ORIGINAL PAPER

Effect of Ta on the corrosion performance of Mo_3Si intermetallic in NaCl solutions

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Abstract The effect of Ta contents on the corrosion performance of Mo_3Si intermetallic in 0.5 M NaCl has been evaluated. Materials included Mo_3Si plus 5, 17, 53, 60, and 74 at% Ta. Techniques included potentiodynamic polarization curves and linear polarization resistance curves. Except for 74 at% Ta, additions of Ta induced a passive region, decreasing the anodic current density, the free corrosion potential, the pitting potential, and the corrosion current density.

Keywords Mo_3Si intermetallic · Aqueous corrosion

Introduction

Molybdenum silicides are of interest for their mechanical and physical properties, due to the need for materials with good properties to support extreme conditions such as high temperature, high stresses, and corrosive environments. $MoSi_2$ is one of the most extensively studied compounds in the Mo–Si binary phase diagram, together with the other two compounds that precipitate in this system, Mo_5Si_3 and Mo_3Si. The low-temperature corrosion behavior of molybdenum silicides, such as Mo_3Si, $Mo_3Si+Mo_5Si_3$, or $Mo_3Si+\alpha$-Mo phases, has not received much attention, with the exception of a few studies [1–3]. In a previous work [4], the corrosion performance of these alloys in 0.5 M sodium chloride (NaCl) and 0.5 M sodium hydroxide (NaOH) was evaluated finding preferential corrosion of one of the phases. Other work on the corrosion

performance of Ta alloys such as Ta–2.5W and Ta–10W alloys (containing 2.5 and 10 wt% W, respectively) showed these alloys to perform better than Ta alone in H_2SO_4 [5] and NaOH [6]. In this work, ternary silicide alloys with Ta additions to a silicide were produced with the purpose to obtain a transition metal with increased corrosion resistance properties.

Experimental procedure

Alloys were prepared by arc-melting of nominally pure elements in a partial pressure of argon, and drop-casting into water-cooled copper molds with a diameter of 12.5 mm. The specimens were annealed in a vacuum of 10^{-4} Pa for 24 h at 1,600 °C and then cooled using a cooling rate of 2.5 °C s^{-1} between 1,600 and 1,000 °C and then furnace cooled. Table 1 shows the nominal composition for the different alloys. To compensate for the possible loss in Si due to evaporation, an extra 0.5 at% of Si was added to keep the final compositions of the alloy after the heat treatment in agreement to the Mo–Si alloy phase diagram (because Mo_3Si is a line compound; i.e., at this chemical composition, a material with only one phase, Mo_3Si, is obtained, whereas for Mo concentrations, either lower or higher than this one, a material with two different phases is obtained). Chemical compositions of the obtained materials and for the different found phases were obtained by X-ray dispersive analysis attached to a scanning electronic microscope (SEM) and, in the case of the different phases, corroborated by X-ray diffraction. For the corrosion experiments, specimens of 5×5×3 mm were obtained by an electrodischarge machine, a machine which produced high voltage and, thus, a spark between the metal to cut an electrode (this spark erodes the metal, cutting it,

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Table 1 Nominal compositions for the tested alloys

Si (at%)	Mo (at%)	Ta (at%)
24.0	71.0	5.0
24.0	59.0	17.0
24.0	23.0	53.0
24.0	16.0	60.0
24.0	2.0	74.0

because these intermetallic alloys are extremely hard to cut by conventional cutting equipment). After that, the specimens were encapsulated in epoxy resin and then polished with diamond paste to a 0.1-μm finish. Electrochemical experiments were performed using a potentiostat from ACM Instruments controlled by a personal computer. Potentiodynamic polarization curves (PCs) were obtained by varying the applied potential from −100 mV with respect to the free corrosion potential, E_{corr}, up to +1,500 mV at a rate of 1 mV/s, using a saturated calomel electrode as reference electrode and a platinum wire as counter electrode. Corrosion rates were calculated in terms of the corrosion current, I_{corr}, by using linear polarization resistance curves, which was done by polarizing the specimen from +10 to −10 mV with respect to E_{corr}, at a scan rate of 1 mV/s, to get the polarization resistance, R_p. By using the Stearn–Geary equation, the I_{corr} value was calculated as follows:

$$I_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)} \cdot \frac{1}{R_p} ,$$

(1)

where b_a and b_c are the anodic and cathodic slopes obtained from the PCs. For the electrochemical current noise (ECN) measurements, a zero resistance ammeter (ZRA) from ACM Instruments was used, which was controlled using a desktop computer. For this, two nominally identical electrodes which were attached to the ZRA equipment readings were taken in blocks of 1,024 points at 1 s intervals. All tests were performed at room temperature (25±2 °C). Solutions used included 0.5 M NaCl prepared from analytical grade reagents. After the experiments, the specimens were cleaned to be observed in the SEM.

Results and discussions

Figure 1 shows the effect of Ta contents on the PCs for the Mo₃Si alloy in 0.5 M NaCl. The alloy without Ta did not show a passive region and exhibited a free corrosion potential value, E_{corr}, near 0 mV. When the silicide was alloyed with Ta, the alloys showed a passive region in all cases and displayed decreases in the E_{corr} value and the anodic current density, the exception being when 74 at% Ta was added, which had the highest anodic current density, even higher than the unalloyed silicide. In some cases, the pitting potential value, E_{pit}, was lowered also.

The effect of Ta contents on the corrosion rate, I_{corr}, for the different silicides is shown in Fig. 2. This figure shows that addition of 5 at% Ta decreased slightly the I_{corr} value of the unalloyed silicide, but by adding 17 at% Ta, the I_{corr} value was decreased by more than three orders of magnitude. With additions of 53 at% Ta, the I_{corr} value
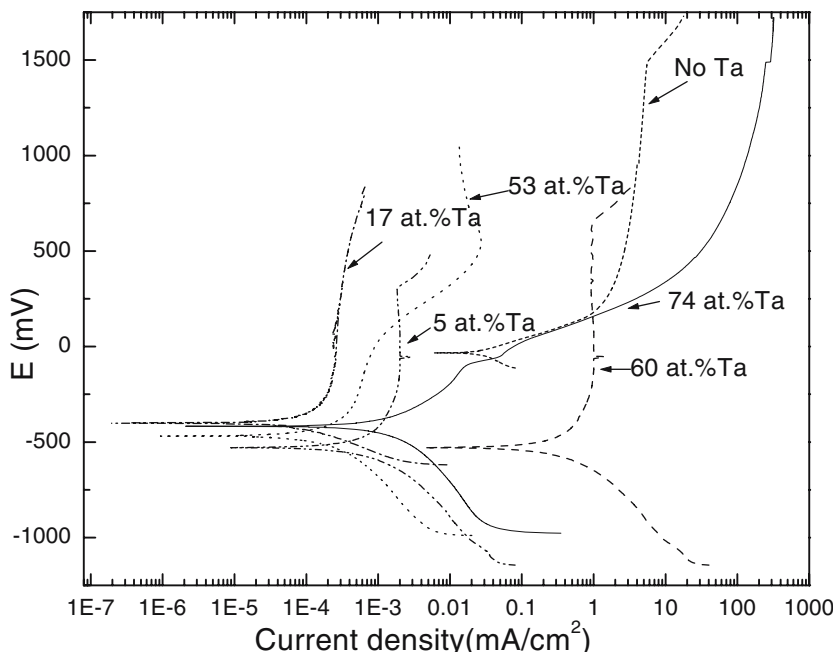

Fig. 1 Effect of Ta concentration on the polarization curves of Mo–24Si alloys in 0.5 M NaCl
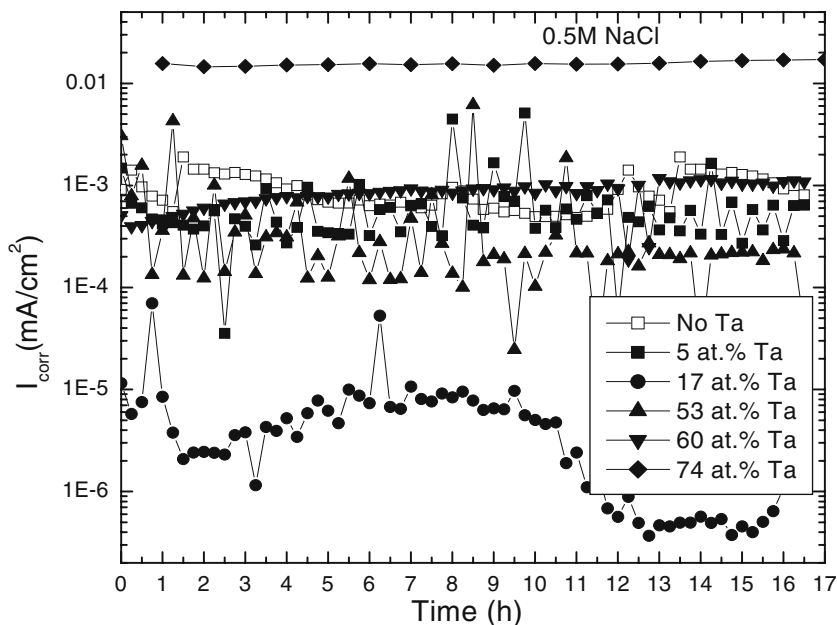
Fig. 2 Effect of Ta concentration on the change of the corrosion current, I_{corr}, with time for Mo–24Si alloys in 0.5 M NaCl

was still lower than the unalloyed silicide; with 60 at% Ta, the corrosion rate was very similar to the unalloyed silicide; and, finally, with 74 at% Ta, the corrosion rate of the unalloyed silicide was increased by more than one order of magnitude.

Because all the passive alloys are susceptible to localized type of corrosion, some tests were carried out to establish this, and a typical graph of the ECN is shown in Fig. 3.

This figure shows transients, where a sudden increase in current and a slow recovery are observed. These types of transients are observed in localized types of corrosion, such as pitting, crevice, and stress corrosion cracking, the result of a film breaking down and reforming. Figs. 4, 5, and 6 show the corroded microstructure of the Si–Mo alloy without additions of Ta and the ones alloyed with 5 at% Ta and 63 at% Ta. The first two figures show a preferential
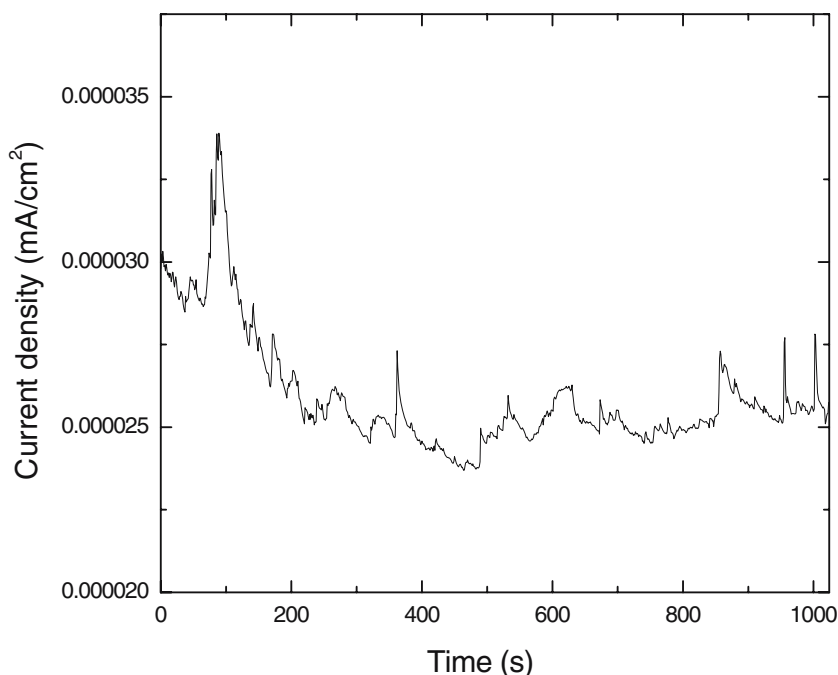

Fig. 3 Electrochemical current noise for Mo–24Si alloy containing 5 at% Ta in 0.5 M NaCl
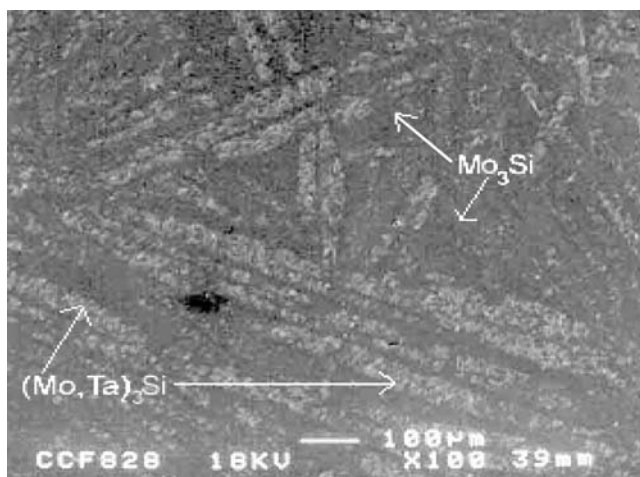
Fig. 4 Micrograph of the Mo–24Si alloys corroded in 0.5 M NaCl

Fig. 6 Micrograph of the Mo–24Si alloy containing 63 at% Ta corroded in 0.5 M NaCl

corrosion of one of the phases, Mo_5Si_3 in the silicide without Ta, and the $(Mo,Ta)_3Ta$ phase in the Ta-containing alloy. The alloy with 74 at% Ta, presented in Fig. 6, shows the fractured passivating film, which was broken and allowed the electrolyte to get in contact with the underlying metal, corroding it.

It is considered that the anodic transients are the result of a film rupture which exposes the metal to the solution. The current transient is the result of exposure of the metal, and its relatively slow current recovery reflects, perhaps, a repassivation process. The transient ceases on reformation of the film. The anodic transients observed suggest that these events are associated with the second nominally identical electrode, which is acting as a cathode. As stated in the "Experimental procedure" section, a two-, nominally identical electrode system was used, and when one electrode was acting as an anode, i.e., dissolving, the second one was acting as a cathode. According to theoretical potential/pH (E/pH) equilibrium diagrams [7]
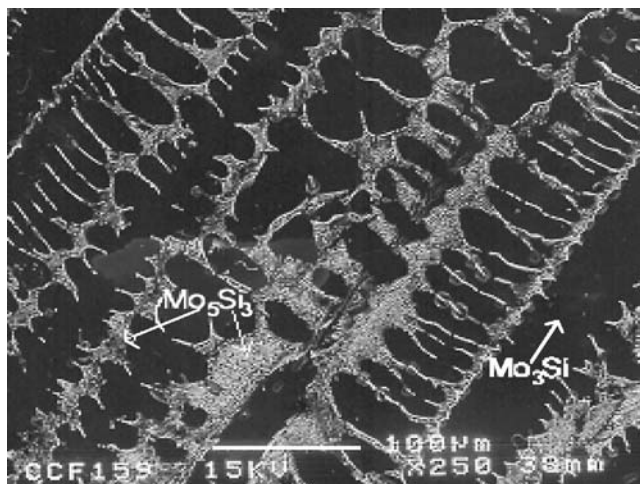
for Mo_3Si and Mo_5Si_3, at the E_{corr} values of this research, the two stable species are MoO_2 and $H_2Si(OH)_6$. So, molybdenum could be oxidized mainly to Mo^{4+} while silicide can be oxidized to silicic acid [8] which can be incorporated into the passive film. This film could contain, thus, both molybdenum and silicon ions. The large area of the cathodic phase, i.e., Mo_3Si, together with a relatively small area of the anodic phases, Mo_5Si_3 and $(Mo,Ta)_3Si$, in combination with an aggressive environment, made favorable conditions for a selective corrosion of the least corrosion-resistant phase to take place.

Conclusions

The effect of additions of Ta on the corrosion behavior of Mo_3Si intermetallic in 0.5 M NaCl has been evaluated using electrochemical techniques. Results showed that additions of Ta to the Mo_3Si intermetallic induced a passive region and decreased the anodic current density, the free corrosion potential, E_{corr}, and the corrosion current density, I_{corr}, but with 74 at% Ta, additions increased the I_{corr} value. There was a preferential, localized corrosion of phases such as Mo_5Si_3 and $(Mo,Ta)_3Si$.

Fig. 5 Micrograph of the Mo–24Si alloy containing 5 at% Ta corroded in 0.5 M NaCl

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