Development of MoSi$_2$ coating with Al doping by using high energy milling method

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Abstract. MoSi$_2$ is well known as a material for high temperature application because it has high oxidation and corrosion resistance. The aim of this research is to develop MoSi$_2$ coating with Al doping on Stainless Steel 316 (SS316) substrate using High-Energy Milling method. Aluminium is added to the coating as a dopant to increase formation of MoSi$_2$ coating layer on the substrate. The variations used here based on the concentrations of doping Al (at.%) and duration of milling. Results show that the MoSi$_2$ coatings with variations of 30 and 50 at.% of Al doping and 3 and 6 hours of milling times were successfully coated on the surface of SS 316 using the high-energy milling method. The most optimum coating result after oxidation test at 1100 °C for 100 hours is shown by MoSi$_2$-30%Al with 3 hours of milling times. From the oxidation results, the Al doping into MoSi$_2$ coating was able to increase the oxidation resistance of the SS 316 substrate.

1. Introduction

MoSi$_2$ is a promising high-temperature material due to its density (6.31 g / cm$^3$) and can operate at high temperatures because MoSi$_2$ has high melting point of 2020 °C. In addition, MoSi$_2$ has a good oxidation resistance at high temperatures. Through thin-layer formation of SiO$_2$, MoSi$_2$ could protect materials from continuous oxidation [1]. Some coating methods have been successfully applied for MoSi$_2$ coatings, such as pack siliconizing, plasma spraying, and chemical vapor deposition [2-4].

For powder materials, mechanical alloying with high-energy milling is one of the most efficient techniques in synthesizing nanomaterials and preparing nanocrystalline alloying. In previous studies, it had been demonstrated that mechanical alloying could also be used in coating processes such as Ni-Al coating [5-7], Fe-Al coating [8-9], and Cr-Al coating [10]. During mechanical alloying with ball milling process, the ball mills together with powder particles collide with the substrate surface with repeated high energy impact resulted in the powder deposition on its surface [11].

Aluminum was a metal element that showed great interest to the oxygen. This was due to the formation of alumina (Al$_2$O$_3$) in high temperature. The Al$_2$O$_3$ oxide layer became a good protective
layer on the surface of the substrate [12]. The addition of Al for coating process affected significantly on the resulted coating formation [8-9].

This research was conducted with the aim to study factors that influence coating process of MoSi$_2$ on Stainless Steel 316 substrate using high-energy milling method with variation of milling time process and concentration of Al (at.%) as doping. In addition, coating on the SS 316 substrate would be tested for oxidation at 1100 °C, which then would be analyzed for its oxidation resistance.

2. Experimental Method

2.1. Material and Coating Process
MoSi$_2$ and Al powder were used as a coating material for Al-MoSi$_2$ coating. Stainless Steel 316 plates with dimension of 10x10x3 mm$^3$ were used as a substrate. Prior to the coating process using high-energy milling method, SS 316 substrates were polished using carbide papers up to 1200 grit. The SS 316 substrates were subsequently cleaned using ultrasonic bath to remove impurities from the surface of the substrate.

The high-energy milling process was carried out in the air atmosphere using shaker mill with vials and stainless steel ball mills. The Al-MoSi$_2$ powder mixture was prepared by mixing MoSi$_2$ powder with Al. Initially, MoSi$_2$ and Al powder with composition of 30 at.% and 50 at.% Al were mixed using shaker mill for 1 hour with 9:1 ball to powder ratio. For the coating process, the SS 316 substrate was milled together with ball mills and mixture of Al-MoSi$_2$ in a vial with variations of 3 and 6 hours of milling times.

2.2. Oxidation Test
The substrate dimension and weight were measured before the oxidation test. The cyclic oxidation test was performed for all coated substrates under air atmosphere with temperature of 1100 °C for 100 hours in a muffle furnace. For each cycle of 20 hours of oxidation time, the samples were removed from the furnace, cooled down to room temperature, and the mass gain was measured, without the spalled oxidation. This cycle was repeated for 5 times until it reached a total of 100 hours of oxidation test.

2.3. Characterization
The coated samples were characterized using optical microscope, X-ray diffraction (XRD), and scanning electron microscope equipped with energy dispersive X-ray analysis (SEM-EDX). The optical microscope was used to view and make sure the samples were free from scratches before the sample was observed using the SEM-EDX. XRD characterization was used to determine phase formation in the deposited MoSi$_2$-Al layer on the surface of SS 316. SEM-EDX characterization was used to observe sample morphology at micro scale and distribution of the detected elements in the sample.

3. Results and discussions

3.1. Coating results with high-energy milling method
XRD characterization results shows that MoSi$_2$ coating with Al doping was successfully formed on the surface of SS 316 substrates after 3 and 6 hours of milling time. It could be seen in figure 1 that all diffraction peaks of substrate surfaces after milling process mostly consisted of MoSi$_2$, and some Mo$_3$SiAl and FeCr phases. The detected FeCr phases are main compositions of the 316 substrates. From the XRD results, Al on this coating was found in the form of Mo$_3$Al [13].
In order to support the XRD results, the cross section of the sample surface was studied using SEM. SEM images on figure 2 reveals that the MoSi$_2$-Al had been successfully deposited on the surface of SS 316, but with some porous and rough surfaces. MoSi$_2$-30%Al coating layer is less porous and rough than that of MoSi$_2$-50%Al coating. The average coating thickness of MoSi$_2$-30Al and MoSi$_2$-50Al was 25.69 µm and 38.32 µm, respectively. The coating layers of MoSi$_2$-Al formed were rough and clearly distinguishable between the coating layer and the substrate. The coating layer was formed by repeated collisions occurring between ball mills, mixed MoSi$_2$-Al powder particles, and the SS 316 substrate.

![Figure 1. XRD pattern of MoSi$_2$-Al coating on the 316 substrates after 3 and 6 hours of milling time.](image)

![Figure 2. SEM images of the cross-sectional 3 h milling MoSi$_2$-Al coating (a) with 50% at.% Al (b) 30% at.% Al.](image)
3.2. Oxidation test

Figure 3 shows the mass change of the SS 316 substrates with MoSi$_2$-Al coating after oxidation test at 1100 °C in air. From all samples, the oxidation rate in the MoSi$_2$-50%Al - 3h sample has relatively the lowest mass decrease compared to the other samples, followed by the MoSi$_2$-30%Al - 3h sample.

![Graph showing mass change over time for different samples.](image)

**Figure 3.** Mass gain after oxidation at 1100 °C in air of the SS 316 substrates with MoSi$_2$-Al coating.

At beginning of the oxidation test until 40 hours, all samples had mass loss due to the instability of the MoO$_3$ formed during the oxidation process and the volatile of MoO$_3$ that made a way for oxygen to reacted with the substrate [14].

After 40 hours, samples with 3 hours milling time were able to minimize the mass loss unlike samples with 6 hours of milling time that showed irregular trends. For the MoSi$_2$-50%Al 6h sample, the mass reduction was relatively low and stable until 80 hours of oxidation test. However, after 80 hours the sample mass decreased significantly. As the MoSi$_2$-30%Al - 6h sample, after 40 hours, the sample mass increased significantly until the end of oxidation test. Although the sample mass increased, figure 4 shows that sample surface began to crack after 60 hours of oxidation process.

![Images showing sample surface after oxidation.](image)

**Figure 4.** MoSi$_2$-30%Al-6h coating layer changing during oxidation at 1100 °C.
The surface morphologies with EDS mapping of a cross section of the 316 substrate with MoSi$_2$-50%Al-3h after oxidation test at 1100 °C for 100 hours is shown on figure 5. After 100 hours of oxidation test, the MoSi$_2$-50%Al-3h surface consisted of 3 layers. Layer 1 is identified as a thick layer of mixed SiO$_2$ and Al$_2$O$_3$ (point 1). Layer 2 consisted of thin layer of Al$_2$O$_3$ (point 2). Meanwhile, at layer 3, thin internal oxidation of mixed MoSi$_2$ – Al is formed (point 3). The detailed composition of each layer is shown in table 1.

![Figure 5. SEM and EDX elemental mapping images of the cross-sectional MoSi$_2$-50%Al-3h coating after oxidation test at 1100 °C.](image)

| Elements | Point 1 (at.%) | Point 2 (at.%) | Point 3 (at.%) |
|----------|---------------|---------------|---------------|
| Al       | 3,862         | 25,498        | 4,418         |
| Mo       | -             | -             | 48,886        |
| Si       | 13,345        | 1,252         | 23,506        |
| O        | 82,74         | 73,251        | 23,118        |

Formation of double SiO$_2$ and Al$_2$O$_3$ layers on the substrate surface with MoSi$_2$-50%Al-3h coating during oxidation test enables the sample to minimize the mass loss during the oxidation test. However, since the layer 1 is not formed as a completely closed layer, this correlates with the oxidation results that the substrate had still mass loss during oxidation test. Thus, the substrate had relied on the thin protective Al$_2$O$_3$ layer against the oxidation attack. This happened because MoSi$_2$ has high coefficient thermal expansion mismatch [15]. With the high-energy milling process, this affected more with the oxidation results of coated MoSi$_2$-Al coating substrates. This explains the results of oxidation test of the substrates with 6 hours of milling times.

4. Conclusions
The MoSi$_2$ coatings with variations of 30 and 50 at. % of Al doping and 3 and 6 hours of milling times were successfully coated on the surface of SS 316 using high-energy milling method. Coating thickness increased with increasing atomic concentration from Al. The most optimum coating result after oxidation test at 1100 °C for 100 hours is MoSi$_2$-30%Al with 3 hours of milling times. From the oxidation results, the Al doping into MoSi$_2$ coating was able to increase the oxidation resistance of the SS 316 substrate.
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