in the $NbSi_2$ (C40) phase may be as low as 27:73. This ratio is near the ratio of 20:80 reported by Nakano et al.[1] Considering the high Nb:Mo ration in the center area of the $NbSi_2$ (C40) phase, it is reasonable to suppose that if the samples were treated at higher temperature for longer time the volume fraction of $NbSi_2$ (C40) phase would have increased. This suggestion may help to explain why a single phase $NbSi_2$ (C40) microstructure was not obtained with the $(Mo_{0.80},Nb_{0.20})Si_2$ composition.

4. Conclusion

1. The effect of Nb addition on the microstructure of $MoSi_2$ alloy was studied.
2. With the compositions of $Mo_{1/3(1-x)}Si_{2/3(1-x)}$–$x$Nb ($x=0.05$, 0.1 and 0.4375) the alloys contain $C11_b$ $MoSi_2$ and Nb_5Si_3 as well as Nb_5Si_3C phases. There are also some unreacted Nb metal phases. The volume fractions of Nb_5Si_3 and Nb_5Si_3C phases increase with Nb addition and become the predominant matrix phase when Nb addition is 43.75%.
3. With the compositions of $(Mo_{1-x}, Nb_x)Si_2$ ($x=0.05$, 0.1 and 0.2) the alloys contain $C11_b$ $MoSi_2$ and C40 $NbSi_2$ phases as well as a small amount of $(Nb,Mo)_5Si_3$ phase. The volume fraction of $NbSi_2$ phase increases with Nb additions. The $C11_b$ $MoSi_2$ phase is the matrix phase and contains small amount of Nb element. The C40 $NbSi_2$ phase contains Mo element. The content of Mo is higher in the area adjacent to $MoSi_2$ phase but decreases to zero in the center of the $NbSi_2$ phase.

Acknowledgements

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