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Defects Interaction on the Mechanical Properties during Transition Formation of $(Mo, Cr)_3$ Si Intermetallic Alloys

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Abstract

Molybdenum silicides alloys with different Mo and Cr additions were produced by the arc cast method. The microstructure revealed mostly single phase structure. Mechanical properties were evaluated in the alloys, showing a decreasing behavior on microhardness. Fracture toughness values were obtained from cracks produced by Vickers indentation technique, showing that ternary alloying did not have a significant effect. Vacancy studies demonstrated that thermal vacancies along the transition line slightly affected the mechanical behavior.

Keywords

Physical Properties, Silicides, Microindentation, Fracture Toughness, X-Ray Diffraction (XRD)

1. Introduction

Molybdenum silicides have received considerable attention for several authors, in such way that these compounds are interesting due to their good response under severe conditions; these authors evaluated the alloys principally under high temperature for applications as furnace elements [1]-[5]. On the other hand, good mechanical properties are also necessary in these materials. Shah *et al*. [6] investigated the intermetallics Nb_3Al and Cr_3Si, evaluated their mechanical properties at room and high temperature and reported that Cr_3Si presented an excellent behavior at high temperature, but with limited possibilities of being alloyed. Raj [7] [8] evaluated

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the mechanical properties of Cr_3Si and Cr-Cr_3Si produced by arc cast and powder metallurgy, where the room temperature fracture toughness was determined in the range of 2.0 and 3.0 MPa $m^{1/2}$, which was comparable with the value reported for Mo_3Si [9]. Fleischer *et al*. [10] studied the mechanical properties of similar intermetallic compounds. They reported the microhardness value of 1200 HVN at room temperature for Cr_3Si, which was lower than the value reported for Mo_3Si [9]. The analysis of the transition of Mo_3Si to Cr_3Si may provide important information about the optimal concentration of Cr to improve the ductility of the Mo_3Si considering the thermal defects affectation. At present, the mechanical and physical properties of this dual phase intermetallic compound have not been fully explored and therefore limited information is available. The purpose of this work is to find the composition range, in which the best alloy performance is produced that may reduce the Mo_3Si brittleness, correlating the thermal defects affectation on the mechanical properties.

2. Experimental Procedures

Alloys with Silicon, Molybdenum and Chromium concentrations, were prepared by arc-melting of nominally pure elements in a partial pressure of argon (99.99% purity). The alloys were drop-cast into water-cooled copper rod molds with a diameter of 6.5 mm and 10mm length. **Table 1** shows the nominal compositions for Si and Cr, obtained by assuming that the weight loss during melting were due to evaporation of Si and Cr, so an extra 0.5 at.% of this elements were added to compensate this weight losses. The specimens were annealed in a vacuum of 10^{-4} Pa for 24 h at 1400˚C, and then furnace cooled using a cooling rate of 2.5˚C·s^{-1} between 1400˚C and 1000˚C. After metallographic polishing, the specimens were etched with Murakami's reagent for 1 - 2 s. The etched specimens were observed in an optical microscope. The lattice parameters were determined by X-ray diffraction of powders with a size < 45 μm and internal silicon standard. The experimental accuracy of the lattice parameter measurements was estimated to be 3×10^{-4} Å. Density values were calculated from the lattice parameter obtained by cell refinement of each alloy and bulk densities were obtained by pycnometric measurements. Vacancy concentrations were calculated from the follow expression [11]:

$$C_v = \frac{\left(\rho_{\text{X-ray}} - \rho_B\right)}{\rho_B}$$

where:

C_v = Vacancy concentration;

$\rho_{\text{X-ray}}$ = Density calculated by X-ray diffraction analysis;

ρ_B = Bulk Density obtained by He Picnometric measurements.

The microhardness was measured on a Buehler microhardness tester using a 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 [11].

3. Results and Discussion [9]

3.1. Microstructures and X-Ray Diffraction

The microstructures of the samples with different Cr content are shown in **Figures 1(a)-(d)**. The single-phase microstructure can be seen along the different ternary alloy compositions, grain boundaries are on the order of 120 μm average. Surfaces crack free were obtained by this method in all range of compositions (dark dots observed on the surface sample probably are impurities from the crucible). **Figure 2** shows the X-ray diffraction patterns obtained from the samples with different Cr compositions. The observed silicon peaks correspond to the standard reference material used to determine the lattice parameter. The diffraction pattern shows a clear transition of the Mo_3Si to Cr_3Si, at 2θ = 46 degrees and after 36 Cr at.%; furthermore, it is observed that the peaks show an increased Bragg angle respect to the sample with 17 Cr at.%, which imply a lattice parameter reduction, no additional phase was observed, except for Mo (211) at 2θ = 73 degrees (see spectrum 2 in **Figure 2**), therefore, it is concluded that the main constitution phases along the transition range are the prototypes Cr_3Si and Mo_3Si which possesses the A15 structure which coexist both in the range of 36 and 60 Cr at.%. These phases are in good agreement with the Cr-Mo-Si ternary phase diagram.

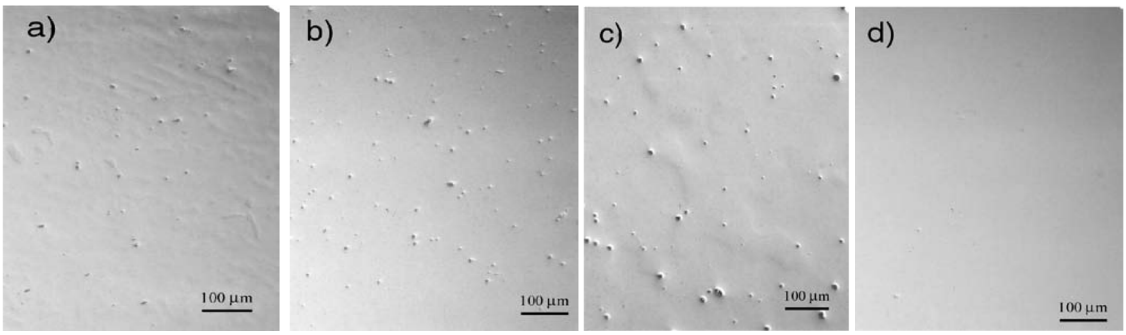

Figure 1. Micrographs of the Cr alloys with a) 17 at.%, b) 36 at.%, c) 60 at.% and d) 76 at.%.

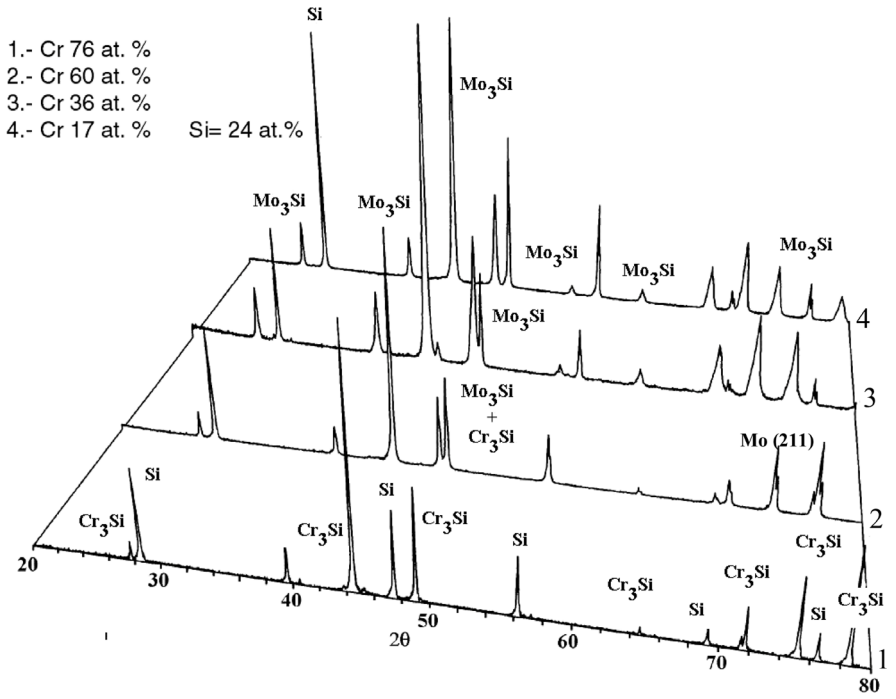

Figure 2. X-ray diffraction pattern from samples with Cr content.

3.2. Mechanical Properties

3.2.1. Hardness Evaluation

Figure 3 shows the plots of the values obtained at room temperature for the microhardness as a function of the Cr concentration. For the alloys with Cr content, the microhardness obtained, presents a decreasing behavior as the Cr at.% increases. In spite of the difference in size of the added atom with respect to the atomic radii of Mo (1.37 Å), it is deduced that Cr (1.25 Å) atoms remain in substitution places in the unit cell, affecting the hardness, due to the lattice distortion that can produce an arrest mode in the dislocation mobility. Fleischer [10] reports a value of 1200 HV at room temperature in samples of Cr_3Si, which is lower (less than 10%) than the results obtained in this study. The hardness obtained in this alloy suggests that one potential application could be in component parts exposed to friction conditions, perhaps by using powder depositions techniques. High hardening can be attributed to an excess of vacancies [12], however, this is not the case for our study, because the vacancy concentration is minimum.

3.2.2. Fracture Toughness Evaluation

Figure 4 presents the values of fracture toughness against the different Cr concentrations. For the alloys with Cr additions the value of fracture toughness decreases as a function of Cr concentration. A reduction of about 40%

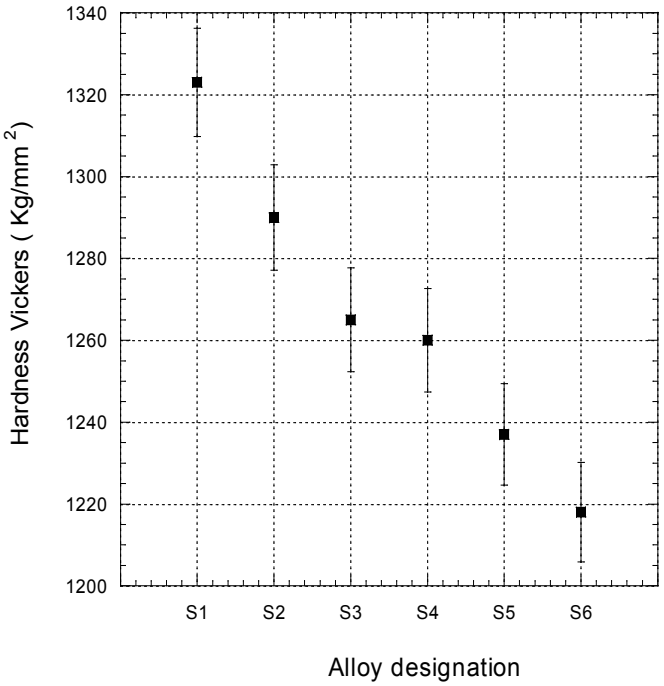

Figure 3. Microhardness as a function of Cr concentration.

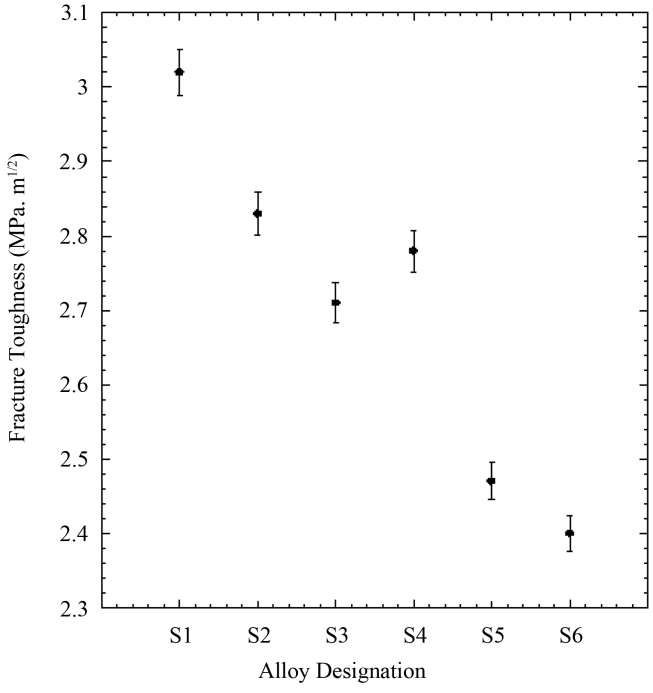

Figure 4. Fracture toughness against different Cr concentrations.

is observed in the fracture toughness between 16 and 76 Cr at.%. This reduction is approximately of 35% in comparison with the value reported for Mo_3Si single phase [9]. It is well known that thermal vacancies may induce some grade of softening in B2 intermetallic compounds [13] and this phenomenon is referred to a solid solution addition. In our case, we have an A15 structure which contain an arrangement of six Mo atoms plus two Si atoms for the Mo_3Si (similar array with the Cr_3Si) which produces a complex structure, thus, the decreasing

behavior of the fracture toughness as a function of the Cr concentration until 48 Cr at.% content, indicates that the presence of point defects can be quite substantial and therefore an effect in the fracture toughness of the materials attributed to this point defect may happen. Other complementary explanation about the toughness increment for sample S4, may be attributed to the interaction of Mo atoms with Cr atoms which are distributed along the A15 lattice where coexists both phases as is shown in the X-ray analyses. Also it has to be mentioned that, since both phases possesses A15 structure, this fact can be considered as highly positive due to the coherency of the lattice parameter, that definitely contribute to reach some grade of plasticity of the alloy.

3.3. Defects Analysis

In **Figure 5**, we present the results of the lattice parameter data as a function of the Cr content. The solid line represents a second order polynomial fit through the lattice parameter data. According to a Rydberg study [14], it is possible to correlate hardness with the reciprocal size of the atoms for pure elements. This conclusion and the underlying experimental results give, in principle, the explanation that the hardness is proportional to the cohesive forces. In the present work, the hardness has a decreasing behavior as a function of the Cr concentration and the lattices parameter decreases with the Cr concentration, so then the relation between hardness and lattice parameter is not reciprocal. Therefore, the present results cannot be explained by this argument. From **Table 1** it can be seen that the density measurements of the alloys with Cr additions have a decreasing behavior as a function of the Cr content.

The Goldschmidt radius of Mo is significantly larger than the Cr radii [15]. Consequently, as seen in **Figure 5**, the Cr_3Si lattice parameter decreases significantly.

The lattice mismatch between Mo_3Si and Cr_3Si of 6.94% almost corresponds to the change of the radius of Mo to Cr (8.76%). On the other hand, in order to obtain a preliminary understanding of the trend of the lattice parameter as a function of the Cr content in the alloy of Mo_3Si, one recalls that the lattice parameter of substitutional solid solutions is usually an average of the interatomic spacing in the pure components weighted according to the atomic fractions present; this observation is known as Vergard's law [16]. We could start with this law to estimate the lattice parameter as a function of the at.%. of Cr in the Mo_3Si alloy. The estimation using this law was carried out in the following steps:

1) The values of the lattice parameter of the alloys Mo_3Si, and Cr_3Si, were taken from the experimental results;

2) The lattice parameter as a function of the Cr content was evaluated from Vergard's law, using the values of the lattice parameter of the alloys Mo_3Si and Cr_3Si.

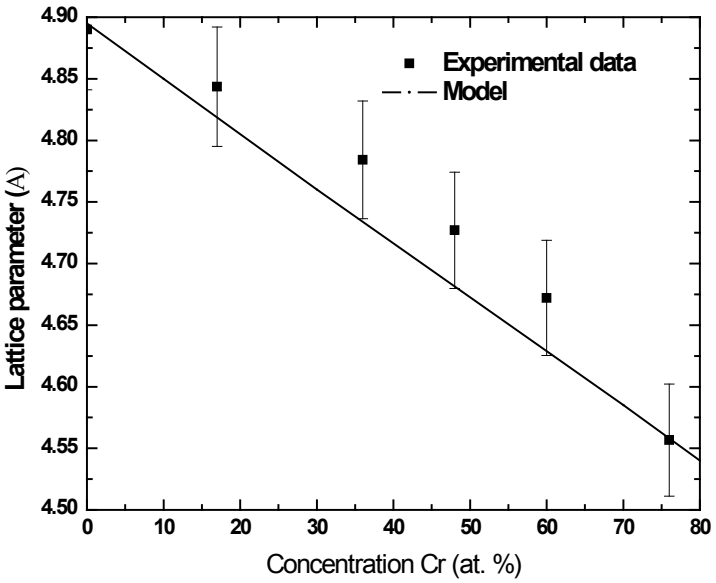

Figure 5. Lattice parameter as a function of Cr, experimentally and using the proposed model.

Table 1. Alloy composition, lattice parameter and densities for the alloys as a function of Mo and Cr additions.

Alloy Designation	Si [at.%]	Mo [at.%]	Cr [at.%]	Lattice Parameter [Å]	X-Ray Density [g/cm^3]	Bulk Density [g/cm^3]	C_v [%]
S1	24.00	76.00	0.00	4.8900	9.00035	8.9985	0.020
S2	24.00	59.00	17.00	4.8436	8.39891	8.3957	0.038
S3	24.00	40.00	36.00	4.7842	7.71521	7.7123	0.037
S4	24.00	28.00	48.00	4.7270	7.33312	7.3302	0.039
S5	24.00	16.00	60.00	4.6721	6.92713	6.9254	0.024
S6	24.00	0.00	76.00	4.5567	6.49180	6.4873	0.069

Although the estimation has some limitations, the model could be used as a first approximation. The results of these estimations are shown in **Figure 5**. Here it can be seen that the estimations and the present measurements are in good agreement. These results permit us to infer that the process for the case of Cr is clearly substitutional. **Table 1** shows the lattice parameter and densities values obtained from X-ray diffraction data analysis for several Cr content, using silicon peaks as references. In the case of alloys with Cr additions, the density results shown a reduction when the Mo content is substituted for the Cr addition (which has a lower atomic mass weight) until the stoichiometric composition of Cr with Si is reached. From the vacancy concentration analysis it is concluded that do not exist enough amount of this defects to promote the lattice deformation, which can be detrimental in the mechanical properties obtained.

4. Conclusion

Ternary alloys with Cr additions on Mo_3Si matrix were produced. The hardness of the alloys in the present study falls in the range of 1200 - 1330 Kg/mm^2. Fracture toughness of the alloys with different Cr additions increases as much as 25%. Density values indicate a low level of thermal defects existing in the alloys. From the studies of the lattice parameter it can be deduced that the variation obtained is attributed to the distortion of the lattice when an atom with different atomic radii is added, not for vacancies concentrations, performing a substitutional process for the case of Cr and for consequence affecting in positive way the mechanical properties during the transition process in a specific range Cr concentration.

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