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Mechanical Behavior of Molybdenum Disilicide-Based Alloys

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ABSTRACT

We have investigated the mechanical behavior of the following single-phase polycrystalline alloys with the MoSi₂ body-center tetragonal structure: MoSi₂ alloyed with ~2.5 at.% Re, MoSi₂ alloyed with 2 at.% Al, MoSi₂ alloyed with 1 at.% Nb, and MoSi₂ alloyed with 1 at.% Re and 2 at.% Al. Several anomalies in the mechanical behavior of alloyed materials were observed. For example, (i) addition of only ~2.5 at. % Re results in an order of magnitude increase in compressive strength at 1600 °C, (ii) additions of Nb and Al cause solution softening at near-ambient temperatures, and (iii) quaternary MoSi₂-Re-Al alloys show strengthening at elevated temperatures and reduction in flow stress with enhanced plasticity at near-ambient temperatures in compression. The mechanisms of anomalous solution hardening and softening are discussed.

INTRODUCTION

Significant increases in the operating temperatures of high-temperature structural components will only be possible if superalloys are replaced with higher melting temperature intermetallic or ceramic materials [1-2]. Refractory metal silicides such as MoSi₂, Mo₅SiB₂, Nb₅Si₃, etc. typically have melting temperatures in excess of 2000 °C and are potential materials for use at temperatures exceeding the melting point of Ni-base superalloys [1-3]. In addition to the low room temperature fracture toughness, the strengths of monolithic silicides at temperatures above ~1400 °C are typically very low. Silicides in the composite form, either with ceramic reinforcements (e.g., MoSi₂-SiC) or eutectics (MoSi₂-Mo₅Si₃), often show enhanced high temperature strengths but the room temperature fracture toughness is still very low [4]. Ductile metallic reinforcements such as Nb react with the disilicide matrix to form other silicides and have limited practical use for long-term high temperature applications, although improvements in toughness have been demonstrated in these composites [5]. This approach, however, may be promising for Si-poor silicides, as shown in systems such as Nb-Nb₅Si₃, Mo-Mo₅SiB₂, etc. [6].

Due to the complex crystal structures and presumably limited deformation capability of these compounds, little work has been done on studying how alloying in the single-phase region influences the deformation behavior. Recent studies on single crystal MoSi₂ have shown compressive plasticity even at temperatures below ambient [7,8]. Furthermore, first principles calculations have predicted that solutes such as Al, Nb, Mg and V may enhance the ductility of MoSi₂ [9]. In the present investigation, we have chosen MoSi₂ as a model material (Fig. 1) to study selected substitutional alloying effects that are anomalous as compared to the classical theories for metals.

Fig.1 Body-centered tetragonal unit cell of MoSi₂; slip vectors are shown by arrows.

EXPERIMENTAL PROCEDURES

Pure MoSi_2 , ternary $(\text{Mo,Re})\text{Si}_2$, $(\text{Mo,Nb})\text{Si}_2$, $\text{Mo}(\text{Si,Al})_2$ and quaternary $(\text{Mo,Re})(\text{Al,Si})_2$ alloys were prepared by arc-melting high-purity elements in an argon atmosphere. The starting melt compositions were MoSi_x , with $x=2.01$ to account for the Si loss during melting. The buttons were turned over and remelted 4 times for homogeneity. Alloying levels were in the 1-2 at.% range. Compression testing was performed on $2 \times 2 \times 4 \text{ mm}^3$ samples, polished to $0.05 \mu\text{m}$ finish, in air using an Instron 1125 machine at an initial strain rate of $\sim 1 \times 10^{-4} / \text{s}$. Transmission electron microscopy (TEM) was performed on a Philips CM30 microscope operating at 300 kV.

RESULTS

All materials tested were polycrystalline with large grain sizes on the order of $100 \mu\text{m}$. Compression testing revealed three unusual phenomena in these alloys that are described below:

Anomalous Hardening

Alloying with Re in the 1-2% level resulted in large increases in the high temperature (T) yield strength of MoSi_2 (Fig. 2). No tests were conducted at $T > 1600^\circ\text{C}$. At $T < 900^\circ\text{C}$, fracture before yield was typically observed and data for MoSi_2 are estimated from tests on single crystals [7,8]. Fig. 2 is a log-linear plot, where linear fits to the data are consistent with a Peierls-stress controlled behavior [10]. Note that the strength of MoSi_2 drops significantly at $T > 1400^\circ\text{C}$, while the Re-alloys show better strength retention. Even at 1600°C , the addition of only 2.5 at.% Re resulted in an order of magnitude increase in high temperature strength.

Fig. 2 Effect of 2.5 at.% Re on the high T strength of polycrystalline MoSi_2 . Data at $T < 900^\circ\text{C}$ are estimated (est.) from single crystal tests [7,8].

Solution Softening

Fig. 2 shows that Re is a potent hardener in MoSi_2 , but the Re-alloys exhibit no plasticity in compression at $T < 1000^\circ\text{C}$. Fig. 3 shows examples of alloying effects that enhance the room temperature compressive plasticity of MoSi_2 . At $T \leq 900^\circ\text{C}$, the yield strength of polycrystalline MoSi_2 is estimated from critical resolved shear stresses for $\{110\}\langle 111 \rangle$ slip at $T > 500^\circ\text{C}$, and $\{011\}\langle 100 \rangle$ at $T < 500^\circ\text{C}$, measured on single crystals. Note that both Nb (1 at.%) and Al (2 at.%) alloys are deformable at room T at strength levels significantly lower than the estimated yield strength of MoSi_2 at room T. At $T < 800^\circ\text{C}$, the temperature dependence of flow stress of MoSi_2 is also lowered by Nb and Al additions.

Fig. 3 Effects of 1 at.% Nb and 2 at.% Al alloying, respectively, on the yield strength of polycrystalline MoSi_2 . The alloys exhibit compressive plasticity at room temperature.

High T Hardening and Low T Softening

Fig. 4 shows two examples where alloying additions have both increased the high T strength and reduced the low T yield strength enough to cause compressive plasticity at room T. This behavior is best exhibited by the quaternary $(\text{Mo,Re})(\text{Si,Al})_2$ alloys that contained only 1 at.% Re and 2 at.% Al. In other words, these alloys combine the beneficial effects of Re (high T hardening) and Al (low T softening) alloying shown in Fig. 2 and 3. Similar effect is seen with Nb additions (Fig. 3 and 4), where only 1 at.% Nb lowers the minimum T at which compressive plasticity is observed from $\sim 900^\circ\text{C}$ to ambient, and resulted in high T hardening. The Al-containing ternary alloys (Fig. 3), however, have insignificant effect on high T strength.

Fig. 4 Quaternary $(\text{Mo,Re})(\text{Si,Al})_2$ alloys with ~ 1 at.% Re and 2 at.% Al are stronger than MoSi_2 at high T and softer at near-ambient T. Ternary Nb-containing alloys exhibit similar behavior.

Dislocation Substructures

In unalloyed MoSi_2 , dislocation substructures were similar to those observed in pure metals deformed at elevated temperatures [11]. Regular cell structures and sub-grains were observed at deformation $T > 1300^\circ\text{C}$ consistent with climb controlled deformation, i.e., glide is easy and climb of dislocations over substructure obstacles is the rate controlling step. The Re-containing alloys show “viscous glide” controlled substructures, i.e., lots of free dislocations and tangles of the $\langle 100 \rangle$ and $1/2\langle 111 \rangle$ type, with little tendency to form cell structures even at 1600°C . Furthermore, weak beam imaging of the $1/2\langle 111 \rangle$ dislocations indicated that Re alloying increases the stacking fault energy [11].

In the ternary $(\text{Mo,Nb})\text{Si}_2$, $\text{Mo}(\text{Si,Al})_2$ and the quaternary $(\text{Mo,Re})(\text{Al,Si})_2$ alloys, the dislocation substructures at temperatures where solution softening is observed (i.e., $T < \sim 600^\circ\text{C}$) consisted primarily of $1/2\langle 111 \rangle$ dislocations, with some $\langle 100 \rangle$ dislocations as shown in Fig. 5. The preferred line direction of the $1/2\langle 111 \rangle$ dislocations appeared to be 60° from screw, consistent with similar observations on unalloyed MoSi_2 [7,8]. While polycrystalline MoSi_2 could not be deformed at low temperatures in compression, studies of dislocations under hardness indents in polycrystalline MoSi_2 have revealed primarily $\langle 100 \rangle$ type dislocations at these temperatures [12]. This suggests that alloying elements such as Nb and Al that cause solution softening at low temperatures may promote $1/2\langle 111 \rangle$ slip in MoSi_2 . A similar inference was made through an analysis of slip traces around room temperature hardness indents on single crystalline $\text{Mo}(\text{Si,Al})_2$ [13], and more recently, through compression testing on single crystals [14]. Another important effect revealed in weak beam imaging of $1/2\langle 111 \rangle$ dislocations in Nb-alloyed materials, Fig. 5, (and also, Al-alloyed materials not shown here) is that partial spacing is increased, i.e., stacking fault energy is lowered, consistent with other studies [14,15].

At intermediate temperatures (~ 800 - 1000°C), when the flow stress increases anomalously with increasing temperatures, still predominantly $1/2\langle 111 \rangle$ dislocations are observed in the Nb and Al-alloyed MoSi_2 . Note that at these temperatures, solution softening is not observed. Most

of the $1/2\langle 111 \rangle$ dislocations on $\{110\}$ planes are in the form of “bundles” at these temperatures, i.e., groups of several dislocations closely spaced, separated by relatively dislocation free regions. These dislocations showed a stronger tendency as compared to 400 °C to be straight and mostly be along the 60° orientation. The anomalous increase in the yield strength with increasing temperature has been interpreted as a Portevin-Le Chatelier effect in unalloyed MoSi₂, presumably caused by interstitial impurities, even though impurity levels as low as 40 wtppm were reported in float-zone crystals studied by Ito *et al.* [7]. An alternate view is that the 60° non-screw dislocations lie along the $\langle 110 \rangle$ directions which are common to several low-index intersecting planes such as $\{110\}$, $\{001\}$ and $\{331\}$. Hence, the possibility of a non-planar dislocation core at these temperatures with segments on planes where the critical resolved shear stress for glide is very high cannot be ruled out. Our present work shows that anomalous yielding is also observed in alloyed MoSi₂. Needless to add, the mechanisms of anomalous yielding in MoSi₂ need to be studied in more detail including first principles and atomistic simulations of dislocations, as shown in a recent study by Mitchell *et al.* [16].

At elevated temperatures (>1200 °C), the Nb-alloyed materials are harder than MoSi₂ and dislocation substructures (Fig. 6) show predominantly $\langle 100 \rangle$ type dislocations and dipole loops that may be pinched-off gliding $\langle 100 \rangle$ dislocations. Several short $\langle 110 \rangle$ dislocation segments are also seen formed as a reaction product between $[100]$ and $[010]$ dislocations. Since this work is on polycrystals, the critical resolved shear stresses for $\langle 111 \rangle$ and $\langle 100 \rangle$ dislocations could not be determined as a function of temperature. Also, more statistics is needed to quantitatively assess the relative amounts of $\langle 111 \rangle$ and $\langle 100 \rangle$ slip at elevated temperatures. From Fig. 6, it does, however, appear that $\langle 111 \rangle$ slip is not as favored as it is at lower temperatures compared to $\langle 100 \rangle$ slip.

Fig. 5 (a) Bright field and (b) weak beam TEM micrographs showing the dislocation substructures in a MoSi₂-1 at.% Nb alloy compressed ~0.5% at 400 °C. The labels a and d correspond to $\langle 100 \rangle$, and b and c correspond to $1/2\langle 111 \rangle$ type dislocations respectively. The weak beam image shows that the $1/2\langle 111 \rangle$ dislocations are dissociated into $1/4\langle 111 \rangle$ partials, with lower fault energy than unalloyed MoSi₂.

Fig. 6 Bright field TEM micrograph from a MoSi₂-1 at.% Nb alloy deformed ~ 1% at 1200 °C. All dislocations in this micrograph have a $\langle 100 \rangle$ type Burgers vector. Reactions between $[100]$ and $[010]$ produce $[110]$ dislocations (e.g., marked with an arrow), and dipole loops, that may have been “pinched-off” from glide dislocations are also seen.

DISCUSSION

The rapid solution hardening of MoSi_2 by Re at elevated temperatures is anomalous and may not be explained within the framework of the classical solution hardening theories based on atomic size and modulus misfits. Since rhenium “disilicide” has a Si-deficient stoichiometry corresponding to $\text{ReSi}_{1.75}$ [17], a Si vacancy may form with every four Re atoms added. The pairing of Re substitutionals with Si constitutional vacancies will result in point defect complexes with elliptical strain fields and hence, strong interaction with both edge and screw dislocations. The fact that hardening is observed even at 1600 °C indicates that these defect complexes are very stable. A dislocation model for this rapid hardening has been presented elsewhere [11], and we only discuss the solution softening here.

With regard to solution softening in MoSi_2 , we note the following features: (i) softening is caused by elements such as Nb, Al, Ta, etc. that change the structure of MoSi_2 from body-centered tetragonal (C11_b) to hexagonal, (ii) softening occurs only at low concentrations (typically < 2-3 at.%) in the single-phase C11_b structure, i.e., at higher concentrations of Nb or Al when the structure changes to hexagonal, the normal hardening behavior is observed, (iii) softening occurs only at low temperatures (< ~600 °C), and (iv) all solutes that soften MoSi_2 lower the stacking fault energy, as inferred from the $1/4\langle 111 \rangle$ partial spacing. Furthermore, Harada *et al* [18] have shown that elements such as Zr with a strong affinity for interstitial impurities did not result in any significant softening. This led Harada *et al* to conclude that the scavenging of interstitial solutes by Al (or, Nb) may not be the dominant mechanism for solution softening in MoSi_2 . The more likely mechanism is the lowering of the Peierls stress and/or easier double kink nucleation in the presence of solutes. Waghmare *et al.* [9] have shown, through first-principles calculations, that elements such as Nb, Al, Mg, and V change the generalized stacking fault energy (γ)-surface of dislocations in MoSi_2 . Since Peierls stress is given directly by the maximum gradient of the γ -surface, the net effect of solutes such as Nb and Al was predicted to be a lowering of the Peierls barrier at low homologous temperatures. Experimentally, we observed that Nb and Al lowered the stacking fault energy, and the increased $1/4\langle 111 \rangle$ partial spacing may result in increased mobility of these partials, consistent with the lower Peierls barrier predicted by Waghmare *et al* [9]. The reason why these solutes segregate to the $1/2\langle 111 \rangle$ dislocation may be related to the higher solubility of these solutes in the hexagonal structure of MoSi_2 . The difference in the tetragonal and hexagonal structures of MoSi_2 is that former has ABAB stacking while the latter has ABCABC stacking of $\{110\}$ planes. The stacking sequence in the fault that separates the two $1/4\langle 111 \rangle$ partials in the otherwise tetragonal MoSi_2 is also ABCABC. Thus, solutes that stabilize the hexagonal structure are likely to segregate to the fault. We further speculate that at elevated temperatures, changes in the core structure (e.g., climb-assisted) and/or solute mobility may reduce the effect of solute on the γ -surface and the Peierls stress.

SUMMARY

The anomalous effects of substitutional alloying, at < 2 at.% level, on the mechanical behavior of polycrystalline MoSi_2 are summarized as follows:

(i) Rapid hardening by Re at elevated temperatures: an order of magnitude increase in compressive strength was observed at 1600 °C, and is interpreted as due to strong interactions of both screw and edge dislocations with Re substitutional-Si vacancy point defect complexes.

(ii) Solution Softening at temperatures $< \sim 600$ °C: alloying with either Nb or Al caused a decrease in yield strength at these temperatures. The Nb or Al-alloyed MoSi₂ exhibited compressive plasticity at room temperature, while the unalloyed MoSi₂ fractured before yield at $T < \sim 900$ °C. We hypothesize that these solutes, through a lowering of the stacking fault energy, are able to lower the Peierls barrier at low temperatures.

(iii) Low Temperature Softening and High Temperature Hardening: observed in ternary (Mo,Nb)Si₂ and quaternary (Mo,Re)(Si,Al)₂ alloys. These results, particularly the quaternary alloys, indicate a non-linear addition of the effects of different solutes, e.g., Al effect dominates at low temperatures and Re effect at high temperatures.

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