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Anomalous Effects of Alloying with Nb on Yield Strength of MoSi₂

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ABSTRACT
The effects of alloying with 1 at% Nb on the yield strength of MoSi₂ were investigated
from room temperature to 1600°C. Anomalous solid solution softening at low temperatures and
rapid solid solution hardening at high temperatures were observed by alloying. The mechanisms
resulting in these anomalies were investigated. Ambient temperature softening may be attributed
to the effects of Nb on stabilizing the 1/2<111> dislocations with lowering the stacking fault
energy. At elevated-temperatures, dislocation substructures were consistent with a viscous-glide
controlled behavior in (Mo,Nb)Si₂ alloys as compared to the easy cell structure formation in
unalloyed MoSi₂. At the intermediate (600-1200°C) temperature range, the anomalous increase
in the yield strength observed in unalloyed MoSi₂ appears to be suppressed by Nb alloying.

INTRODUCTION
The efficiency of a gas turbine engine is determined largely by its operating temperature.
Engine materials that can operate at temperatures above those of superalloys, ≈1100°C, are
needed for higher efficiency engines. Molybdenum disilicide (MoSi₂) –based alloys are
potential candidates to replace superalloys as structural materials for high-temperature
applications [1]. MoSi₂ has superior oxidation resistance, higher melting point, and lower
density in comparison with superalloys but inferior low temperature (< 900°C) ductility.
Furthermore, MoSi₂ exhibits a low strength at high temperatures (>1200°C). For example,
below ≈900°C, the fracture toughness of MoSi₂ is in the range of 2-4 MPa√m [2] and the 0.2%
offset yield strength of MoSi₂ at 1600oC is about 20 MPa [3]. The problem with pest oxidation
of MoSi₂ in the temperature range of 500°C to 800°C may be alleviated by alloying [4, 5].

Single crystals of MoSi₂ can be deformed plastically in compression down to ambient
temperatures in all major crystallographic directions except the [001] orientation [6]. However,
polycrystalline MoSi₂ is brittle at temperatures below ≈900°C due to the lack of sufficient
number of slip systems [6]. Alloying or reinforcing with a second phase may lower the brittle-
to-ductile transition temperature (BDTT) of MoSi₂. Ductile-phase toughening with metallic
phases has limited applicability in MoSi₂ due to the chemical reaction with silicon to form
silicides, and reinforcing with ceramic second phases such as SiC and ZrO₂ has only a modest
effect on enhancing plastic flow and increasing toughness [7].

Investigations on the alloying of MoSi₂ while maintaining its body-centered tetragonal
(C11₅) structure have indicated an improved low temperature ductility with Al or Nb alloying
and an increased high-temperature strength with Re alloying [3, 8-12]. It has also been shown
that MoSi$_2$ may be alloyed with both Al and Re to obtain concurrently improved low-temperature ductility and high-temperature strength [13]. Preliminary investigations have indicated that the combined effects of Al and Re on mechanical properties of MoSi$_2$ may be obtained by Nb alloying alone [14].

The possibility of obtaining concurring ambient-temperatures and high-temperatures improvements in the mechanical properties of MoSi$_2$ by Nb alloying is investigated here. The high temperature investigations are focused on improving the yield strength and the low temperature studies are concerned with increasing the ductility. Ductility and yield strength do not go hand in hand and an increase in one in general results in a decrease in the other. Microalloying techniques are employed to take advantage of anomalous solid solution hardening and softening to obtain concurrently enhanced room-temperature (RT) ductility and high temperature strength in single-phase polycrystalline MoSi$_2$.

**EXPERIMENTAL PROCEDURE**

Unalloyed polycrystalline MoSi$_2$ and samples alloyed with 1 at% niobium, (Mo$_{0.97}$ Nb$_{0.03}$)Si$_2$, were prepared by arc-melting elemental Mo, Si, and Nb in an argon atmosphere. Each sample was turned over and remelted 4 times to ensure homogeneity. The samples were polished with SiC paper up to 4000 grit and finished with 0.05 \( \mu \text{m} \) colloidal silica. Compression testing was performed on 2 \( \times \) 2 \( \times \) 4 mm$^3$ samples in air using an Instron 1125 machine at an initial strain rate of $\approx 1 \times 10^{-4}$ s$^{-1}$. Dislocation structures were characterized by transmission electron microscopy (TEM).

**RESULTS**

The results of compression testing for polycrystalline samples of unalloyed MoSi$_2$ and those containing 1 at% Nb are shown in Fig. 1. Unalloyed MoSi$_2$ would not yield prior to brittle fracture below 900°C. The RT yield strength of polycrystalline MoSi$_2$ estimated from the CRSS for operative slip systems in single crystals is about 1045 MPa [15]. The experimental compressive 0.2% offset yield strength of polycrystalline unalloyed MoSi$_2$ ranged from 276 MPa at 900°C to 14 MPa at 1600°C and those of (Mo$_{0.97}$ Nb$_{0.03}$)Si$_2$ samples from 500 MPa at 25°C to 143 MPa at 1600°C. Alloying MoSi$_2$ with 1 at% Nb lowered the BDTT (in compression) from 900°C to RT or below RT. RT was the lowest deformation temperature for these investigations. Compared to the estimated value from single crystals, the RT yield strength of MoSi$_2$ decreased by more than a factor of two. Nb alloying also improved the yield strength at 1600°C by an order of magnitude.
DISCUSSION

The effects of alloying with 1 at% Nb on the 0.2% offset yield strength of MoSi$_2$ may be divided into three distinctly different effects at three temperature regimes. Those effects are: (1) solid solution softening at T < 600°C, (2) solid solution hardening at T > 800°C, and (3) insignificant temperature dependence of yield stress at 600°C < T < 1200°C. These effects are discussed in the following sections.

**Low-Temperature Solid Solution Softening**

The tetragonal C11$_b$ structure of MoSi$_2$ is closely related to its hexagonal C40 structure and easy transformation from tetragonal to hexagonal is possible. It is known that the 1/2⟨111⟩ dislocations dissociate into two co-linear 1/4⟨111⟩ partials separated by a stacking fault on {110} [16]. The stacking sequence in the fault is ABCABC, which is also the stacking sequence in the C40 structure. Thus, the alloying elements such as Nb that stabilize the C40 structure with respect to C11$_b$ are likely to lower the stacking fault energy, thereby increasing the width of the faulted region. This change in the stacking fault energy surface ($\gamma$-surface) by alloying is likely to affect the Peierls stress and dislocation nucleation and mobility [9]. At low temperatures (<600 °C) where softening is observed, dislocation substructures in 1 at% Nb alloyed MoSi$_2$ predominantly exhibited the 1/2⟨111⟩ slip with some ⟨100⟩ slip. Investigations on the dislocations under the hardness indents in unalloyed MoSi$_2$ at these temperatures have revealed predominantly ⟨100⟩ slip [16]. Therefore, Nb alloying promotes 1/2⟨111⟩ slip in MoSi$_2$ at low
temperatures. The dislocation substructure of (Mo\textsubscript{0.97} Nb\textsubscript{0.03})Si\textsubscript{2} alloy compressed \( \approx 0.5\% \) at 400°C is shown in Fig. 2.

In a separate investigation, an increase in the separation distance between 1/4\{111\} partials by alloying with Nb was observed [15]. Addition of 1 at% Nb to MoSi\textsubscript{2} increased the stacking width to 7.5 -8.5 nm for the 60\(^\circ\) from screw orientation 1/4\{111\} compared to \( \approx 6.8 \) nm for the unalloyed MoSi\textsubscript{2} reported by Ito et al. [17]. Presumably Nb solute atoms segregate to the fault increasing the spacing between the partials and resulting in a lower stacking fault energy and hence, an enhanced dislocation mobility and a decreased flow stress. The stacking fault energies for the 1/2\{111\} dislocations in unalloyed and 1 at% Nb alloyed MoSi\textsubscript{2} were determined to be 269 and 207 mJ/m\(^2\), respectively, by \textit{ab initio} calculations [18]. Segregation of Nb solute atoms to the dislocation core may also promote kink nucleation resulting in an enhanced ductility at low temperatures.

![Fig. 2. Bright field TEM micrograph showing the dislocation substructure in a (Mo\textsubscript{0.97} Nb\textsubscript{0.03})Si\textsubscript{2} alloy compressed \( \approx 0.5\% \) at 400 °C. The labels 1 and 2 correspond to \langle100\rangle and 3 and 4 correspond to 1/2\{111\} type dislocations, respectively.](image)

\textit{Solid Solution Hardening}

Unalloyed MoSi\textsubscript{2} has very low yield strength at high temperatures \((T>1200\textdegree\text{C})\). Glide of dislocations in MoSi\textsubscript{2} at high temperatures is easy and the climb of dislocations is the rate
controlling mechanism as inferred from the well-defined dislocation cell structures [3]. The dislocation structure of 1 at% Nb containing samples deformed at 1200°C for ≈1% under compression is shown in Fig. 3. Deformation of (Mo₀.₉₇ Nb₀.₀₃)Si₂ at 1200°C resulted in dislocations with predominantly ⟨100⟩ and a few 1/2⟨111⟩ Burgers vectors and dipole loops that may be pinched-off the gliding ⟨110⟩ dislocations. ⟨110⟩ type sessile dislocations were formed from the [100]+[010]=⟨110⟩ reaction. The dislocation substructures were consistent with the increased glide resistance due to Nb alloying.

Nb alloying of C11b structure of MoSi₂ results in opposite effects at low (T < 600 °C) and high (T > 1200°C) temperatures. At low temperature enhanced 1/2⟨111⟩ mobility, decreased stacking fault energy, and perhaps enhanced kink nucleation by Nb alloying results in improved plasticity. At high temperatures, thermal activation of kink nucleation is easier than activation by Nb solutes as nucleation sites. Therefore, there is no softening effect at high temperatures because of the presence of Nb solutes. However, suppressed dislocation mobility with strain fields due to the presence of solute Nb results in a viscous glide controlled deformation mechanism in (Mo₀.₉⁷ Nb₀.₀₃)Si₂ instead of a climb controlled deformation mechanism observed in MoSi₂. The point defect structure in Nb alloyed samples need to be studied in more detail to interpret the high hardening rates at elevated temperatures.

![Micrograph](image_url)

Fig. 3. Bright field TEM micrograph from a MoSi₂-1at% Nb alloy compressed ≈1% at 1200°C. All dislocations in this micrograph have a ⟨100⟩ type Burgers vector. Reactions
between [100] and [010] produce [110] dislocations (e.g. marked with a black arrow), and dipole loops that may have been “pinched-off” during glide of dislocations.

**Intermediate Temperature Range**

Monocrystalline silicides exhibit anomalous increase in the yield stress with increasing temperature at different temperature ranges depending on the crystal orientations. The phenomenon of anomalous increase in yield strength with increasing temperature is not well understood. Recent investigations indicate a change in the dislocation core structure with temperature as the mechanism for this anomaly [19]. In MoSi$_2$, this anomalous yield stress behavior occurs at the temperature range of about 600-900°C for the \{011\}(100) and \{010\}(100) slip systems [20]. Similar behavior is observed at temperature range of about 800-1100°C for the \{110\}(111) slip system. Crystals with hard orientation, i.e. [001], exhibit anomalous yield behavior at 1000-1200°C with high CRSS for \{013\}(331) slip system. Therefore, the anomalous yield stress temperature range (AYSTR) in monocrystalline MoSi$_2$ samples varies from 600-1200°C depending on the sample orientation during compression testing.

The AYSTR for 1 at% Nb containing MoSi$_2$ shows insignificant variation in the yield strength with temperature. The 0.2% offset yield strength at 600-1200°C remains constant at 343±9 MPa. Similar behaviors were observed for 2 at% Al and 2 at% Al+1 at% Re containing MoSi$_2$ at 600-800°C published previously [14]. The behavior of polycrystalline (Mo$_{0.97}$Nb$_{0.03}$)Si$_2$ at the AYSTR may be elucidated by considering the yield anomaly of the aforementioned slip systems for soft orientations obtained by Ito et al. [20] as shown in Fig. 4.

First, at the AYSTR, i.e. 600-1200°C, \{011\}(100), \{110\}(111), and \{010\}(100) slip systems are the easy slip systems. In polycrystalline MoSi$_2$, since more than one slip system is active at a specific temperature because of the random orientation of the grains, the yield stress should be the weighted average of the yield stress for all the individual active slip systems. Starting at 600°C, the CRSS increases for \{100\} slip and it decreases for \{111\} slip. Therefore, the plot of yield strength vs. temperature becomes flat for polycrystalline samples.

Second, alloying polycrystalline MoSi$_2$ with Nb shifts the temperature for activation of the 1/2\{111\} type slip to lower temperatures and impedes the easy glide of dislocations at higher temperatures. This results in the enhancement of plasticity and strengthening below and above some intermediate temperature range, respectively. For polycrystalline (Mo$_{0.97}$Nb$_{0.03}$)Si$_2$ this intermediate temperature corresponds to the AYSTR. At 600-1200°C the softening and hardening effects of Nb on MoSi$_2$ are competing. The combined effects of the first and second phenomena is a temperature region at which yield strength remains relatively constant.
Fig. 4. Yield strengths for single crystals with $[\bar{1}10]$ and $[0\ 15\ 1]$ orientations from Ref. [20] and the 0.2% offset yield strength of polycrystalline MoSi$_2$ and 1 at% Nb alloyed MoSi$_2$.

SUMMARY
Alloying polycrystalline MoSi$_2$ with Nb within the solubility limits in C11$_b$ structure had a significant effect on the yield strength in compression. 1 at% Nb alloying resulted in enhanced ambient temperature ductility and high temperature strengthening. At the temperature range of 600-1200°C, the yield strength of (Mo$_{0.97}$ Nb$_{0.03}$)Si$_2$ remained constant at 343±9 MPa.

ACKNOWLEDGEMENTS
This research was funded by department of energy, Office of Basic Energy Sciences. The first author was also supported by the Rackham Award from Horace H. Rackham School of Graduate Studies and Office of Research at University of Michigan.

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