Defects analysis on the strengthening of solid solution Nb additions in Mo₃Si alloys

Isai Rosalesᵃ,∗, Mara J. Garcia-Ramirezᵃ, Constancio Diaz-Reyesᵃ, Horacio Martínezᵇ

ᵃ Centro de Investigación en Ingeniería y Ciencias Aplicadas, UAEM, Av. Univ. 1001 Col. Chamilpa, 62210 Cuernavaca, Morelos, Mexico
ᵇ Centro de Ciencias Físicas, UNAM, Av. Univ. s/n Col. Chamilpa, 62210 Cuernavaca, Morelos, Mexico

A R T I C L E   I N F O

Article history:
Received 5 June 2017
Accepted 7 November 2017
Available online xxx

Keywords:
Physical properties
Hardness
Mechanical properties
Molybdenum silicides

A B S T R A C T

Molybdenum silicides alloys with different Nb additions were produced by the arc-melting technique ranging from 0 to 20 Nb at.%. Physical characterization has been performed for each one of the alloys. Experimental and calculated density showed a decreasing value when Nb additions increment up to 20 Nb at.%, showing the effect produced by the atoms additions with lower atomic weight. Vacancy concentration indicates that point defect do not strongly affect the alloy performance. Mechanical evaluation showed positive strengthening, which is attributed to the lattice distortion, increasing with Nb content. TEM analysis supports such assumption by the observation of dislocations network. Results in this work are interpreted in terms of substitutional process.

© 2017 Published by Elsevier Editora Ltda. on behalf of Brazilian Metallurgical, Materials and Mining Association. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The global needs of improved materials to support severe service conditions in combination with good mechanical properties are constantly been required. Intermetallic compounds based on the Mo-Si system can be these promising materials to be applied as structural and high temperature resistant materials due to their high melting point. Until now, in this direction, MoSi₂ is commercially being used as heating element [1–3]. It is well known that the main problem of these intermetallic compounds is their low ductility at room temperature, which are the cause of the limitations in structural applications. Specific attention has been given to Mo₃Si₃ with B addition, where a considerable improvement in their oxidation resistance was observed [3–6], also significant increment of fracture toughness at room temperature on Mo₃Si₃ with a continuous α-Mo matrix was reported. Kružić [7] investigated similar alloys, reporting an improved fracture toughness value.

In a previous work, we have reported the tensile behavior at high temperature of this material Mo₃Si intermetallic alloy with Nb additions, finding that Nb truly affects the alloy performance [8]. Until now the analysis of point defects of the intermetallic Mo₃Si compound with Nb solid solution additions and the interaction with mechanical and physical properties has not been developed, therefore, the purpose of the present work is to understand these phenomena by

∗ Corresponding author.
E-mail: faye12@uaem.mx (I. Rosales).

https://doi.org/10.1016/j.jmrt.2017.11.003
2238-7854/© 2017 Published by Elsevier Editora Ltda. on behalf of Brazilian Metallurgical, Materials and Mining Association. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
using a modeling tool to characterize such effect at room temperature.

2. Experimental procedures

Alloys with nominal silicon concentration of 24 at.% and Nb additions were prepared by arc-melting technique, using nominally pure elements in a partial pressure of argon (99.999% purity). The alloys were drop-cast into water-cooled copper molds with a diameter of 12.5 mm. As is pointed out by Huebisch [9], calculations from the weight losses resulted as the best option for determining the precise alloy compositions. Table 1 shows the nominal compositions calculated by assuming weight losses during melting and casting processes. The specimens were annealed in a vacuum of 10⁻⁴ Pa for 24 h at 1400 °C furnace cooled. After metallographic polishing, the specimens were etched with Murakami’s reagent for 1–2 s. The etched specimens were observed in an optical microscope as well as with a scanning electron microscope equipped with an energy dispersive spectroscopy (EDS) system. X-ray diffraction analyses were carried out in a Siemens D5000 diffractometer with cooper radiation CuKα (λ = 1.5405 Å), lattice parameters were determined by X-ray diffraction of the powders, with a size lower than 45 μm and an internal silicon standard. The experimental accuracy of the lattice parameter measurements was estimated to be 3 × 10⁻⁴ Å. The hardness was measured on a Buehler microhardness tester using a constant load of 500 g with a holding time of 15 s. Fracture toughness evaluation was performed using the indentation method with a Vicker’s indenter [10]. For best precision, the length cracks were measured in a SEM JEOL 6400. For TEM analyses, samples with 3 mm in diameter were obtained and polished with paper grinding up to 200 μm thickness, then, focused ion beam (FIB) process was employed to obtain samples with 40–50 μm thickness. The samples were electropolished with 5 vol% hydrochloric acid in methanol at –10 °C.

3. Results and discussion

3.1. Microstructural observation

Micrographs were taken in perpendicular plane to the solidification direction, in Fig. 1a and b it can be observed the representative surface microstructures of the samples with 5 and 20 at% Nb respectively in annealed condition. Fig. 1a shows the microstructure with equiaxed grains and average size of 200 μm, while Fig. 1b presents enlarged grains with an average size of approximately 150 μm. Fig. 1a shows a single-phase structure after heat treatment, which is in good agreement with the ternary alloy phase diagram for this system [11]. This enlarged grain sizes were produced during the annealing process due to the fact that there are no barriers such as precipitates or second phases in combination with the slow cooling rate. In samples with 20 at% Nb, it can be observed few dark dots on the surface sample probably developed during metallographic preparation, postulating that Nb solubility limit in the alloy is below this concentration.

Fig. 2 shows the X-ray diffraction patterns from samples with 5 and 20 at% Nb, it is evident that no extra phase was formed during the solidification process, only Mo₅Si phase was detected conserving the solid solution state. It is also observed that peaks obtained for the alloys with a content of 20 at.% Nb are shifted to the left (decreased Bragg angle) indicating that if Nb concentration is incremented, thereby, it is expected that lattice parameter may increases proportionally as Nb increases, on the other hand, extra peaks may correspond to a niobium that segregates to the grain boundary due to an oversaturation, then solid solution is exceeded and as consequence small extra peaks appear in spectrum at this concentration.

The microstructural characterization was finalized with the EDS chemical analysis of the different samples after annealed annealing. The spectra in Fig. 3 shows the presence of very small Nb peaks at higher Nb concentration (from 10 to 20 at.% Nb). This result, combined with metallographic observations, confirms that Nb solid solution in annealed samples at 1400 °C effectively occurs below 10 at.% Nb. along of single phase compositions marked in the ternary alloy phase diagram [8].

3.2. Mechanical behavior evaluation

The strengthening behavior of the alloys with Nb additions is presented in Table 2, where it can be observed the microhardness results for the different alloys, noticing an important variation, starting with the reported value of 1324 kg/mm² for the alloys with 0 at.% Nb [12], up to 1428 kg/mm² for sample with 20 at.% Nb. Then, it is observed that hardness proportionally increases when Nb percent is incremented in the alloys. The explanation of this hardness increment may be associated to the lattice distortion produced by the incorporation of an atom with higher atomic size and therefore exist the possibility of dislocations generation in the lattice, produced during the melting and casting process. Table 2 includes the values of the fracture toughness of the alloys at room temperature. The initial reported value for samples without Nb additions represents the single phase Mo₅Si [12] of approximately 2.34 MPa m¹/₂; after Nb addition, the toughness of the alloys shows a small decrement in the value when the Nb additions are incremented. The differential values between 0 and 20 at.% Nb, are approximately of 1.0 MPa m¹/₂. The values obtained for alloys with 10 and 20 Nb at.% are in the same order much lower than the reported for other silicides niobium alloys [6] (14 MPa m¹/₂). This behavior can be explained by the fact the A15 structure has been deformed creating a distorted structure, taking an important role in this toughness reduction when an external stress is applied.

| Table 1 – Nominal compositions for Mo-Si-Nb alloys showing the niobium additions. |
|-----------------|-----------------|-----------------|
| Si (at.%)       | Mo (at.%)       | Nb (at.%)       |
| 24.0            | 71.0            | 5.0             |
| 24.0            | 66.0            | 10.0            |
| 24.0            | 61.0            | 15.0            |
| 24.0            | 56.0            | 20.0            |
3.3. Physical properties

Density results obtained from X-ray analysis and values obtained from He-pycnometric evaluations (bulk density) are shown in Fig. 4. It can be observed that bulk density and X-ray densities of the alloys, decrease slightly as the Nb content increase. This decrement normally may indicate the presence of a large amount of thermal vacancies generated at the time the solidification begins; however, as will be shown in the analysis of vacancy concentrations in the next section, the vacancies are essentially zero on the alloys, thereby, the reason for the decrement in density, is attributed to the lower atomic weight of Nb atoms (≈3% lower) in comparison with Mo atoms. It can be noted that basically there is no significant difference between both experimental and calculated results.

Fig. 5 shows the plot of the lattice parameter obtained from the calculation in each alloy and the lattice parameter obtained by X-ray diffraction technique, using silicon peaks as standard reference. Experimental results show a small discrepancy in comparison with the lattice parameter calculated from both techniques.

In order to understand the mechanical behavior of the alloys, by the variations in the dimensions of the unit cell, a specific study was carried out. It well known that the A15 crystal structure of the (Mo, Nb)3Si possesses a simple cubic lattice with eight atom structure [13,14]. This structure can be described in terms of three different types of atomic layers (Fig. 6) parallel to the cube faces: those containing two

<table>
<thead>
<tr>
<th>Nb at.%</th>
<th>CV measured (%)</th>
<th>CV calculated (%)</th>
<th>Microhardness HVN (0.5)</th>
<th>Fracture toughness MPa m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.01</td>
<td>0.011</td>
<td>1324 ± 7</td>
<td>2.34</td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>0.016</td>
<td>1371 ± 5</td>
<td>2.01</td>
</tr>
<tr>
<td>10</td>
<td>0.02</td>
<td>0.032</td>
<td>1374 ± 12</td>
<td>1.76</td>
</tr>
<tr>
<td>15</td>
<td>0.05</td>
<td>0.048</td>
<td>1395 ± 8</td>
<td>1.57</td>
</tr>
<tr>
<td>20</td>
<td>0.06</td>
<td>0.064</td>
<td>1428 ± 13</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Mo(Nb) and one Si atom per unit cell intersected denoted a or b, and those containing one Mo atom denoted c. These stack in a …abcabcba… sequence and thus the layers correspond to (004) planes in the structure [14]. The estimation of the structure of the systems studied in this work is particularly defined for the unit cell. The dimensions of the unit cell are fixed by the atoms size in the cell. In the case of the FCC unit cell, atoms lying along the diagonal of each face are in contact each other. A feature of close-packed structures is that packs and modeled as a collection of hard spheres [15,16]. We evaluated the variations of the lattice parameter for different Nb concentrations taking into account the previous considerations and using the $r_{\text{Si}}, r_{\text{Nb}}$ and $r_{\text{Mo}}$ lattice parameters obtained by X-ray measurements. The value obtained for Mo$_2$Si layer is 5.0% higher than the value obtained for Nb$_2$Si layer which is consistent with the increment of the Goldschmidt radii of Mo (1.40 Å) to Nb (1.47 Å) [13]. This effect is attributed to the interaction of Nb inner atoms in the A15 structure, when Mo atoms are substituted by Nb atoms in the melting process, where the difference in atomic radii between Mo and Nb is 0.07 Å. There is a variation less than 0.2%, clearly indicating that only can exist a substitutional mechanism during the solidification process; Ray et al. [17] studied the effect of Nb substitution on the stability of Mo$_3$Si, stabilizing that A15 phase is destabilized in approximately 27.5 at.% Nb considering the energy formation and the interaction between Mo-Nb instead of Mo-Si pairs.

In order to evaluate the changes that occur in the lattice, calculations of the deformation parameter $d$ were performed, which was defined as

$$d = (D_0 - D) \times 100/D_0 \quad (1)$$

where $D$ and $D_0$ denote the distance between atoms with and without distortion respectively, i.e., with and without Nb substitution. Taking the inter-atomic distance as $r_{\text{measured}}/2$, the distortion parameter $d$ is 0.31, 0.48, 0.72 and 0.90 for Nb 5 at.%, 10 at.%, 15 at.%, and 20 at.% respectively.

The obtained results indicate an increment in the distortion of the lattice parameter for the layer with Nb 20 at.% is approximately 3 times bigger than the Nb 5 at.% a higher lattice parameter increment for the alloy with 20 at.% Nb of approximately 3 times in comparison with the sample with 5 Nb at.%, which can be related with the resulting mechanical behavior of the alloys.

### 3.4. Defects analysis

It is well known that defects are directly related to physical and mechanical properties, such as diffusivity, hardness, and ductility among others. Many efforts have been developed to understand the defect types in B2 structures [18,19], laves phases [20,21] but very few studies have been undertaken to clarify the point defect mechanisms in A15 structures. As is showed in Fig. 5, the lattice parameters for (Nb,Mo)$_3$Si compee.
sitions increase with the increasing of Nb concentration. This is not surprising since Nb has a larger atomic size than Mo.

The atomic size ratio, $R_A/R_B$, of the AB₃ structure studied in this work can be calculated and found to be 0.96 and 0.91 for Mo₃Si and Nb₃Si, respectively. Here, $R_A$ and $R_B$ are the atomic radii of the A and B atoms with a coordination number of 12 [13,22]. The measured vacancy concentrations as a function of Nb atomic concentration by using the method proposed by Zhu et al. [20] are presented in Table 2. Since the constitutional defects in this compound have been established, it is possible to conclude that these defects are thermal vacancies, indicate that the quadruple defects may be formed in this compound by heating; however, a useful analogy can be found when considering triple-defect in B2 phases. This class of compounds possesses constitutional defects as thermal vacancies [23]. Such systems will be suitable for examination if the vacancy-assisted synchro-shear deformation and toughness improvement are possible in (Nb,Mo)₃Si compounds. Neumann [24] reported that B2 compounds with negative $\Delta H$ smaller than 75–90 kJ/mol generally exhibit the anti-site defect structure, while compounds with a greater value generally exhibit the triple defect structure and have constitutional vacancies. In other words, constitutional vacancies are the preferred defect mechanism in compounds that are more strongly ordered, i.e. with higher absolute $\Delta H$ values.

3.5. Transmission electron microscopy analysis

In order to reinforce and support the results obtained in the previous sections for strengthening in the alloys and the modifications of the physical properties generated by the Nb solid solution additions, a TEM work was performed in samples with two different Nb concentrations i.e. 5 and 20 Nb at.%. 

Fig. 7a and b shows the bright field TEM image of the alloy with low Nb concentration (5 Nb at.%) where a low density of planar defects is observed. Because stacking fault dislocations are produced for the distortion of the lattice, in both images are shown a series of pile up dislocations which are developed as a product of the introduction of the Nb atom in the crystal structure, generating a distortion in the lattice and therefore, an increment in dislocations per surface area fraction.

Fig. 8 shows a bright field image by TEM of the sample with 20 Nb at.%, where stacking planar dislocations runs near to <012> orientation; on the work zone also are observed a considerable amount of edge dislocations. As expected, the density of the fault produced on the alloys is increased
proportionally with the Nb addition. This kind of planar defects has been observed in Nb₃Al compounds [14].

The increment in dislocations is produced not only by the increment of the stacking fault energy which is directly produced by the lattice distortion when the alloy is exposed under mechanical or thermal stresses, also can be produced by the vacancies generation which produce this energy increment, so the produced dislocation are either by removal or insertion of a plane of atoms, in our case this distortion it is attributed to the insertion of the Nb atom which possesses a bigger atomic radii.

The observation of this kind of defects in Fig. 7 is important to clarify the mechanical and physical behavior obtained by the experimental results.

4. Conclusions

Mo₃Si with different Nb additions have been successfully produced in agreement with the ternary alloy phase diagram. Very good concordance was found between the determination of the lattice parameter by X-ray measurements and the calculations based in calculations by using the atomic radii. Point defects in A15 structure have been clarified using the X-ray lattice parameter measurements, finding by this method that the vacancy concentrations in the alloys is close to zero. As the Nb content in the structure increases, the lattice parameter as well increases, on the other hand, as the Nb content increases, density decreases in the structure. Fracture toughness of alloys has not been affected significantly for vacancy concentrations, consequently the observed strengthening in alloys measured by Vickers indentations is mainly attributed thus to a lattice distortion. TEM analysis supports the postulation of dislocation interaction.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors are grateful with ORNL for sample preparations, we want to thank R. Guardian, and A. Bustos for their technical assistance. This research was partially supported by CONACyT and PRODEP under Grant PTC-074.

REFERENCES


