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Materials Science and Engineering A 463 (2007) 107–114

MATERIALS SCIENCE & ENGINEERING A

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# The influence of silicon on the strength and fracture toughness of molybdenum

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Received 17 April 2006; received in revised form 18 July 2006; accepted 22 July 2006

**Abstract**

Mo–Si alloys containing up to 1 wt.% Si were fabricated by powder-metallurgical processing and their lattice parameters, elastic constants, densities, grain sizes, strengths, ductilities, and fracture toughness values were measured. The yield strength was insensitive to the grain size, i.e., a Hall–Petch relationship was not observed. Generally, Si additions caused pronounced solid solution strengthening. However, for small Si concentrations ($\leq$0.1 wt.%) solid solution softening was observed at room temperature and below. With increasing Si concentration, the room temperature ductility and fracture toughness dropped precipitously. This is attributed to the increase in strength and a transition from transgranular to intergranular fracture.


*Keywords:* Molybdenum; Solid solution strengthening; Solid solution softening; Hall–Petch relationship

## 1. Introduction

Molybdenum borosilicide alloys are a new class of potentially oxidation-resistant ultra-high temperature materials receiving substantial interest in both the industrial as well the scientific community [1–4]. In this respect, they were the subject of a recent symposium entitled "Beyond Nickel-Base Superalloys" [5]. Usually, molybdenum borosilicides consist of three phases: a molybdenum solid solution phase ($Mo_{ss}$), an intermetallic $Mo_3Si$ phase, and a ternary intermetallic $Mo_5SiB_2$ phase ("T2-phase"). The two intermetallic phases are brittle—their room temperature fracture toughness values are around 2–3 MPa $m^{1/2}$ [6,7]. However, they are very strong at high temperatures [7,8] and provide the necessary oxidation resistance due to the potential for forming a protective borosilicate glass layer at temperatures above 1000 °C [9]. While the $Mo_{ss}$ is not oxidation-resistant, it contributes greatly to the room temperature fracture toughness of molybdenum borosilicides: the room temperature fracture toughness and crack growth resistance of molybdenum borosilicides increase with increasing $Mo_{ss}$ volume fraction and reach values as high as 21 MPa $m^{1/2}$ [3,10].

The ductility and fracture toughness of the $Mo_{ss}$ is very important for the properties of molybdenum borosilicides; on the one hand, the higher the ductility and fracture toughness of the $Mo_{ss}$, the less is needed to achieve a particular value of the fracture toughness [3]. On the other hand, a smaller $Mo_{ss}$ volume fraction translates into improved oxidation and creep resistance. According to the ternary Mo–Si–B phase diagram, the $Mo_{ss}$ contains a negligible amount of B and up to 0.87 wt.% Si (2.9 at.%) at 1600 °C [11]. The binary Mo–Si phase diagram indicates a value of 0.65 wt.% (2.2 at.%) Si at that temperature [12]. It has been known for more than half a century that silicon significantly increases the room temperature strength of Mo. At the same time, it reduces its ductility. For example, according to Bruckart et al. and Northcott, an addition of 0.5 wt.% Si reduces the room temperature ductility of Mo from 25 to 3% [13,14]. However, no systematic investigations were carried out so far regarding the temperature and composition dependence of the tensile properties of binary Mo–Si alloys. Therefore, the purpose of the present work is to evaluate the microstructure and mechanical properties of Mo–Si solid solutions in considerably greater detail.

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doi:10.1016/j.msea.2006.07.153

Table 1
Room temperature lattice parameters, elastic moduli, density values, porosity, and grain sizes of Mo–Si solid solution alloys after hot isostatic pressing (HIPing)

| Si (wt.%) | Si (at.%) | Lattice parameter (nm) | Young's modulus $E$ (GPa) | Shear modulus $G$ (GPa) | Density (Mg/m$^3$) (Archimedes) | Density (Mg/m$^3$) (lattice parameter) | Porosity volume fraction (%) | Grain size (μm) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0.31478(2) | 302.6 | 117.4 | 10.09 | 10.22 | 1.3 | 97(8) |
| 0.1 | 0.34 | 0.31468(2) | 307.5 | 119.9 | 10.07 | 10.20 | 1.3 | 54(4) |
| 0.5 | 1.69 | 0.31443(1) | 298.1 | 115.0 | 10.00 | 10.13 | 1.3 | 35(5) |
| 1.0 | 3.34 | 0.31412(10) | | | 9.97 | 10.04 | 0.7 | 82(5)[a] |

Estimated errors are indicated in brackets.
[a] This alloy was annealed for10 h/2000 °C after the HIPing; prior to the HIPing the grain size was 26 μm.

## 2. Experimental procedure

Mo–Si alloys with 0, 0.1, 0.5, and 1.0 wt.% (0, 0.34, 1.69, 3.34 at.%) Si were fabricated from Mo standard powder (Plansee AG, Reutte, Austria) and Si powder (H.C. Stark). For each alloy, 10 kg of powder were mixed, cold isostatically pressed into rods, and sintered in hydrogen for 5 h at 1850 °C. After removing the surface layer, the rods were vacuum-encapsulated in Ti cans and hot isostatically pressed (HIPed) for 5 h at 1500 °C and a pressure of 200 MPa. After the Ti cans were removed by machining, the rods had final lengths and diameters of approximately 200 and 45 mm, respectively. The Mo–1 wt.% Si alloy was hydrogen-annealed for 10 h at 2000 °C after the HIPing in order to dissolve residual $Mo_3Si$ and to increase its grain size. Unalloyed Mo as well as Mo–0.1 wt.% Si materials were hydrogen-annealed for 10 h at 1800 °C or 10 h at 2000 °C to provide a range of grain sizes. The chemical compositions of the alloys were determined by fusion analysis, combustion analysis, and inductively coupled plasma–optical emission spectroscopy (ICP–OES). The Si concentration was confirmed using wave-length dispersive analysis in a scanning electron microscope (SEM). The lattice parameters were determined by X-ray diffraction of polished specimens. Density values $\rho_A$ were measured with paraffin-coated specimens using Archimedes principle. Density values $\rho_{xrd}$ were also calculated from the composition and the measured lattice parameters. The residual porosity was calculated as $100\% \times (\rho_{xrd} - \rho_A)/\rho_A$. Elastic constants were determined using a resonance technique in which a bend bar was suspended on two carbon fiber loops in vacuum. The characteristic resonance frequencies were determined with a piezo-electric actuator/detector system and evaluated according to Lins et al. [15]. Grain sizes were determined as the average linear intercept length on polished and electrolytically etched specimens. For each alloy, several pictures were analyzed in order to obtain a standard deviation. Likewise, 10 Vickers hardness values with a load of 1 kg were measured for each composition. Tensile and compression testing was carried out at a strain rate of $2.2 \times 10^{-3}\ s^{-1}$. The tensile specimens had gage lengths and gage diameters of 15 and 3, or 25 and 5 mm, respectively. Testing at temperatures up to 538 °C was carried out in air, and at higher temperatures in vacuum. The compression specimens were 8 mm high with a diameter of 5 mm. Fracture toughness values were determined using 10 mm × 10 mm × 55 mm bend bars notched 4 mm deep by electro-discharge machining (fatigue pre-cracking of pre-notched specimens was not successful). The fracture toughness was determined from three-point bending experiments on these specimens using standard relationships and the specimen geometry, span, and maximum load [16]. Five values were determined for each alloy. The fracture surfaces of selected specimens were examined in a SEM.

## 3. Results

The measured lattice parameters, elastic constants, densities, and grain sizes are listed in Table 1. The lattice parameter decreases linearly with the Si concentration. Examples of the microstructure and residual porosity are visible in Fig. 1. Table 2 shows the result of the chemical analysis. As in commercially pure Mo, the concentration of all interstitial elements such as C, O, N, and H is very low, with values less than 5 wppm. It

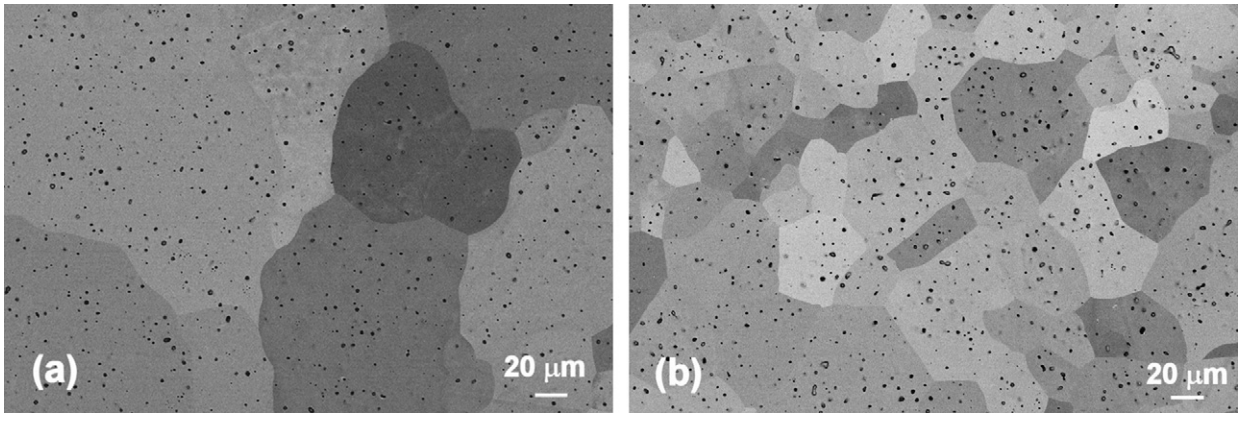


Fig. 1. SEM images of electrolytically etched Mo (a) and Mo–0.5 wt.% Si (b). The black spots indicate the (overetched) residual porosity.