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The influence of silicon content on microstructure and hardness of Mo–Si alloys

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ABSTRACT

Mo–Si alloy sheets with different silicon content were fabricated by powder-metallurgical and thermo-mechanically processing. The effect of Si content and annealing temperature on microstructure and hardness of the Mo–Si alloys were studied by using optical microscopy (OM), transmission electron microscopy (TEM) and Vickers hardness tester, respectively. The results indicated that the presence of Si can effectively refine the grain sizes and improve the hardness of Mo–Si alloys. Si can also increase the recrystallization temperature of alloys and play a significant role in restraining the grain growth at high temperatures. Increasing the annealing temperature, the microstructure of Mo–Si alloy sheets is gradually coarsened and changed from fibrous to equiaxed structure, causing reduction in hardness. The hardening effect in the Mo–Si alloys came from the refined grain strengthening, solid solution strengthening, and second phase particle strengthening, which are closely dependent on the Si content and annealing temperature.

1. Introduction

With rapid development of aerospace and air craft engine communities, more stringent requirements on the mechanical properties were proposed to the structural materials used at elevated temperatures. Thus, speeding up the research progress of high temperature structural materials and improve its performance are the crucial problems that need to be solved urgently. In the past few years, intermetallics and most ceramics has been the focus of research attention. The intrinsic brittleness of these materials has guided research in the direction of multiphase refractory alloys which contain a matrix phase that is capable of providing ductility, and a suitable volume fraction of second phase(s) that enhances the creep resistance of the alloy at elevated temperature [1]. The current investigations indicated that the molybdenum borosilicide alloys are potential candidate materials for the next generation of high temperature structural material [2–4].

Usually, molybdenum borosilicide alloys composed of three phases: a molybdenum solid solution phase (Mo_{ss}), brittle intermetallic phases Mo_5SiB_2 (T_2 phase) and Mo_3Si. The two intermetallic phases are very strong at high temperatures and provide the necessary oxidation resistance due to the potential for forming a protective borosilicate glass layer at temperatures above 1000 °C [5]. While the Mo_{ss} is not oxidation-resistant, Mo_{ss} has excellent ductility and toughness that is very important for the mechanical properties of molybdenum borosilicide alloys [6]. According to the binary Mo–Si and Mo–B phase diagram, the solubility of Si in Mo depends on temperature, and the Mo_3Si particle can be precipitated when the Si content is higher than 3 at.% at 1600 °C, while that of B in Mo is thought to be negligible and its effect on the mechanical properties of the solid solution molybdenum alloy is thought to not be critical [7,8]. It has been known that silicon significantly increases the room temperature strength and reduces the ductility of Mo. However, no systematic investigations have been carried out so to reveal the annealing temperature and composition dependence of the microstructure and hardness of binary Mo–Si alloys. Thus, the purpose of the present work is to systematically study the microstructure and hardness of Mo alloy sheets with the addition of different silicon concentrations and discuss the hardening mechanism of the solid solution of Si and molybdenum silicide as well as annealing temperature.

2. Experimental procedures

The Mo alloy sheets added with 0, 0.1, 0.3, 0.6 and 1.0 wt.% (0, 0.34, 1.02, 2.04 and 3.4 at.%) Si were fabricated by powder-metallurgical and thermo-mechanically processing. Elemental powders of Mo and Si has 99.96 wt.% and 99.5 wt.% purity, respectively. For each alloy, 2 kg of powder was mixed. A milling process was carried out for 48 h in stainless container with Mo milling balls in a planetary ball mill with a rotational speed of 40 rpm. Homogeneously mixed powders were statically cold pressed into slab compacts, and sintered at 1900 °C for 6 h in flowing dry hydrogen. The resulting sinter billets were then thermo-mechanically processed at 1330–1270 °C into sheet with the thickness of 2.5 mm (ε>80%). Finally the sheets were

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carefully annealed at 850, 950, 1050, 1150, 1250, 1350, 1450 and 1550 °C in a dry hydrogen atmosphere for 1 h.

The density (ρ_A, measured density) of the sintered billets was measured on paraffin-coated specimens using Archimedes principle. Density (ρ_{XRD}, theoretical density) was calculated from the composition and the measured lattice parameters [8]. The results are listed in Table 1. The sheet samples were polished along the rolling direction and etched with Murakami's etchant (10 g potassium ferricyanide, 10 g sodium hydroxide, and 80 ml distilled water) for optical metallographic examinations. Optical microscopy (OM) observations were performed by using an OLYMPUS metalloscope. Grain sizes of samples were determined as the average linear intercept length on polished and etched specimens. For each alloy, more than 10 pictures were analyzed in order to obtain an accurate value. In addition, the hardness test was examined by a TUKON-2100 with a standard deviation of approximately ± 3%. At least five Vickers hardness values, with a 0.1 kg load and a 10 s dwell time, were measured for each sample. The microstructure observations of alloys were performed by using a JEM-3010 transmission electron microscopy (TEM).

3. Results and discussion

3.1. Optical microstructure observation

The variation in microstructure and grain size with Si concentration and annealing temperature is discussed first. Fig. 1 shows the optical micrographs of grain structure in sinter billets of Mo–Si alloys with different Si content. These samples have completely equiaxed grain structure and some residual porosities are visible inside the grain and on the grain boundaries. It is clearly revealed that the addition of Si has remarkable effects on the grain size, i.e. increasing the Si concentration reduces the grain size, as shown in Table 2. When the Si content is lower than 0.3 wt.%, the refining of grain size is not obvious. Beyond the critical point of 0.3 wt.%, the grain size decreases sharply with any further increase in the Si mass fraction.

Fig. 2 shows the microstructures of the as-deformed Mo–Si alloy sheets, where the horizontal is the rolling direction. Compared with the sinter billets, the as-deformed sheets have elongated grains and fibrous structures along the rolling direction. The statistical measurements on grain sizes are list in Table 2. The results show that the grain sizes of Mo–Si alloy sheets decreased sharply after deformation (more than 50% smaller than sinter billet with the same Si concentration). The grain boundaries of sheets are clear and straight at relatively lower Si content, but by increasing the Si concentration, black particles (possibly molybdenum silicide or silica) are observed within grains and distributed in chain-like along the rolling orientation. At the same time, the grain boundaries become blurry and it is hardly to distinguish the grains. One can clearly see that the grain sizes are significantly smaller than those of the alloys with low Si concentration.

Representative optical photomicrographs are shown in Fig. 3 to reveal the variation of pure Mo grains with annealing treatments. By increasing the annealing temperature, the elongated grains and fibrous structure gradually widen and changed to equiaxed grains. When the pure Mo sheet is annealed at a low temperature (850 °C and 950 °C), the grain structure changes slightly compared to the as-deformed sheet. However, the aspect ratio of the grains is decreased. After annealed at 1050 °C, obvious recrystallization is observed. The grains change to totally equiaxed and tend to grow up after annealed at 1150 °C. The grain size sharply increases when the annealing temperature is 1250 °C.

The photomicrographs of Mo–0.3Si sheets (annealed at 850–1550 °C, respectively) were chosen in order to systematically illustrate the microstructure variation of Mo–Si sheets with annealing treatments (Fig. 4). Because of fine grains, Mo–0.3Si sheets have more narrow fibrous structure than pure Mo after deformation. When annealed at 850 °C and 950 °C, the microstructures of Mo–0.3Si evolved in a similar way to the pure Mo but remained fibrous with an elongated shape. After annealed at 1050 °C, as seen in Fig. 4c, few fine equiaxed grains are present within the fibrous structure, indicating that the recrystallization is started at this annealing temperature. Increasing the annealing temperature to 1150 °C, the recrystallization is completely achieved and many equiaxed grains can be observed as in Fig. 4d. Further increase in the annealing temperature does not change the microstructure greatly. As a result, the grain size grows slowly.

The influence of the Si concentration on the grain sizes of Mo–Si alloys is shown in Fig. 5 as a function of annealing treatments. One can clearly see that Si can effectively refine the grains of Mo, especially at content higher than 0.6 wt.%. Increasing the annealing temperature, the grain shape of Mo–Si alloy sheets changes from narrow fibrous to equiaxed structure. When annealed at 850 °C and 950 °C, the grain size changes about 1 μm between the pure Mo and the Mo–Si alloys. After annealed at 1050 °C, the grains of pure Mo grow quickly up to 19.4 μm and the grain shape changed to equiaxed. In contrary, there is no sharp change in the Mo–Si alloys sheet annealed at the same temperature. As a result of the recrystallization, the grain size of Mo–Si sheets show a visible increase after annealed at 1150 °C. In addition, the grains size of Mo–Si alloys sheet change within 2–3 μm when annealing temperature increased from 1350 °C to 1550 °C. However, the grain size of pure Mo increases sharply reaching more than 53.4 μm at 1250 °C.

3.2. TEM microstructures observation

In Fig. 6, the TEM bright-field images show the microsturctural morphology and dislocations of the as-deformed Mo–Si alloys sheet. One can see that the Mo–Si alloys have an elongate grain structure because of the heavy deformation. These elongated grains are composed of several sub-grains which are formed by dislocation cells. In Fig. 6b, there are a large number of dislocations arranged within the grains.

Fig. 7 shows the TEM bright-field images for the microstructure of Mo–Si alloy sheets after annealing treatments. After annealed at 850 °C, the density of the dislocations decreased, which may be attributed to the annihilation of dislocations. At the same time, elongated grains were gradually widened, but still remained the fibrous structure (seen in Fig. 7a). By further increasing the annealing temperature, a number of tangled dislocations formed irregular cell wall with a certain width, which constructed sub-grain structure by surrounding and splitting the low dislocation density areas (Fig. 7b). These structures are ready to polygonize at high temperature recovery.

For the Mo–Si alloy sheet samples annealed at 1350 °C (Fig. 7c), obvious changes in microstructure can be found. Only a few dislocation lines exist in the vicinity of the grain boundary. The tangled dislocations inside of grain also decreased dramatically and the dislocation-free regions increased. The sub-grain boundaries, formed by dislocations, disappeared and the sub-grain combined. Then the grain boundaries became thinner and straighter.

Table 1
The room temperature composition and density values of sinter billet of Mo–Si alloys.

Material	Mo (wt.%)	Si (wt.%)	Si (at.%)	ρ_A(g/cm^3)	ρ_{XRD}(g/cm^3)
Mo	100	0	0	9.866	10.19
Mo–0.1Si	99.9	0.1	0.34	9.873	10.15
Mo–0.3Si	99.7	0.3	1.02	9.858	10.14
Mo–0.6Si	99.4	0.6	2.04	9.724	10.06
Mo–1.0Si	99.0	1.0	3.4	9.409	10.01

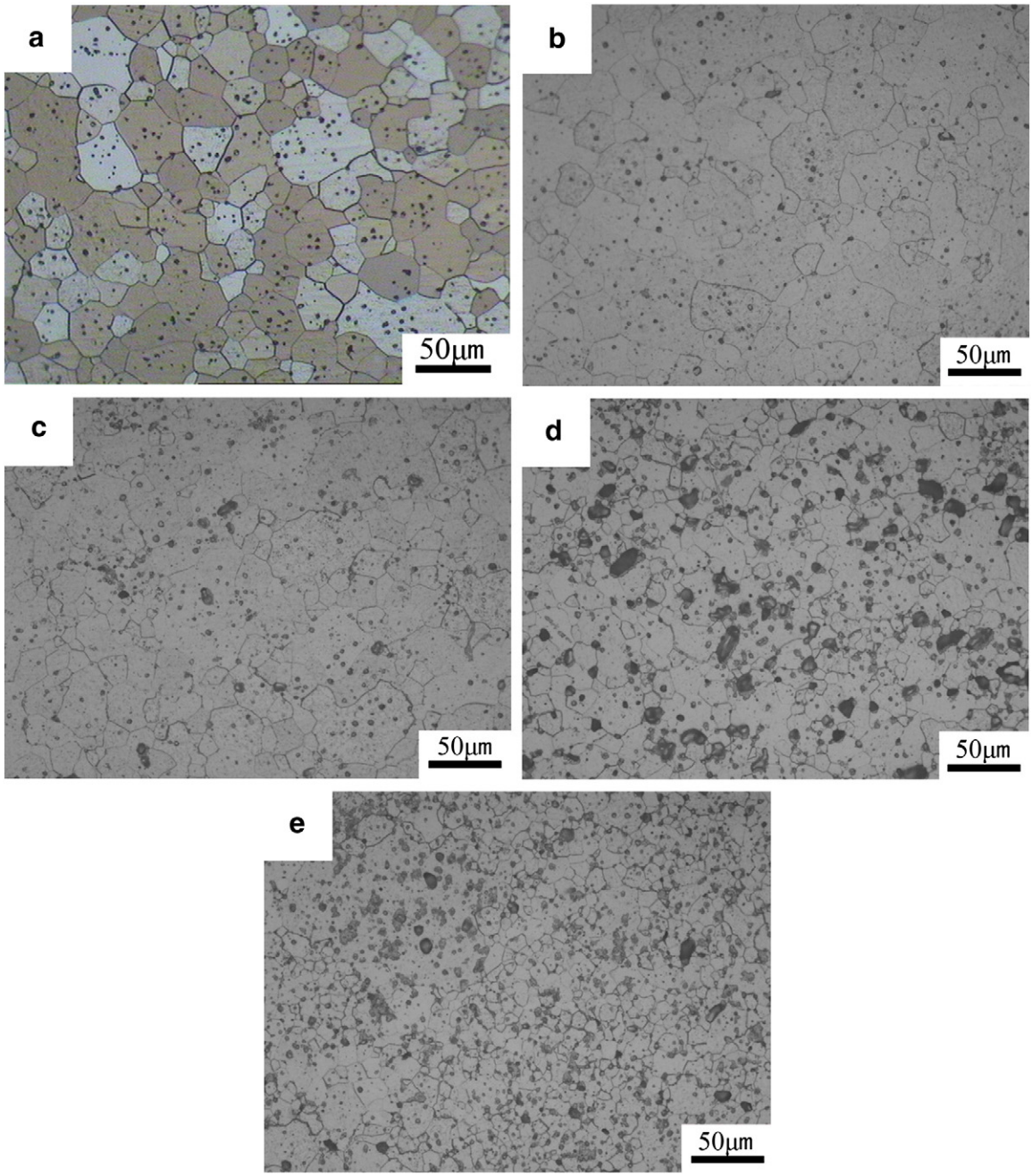

Fig. 1. The grain sizes changes with silicon concentration in sinter billet of Mo–Si alloys. (a) Pure Mo; (b) Mo–0.1Si; (c) Mo–0.3Si; (d) Mo–0.6Si; and (e) Mo–1.0Si.

3.3. Hardness

The measured Vickers hardness with respect to the Si concentration of both the sinter billets and the as-deformed Mo–Si alloys are presented in Fig. 8. It is found that the addition of Si can improve the hardness of Mo alloys, particularly in as-deformed sheets. The hardness of the Mo–Si alloys is increased by raising the Si concentration. The solid solution softening in Mo–Si alloys, reported by D. Sturm et al. [9], does not appear in our present work. In their study, the hardness of the sinter billet of Mo–Si alloy decreased at 0.1 wt.% Si concentration. They called this solid solution softening which may have been caused by those elements having higher electron numbers. Compared to sinter billets, the as-deformed sheets have hardness higher than 80 HV at the same Si concentration.

Table 2
Grain sizes in sinter billet and as-deformed sheet of Mo–Si alloys.

Material	Sinter billet (μm)	As-deformed sheet (μm)
Pure Mo	24.83	11.72
Mo–0.1Si	23.35	11.42
Mo–0.3Si	22.08	6.99
Mo–0.6Si	14.11	5.17
Mo–1.0Si	11.82	4.25

Fig. 9 shows the dependence of Vickers hardness on the annealing temperature for pure Mo and Mo–Si alloy sheet, respectively. By increasing the annealing temperature, both the pure Mo and Mo–Si alloys show a decrease in hardness. However, the decrease is slow when annealed between 850 °C and 950 °C. Due to recrystallization, the hardness values decrease significantly after annealed at 1050 °C

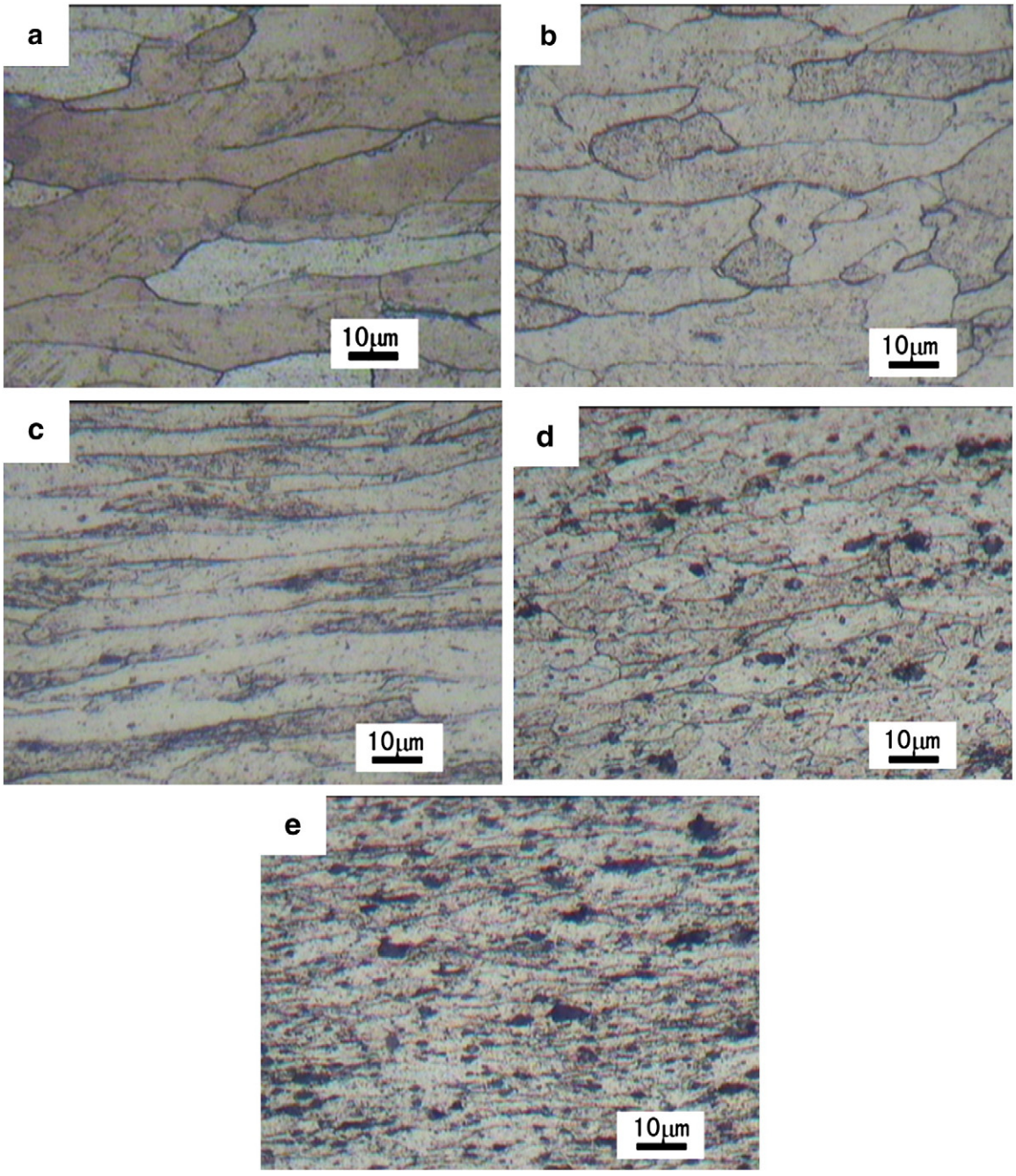

Fig. 2. The photomicrographs of Mo–Si sheets along the rolling direction (a) Pure Mo; (b) Mo–0.1Si; (c) Mo–0.3Si; (d) Mo–0.6Si; and (e) Mo–1.0Si.

and 1150 °C, which is the range of recrystallization temperature for Mo–Si alloy sheets. After recrystallization temperature, although the high Si concentration of Mo–Si sheets have a relative high hardness, almost all the alloys with different compositions maintained a hardness of about 200 HV, with very small fluctuation, when the annealing temperatures within the range 1350 °C to 1550 °C.

3.4. Discussion

The presences of Si can refine grain size of sinter billets Mo–Si primarily due to two reasons. First, Si is a substitutional solid solution element in Mo lattice when the concentration is relative low. Because of mismatch in atom scales, the local stress filed are formed around Si substitutional atoms which will provide energy for nucleation in sinter processing. The increased nucleation rate promotes grain refinement, although this effect is not obviously. Second, there are spherical-like second phase particles present in the alloys, which determined from the lattice constants of diffraction pattern shown in Fig. 10, is characterized to be Mo_3Si. This demonstrates that Si is already saturate in the Mo lattice when its concentration reached 0.3 wt.% at room temperature. Further increasing the Si content, e.g. to 0.6 wt.%, there will be precipitated a large number of Mo_3Si particles. These particles not only offered nucleation cores, but also impede grain boundary movement effectively. This can explains why the grain size is visibly refined in higher Si concentrations.

The presence of Si promotes the recrystallization temperature of Mo alloys (Fig. 4), because the impurity atoms, like Si atoms in our work, can inhibit migration of dislocations and grain boundaries through segregation around dislocations and the grain boundaries.

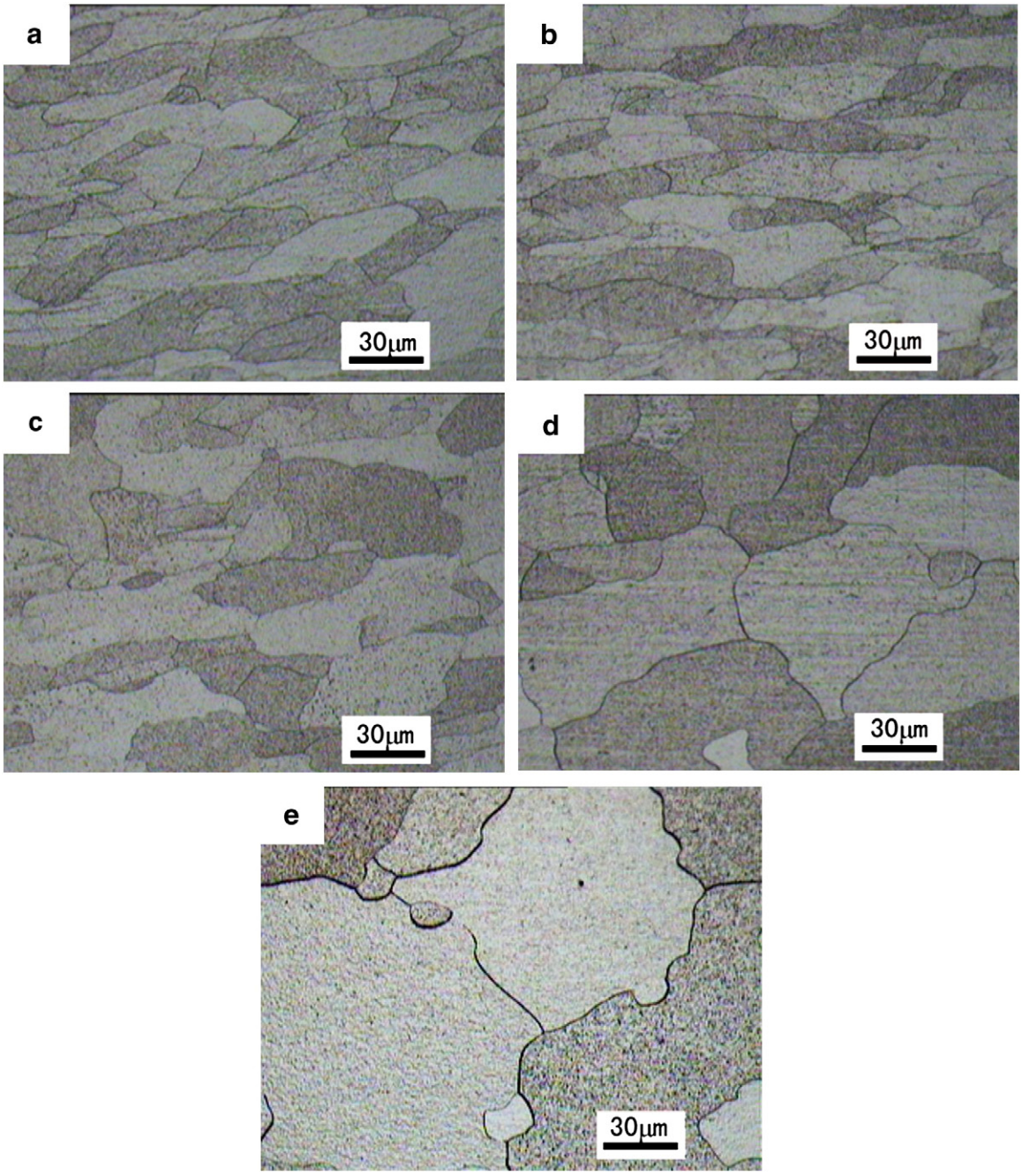

Fig. 3. The photomicrographs of pure Mo sheet during annealing treatments (a) 850 °C; (b) 950 °C; (c) 1050 °C; (d) 1150 °C; and (e) 1250 °C.

The impurity atoms also prevent diffusion of Mo atoms. Therefore, more activation energy is necessary to motivate the recrystallization.

During the thermo-mechanically processing, porosities within the as-deformed sheets are significantly decreased. The pre-existence of a large number of tangled dislocations causes further plastic deformations more difficult, which is responsible for the improvement in the hardness of material. Moreover, the thermo-mechanically processing caused residual stresses inside the sheet. These factors contribute to the Vickers hardness, causing as-deformed sheets to have a hardness of about 80 HV higher than the sintered billets even at the same Si concentration.

The contributing hardening mechanisms are as follows. First, the stress field around solid solution Si atoms, which is created due to electron-negativity and size mismatch ($R_{Si}/R_{Mo} = 0.73$), interact with dislocations and hindered its slipping, this gives provides improved plastic deformation resistance of Mo–Si alloy sheets. Next, the precipitation of Mo_3Si has high hardness and can hinder dislocation slipping. Also grain boundaries migrate as obstacles that are also contributors to the hardness of alloys [10]. Therefore, the hardness of Mo–Si alloys increased with Si concentration is a coupled effect of Solid solution strengthening and particle dispersion strengthening.

The hardness of Mo–Si alloy sheets decreased slowly at the outset of annealing because at that temperature it is at the recovery state (seen in Fig. 4a and b), and the mechanical properties of Mo–Si alloy sheets changes slightly. Fig. 4c and d illustrates that the recrystallization temperature range is about 1050 °C–1150 °C for Mo–Si alloy sheets for our work. Because the number of dislocations as well as grain boundaries is greatly reduced, the hardness of Mo–Si alloy sheets decreases, especially in the Mo–1.0Si with a reduction by more than 150 HV. After the recrystallization annealing, the content of the defects, such as dislocations and vacancies, are obviously decreased at

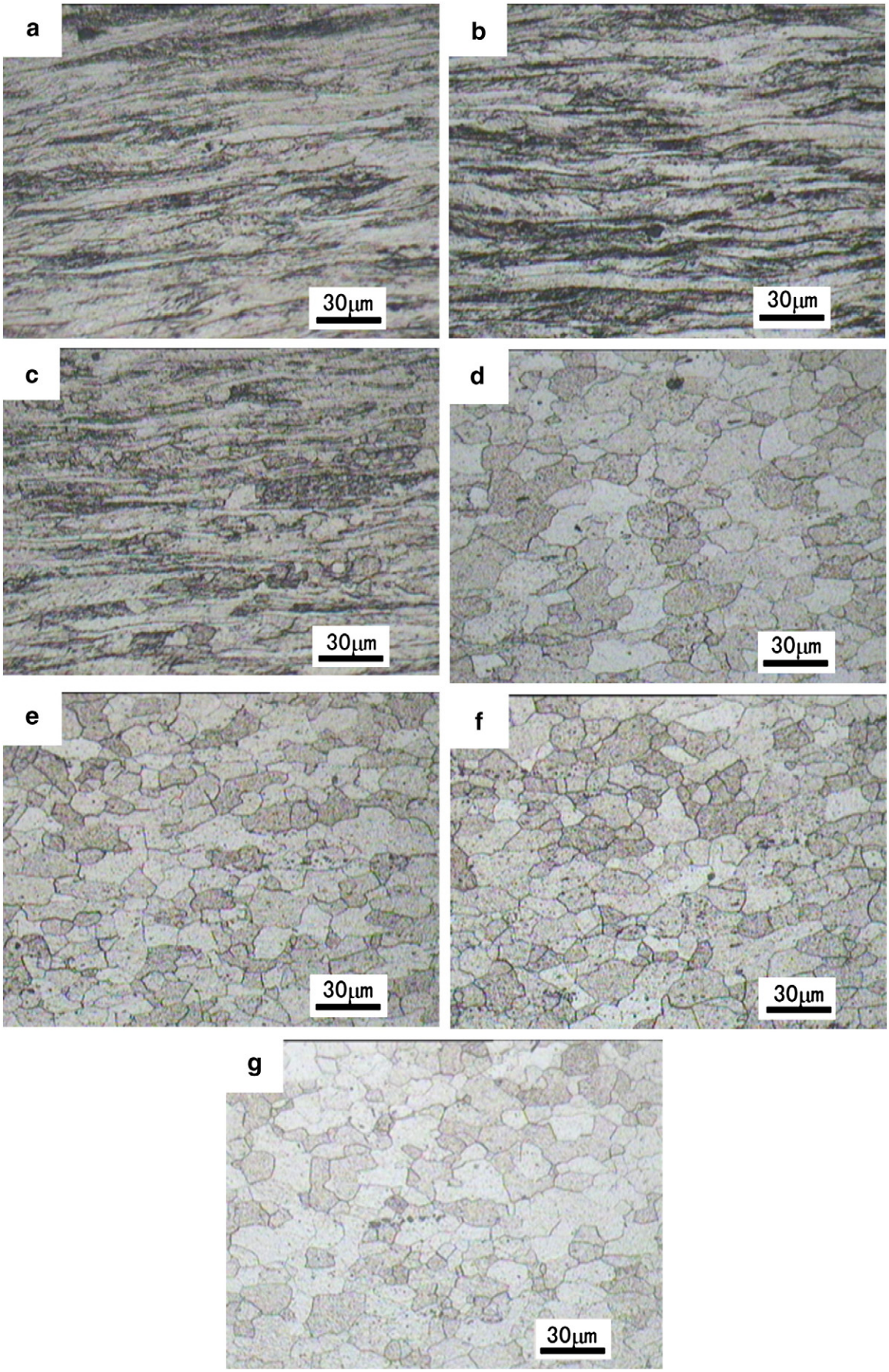

Fig. 4. The photomicrographs of Mo–0.3Si alloy sheet during annealing treatments (a) 850 °C; (b) 950 °C; (c) 1050 °C; (d) 1150 °C; (e) 1350 °C; (f) 1450 °C; and (g) 1550 °C.

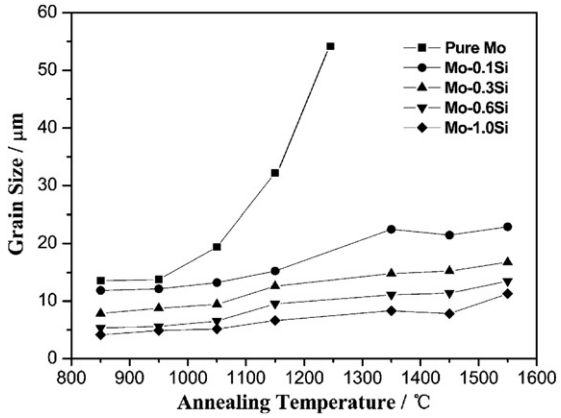

Fig. 5. The influence of Si concentration and annealing temperature on grain size of Mo–Si sheets.

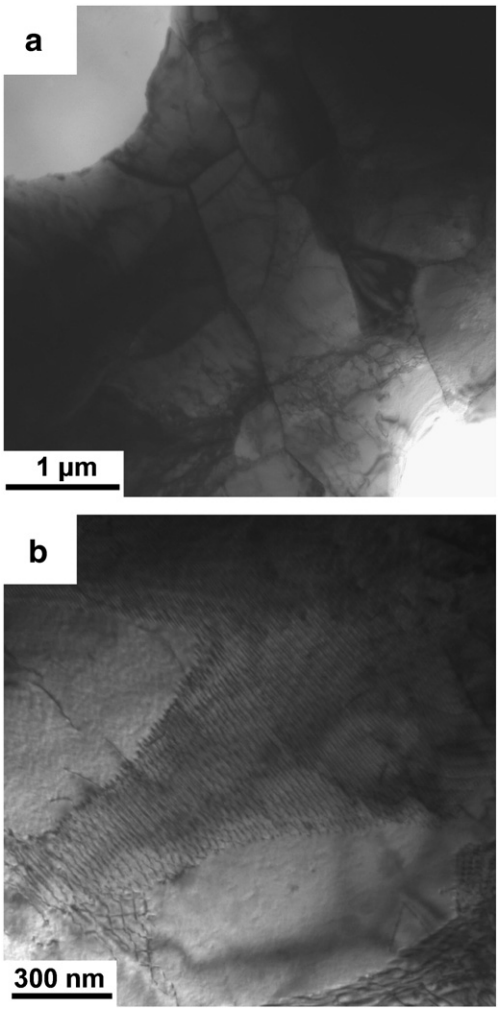

Fig. 6. The TEM images for microstructure morphology (a) and dislocations (b) of the as-deformed Mo–Si sheet.

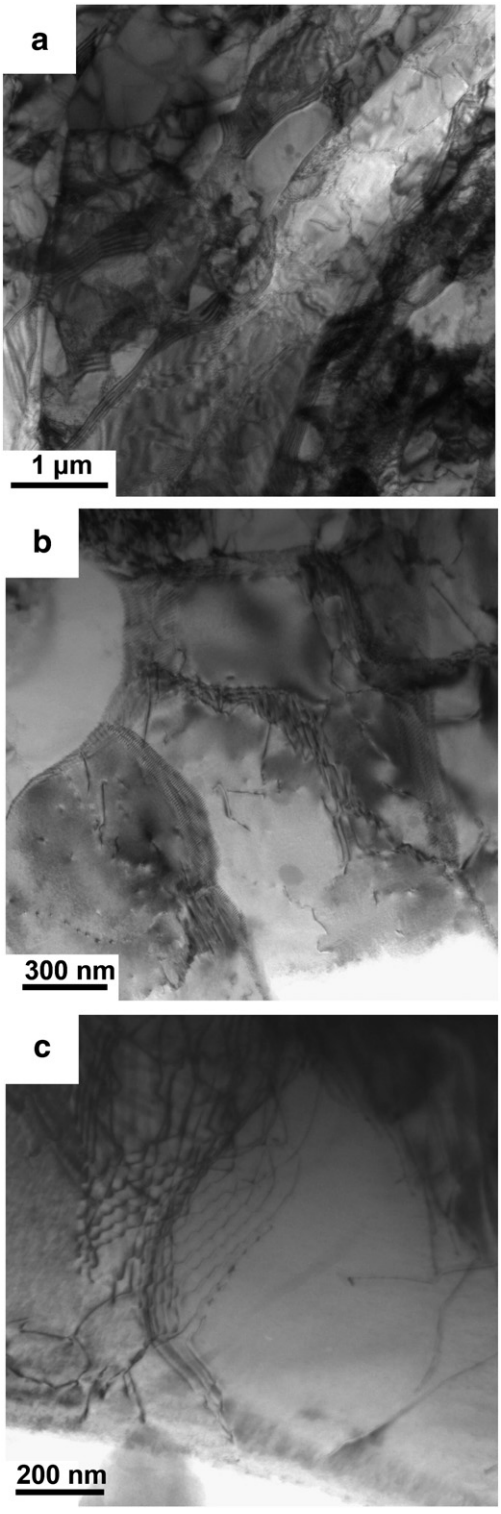

Fig. 7. The TEM images for microstructure of Mo–Si sheet at different annealing temperature (a) 850 °C; (b) 1050 °C; and (c) 1350 °C.

the same residual stress and distortion energy in the grains, which is the reason for a slow decrease in hardness.

4. Conclusions

(1) The grain size of Mo–Si alloys was significantly refined by adding Si and, at the same time, the phase composition changes from monolithic Mo_{ss} to Mo_{ss} and Mo_3Si with an increase in the Si concentration.

(2) The presence of Si can promote the recrystallization temperature of Mo alloys (1150 °C), which is responsible for restraining the grain sizes at high temperature. Solid solution strengthening, particle dispersion strengthening and fine-grain strengthening are the main strengthening mechanisms in Mo–Si alloys.

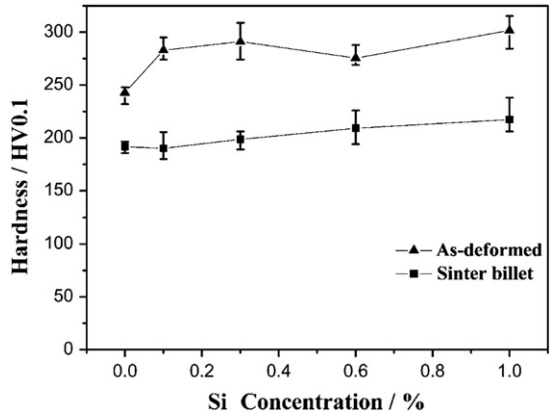

Fig. 8. The Vickers hardness for sinter billets and as-deformed of Mo–Si alloys.

(3) With increasing the annealing temperature, the elongated grains and fibrous structure of the pure Mo and Mo–Si alloy sheets are gradually widened and transited to equiaxed grains. The grain of pure Mo grows quickly after annealed at 1250 °C, however, the grain size of Mo–Si alloy sheets changes slightly even after annealed at 1350 °C or higher temperature.

(4) The hardness of pure Mo and Mo–Si alloy sheets is reduced with increasing the annealing temperature. The hardness decreased slowly when annealed at 850 °C and 950 °C because it is in the recovery state for alloys; when the annealing temperature is up to 1050 °C and 1150 °C, the recrystallization makes hardness decrease remarkably. At the annealing temperature of 1350 °C and above, the influence of temperature on hardness is weakened, resulting in an almost constant hardness.

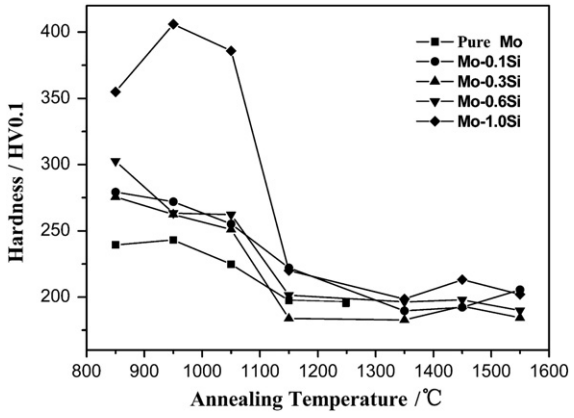

Fig. 9. The Vickers hardness of pure Mo and Mo–Si sheet alloys decreased with annealing temperature.

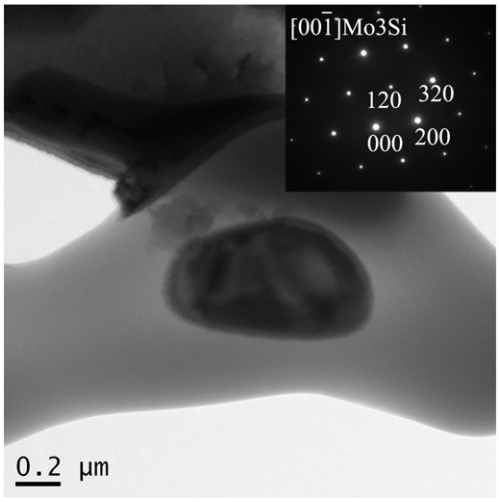

Fig. 10. The TEM bright-field image with selected area diffraction pattern of the Mo_3Si in Mo–0.3Si sheet.

Acknowledgments

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