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Characterization of the Structure of Plasma-Sprayed Metallic Silicide Coatings†

Akira Ohmori*, Nobuhiro Ohnishi**, Chang-Jiu Li*** and Hiroaki Shoyama****

Abstract

MoSi₂ and TiSi₂ coatings are deposited by low pressure plasma spraying processes. The structures of the deposited coatings are characterized by using X-ray diffraction. The effects of annealing treatment on the structures of the coatings under vacuum and under ambient atmospheres are examined. It is found that the MoSi₂ coating is consisted of a meta-stable hexagonal MoSi₂ and a stable tetragonal MoSi₂₃ while TiSi₂ coating is constituted from meta-stable orthorhombic base centered phase (C49) and stable orthorhombic face-centered phase (C54). The annealing of both silicide coatings under the temperatures from 873K to 1073K leads to the phase transformation from meta-stable silicides to stable silicides. The annealing of the TiSi₂ coating at ambient atmospheres results in the oxidation of silicide and formation of TiO₂ and SiO₂ which fills up the pores in the coating and leads to densification of the coating. The annealing treatment also causes the diffusion of silicon towards the substrate from the coating to form a strong bond between coating and substrate. However, the diffusion of silicon depletes the silicon in the coating and may reduce the instability of the silicide coating.

KEY WORDS: (Plasma Spraying) (Coating) (Titanium Silicide) (Molybdenum Silicides) (Structure)

1. Introduction

Refractory metal silicides are receiving interest as potential high temperature structural materials. Because of its high melting point, low density, excellent high temperature oxidation resistance and metallic-like thermal and heat conductivities, MoSi₂ is expected to be most promising of those materials1. Many investigations have aimed at the improvement of fracture toughness and resistance to creep at high temperature2,3. There are several processes which are usually used for forming and processing of metal silicides. The thermal spray process is preferable for depositing silicide coatings.

Compared with the broad interest in MoSi₂ as a high temperature structural material, titanium silicides are mainly creating interest as electronic materials4. Therefore, titanium silicides are mainly produced by thermal diffusion processes with diffusion of Si into titanium. As a result of the high melting point of Ti₅Si₅ (upto 2403K)5 and excellent oxidation resistance of titanium silicides, titanium silicide may be expected to become one of the candidates for high temperature structural materials. In particular, the metal silicides with such high melting points are expected to be used as high temperature coatings.

It is well known that any material with a physical melting point can be easily coated on a coating by the thermal spray process. Therefore, the deposition of MoSi₂ coating has been attempted by plasma spraying processes6,7. Main interests have been concerned with the mechanical properties of sprayed MoSi₂ coatings. When the coating of a material is deposited through plasma spraying, it has to be subjected to rapid heating up to the melting point and then experience a rapid cooling when spray particle impacts on the substrate. Such a rapid thermal cycle generally leads to the formation of a meta-stable structure8. As a candidate for high temperature structural materials, silicide coatings should have a stable structure at high temperatures. However, there are few reports concerning the structure of thermal sprayed metal silicide coatings, especially, titanium silicides.

In this paper, MoSi₂ and TiSi₂ coatings were deposited using a low pressure plasma spraying process.

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and the structure of both MoSi$_2$ and TiSi$_2$ coatings were characterized, and the effect of annealing treatment on the structure of silicide coatings was investigated.

2. Materials and Experimental Procedure

2.1 Materials

Both molybdenum disilicide (MoSi$_2$) and titanium disilicide (TiSi$_2$) powders used in the experiment had a grain size ranging from 10 $\mu$m to 63 $\mu$m. MoSi$_2$ has a nominal composition of 62.5 mass% Mo-37.5 mass% Si, while the nominal composition of TiSi$_2$ was 47.6 mass% Ti-52.4 mass% Si. Mild steel was primarily used as substrate.

2.2 Low pressure plasma spraying

Plasma spraying was carried out using a commercial spraying torch (Metco 7MB). Plasma torch operated using Ar as primary gas and H$_2$ as secondary gas. Table 1 shows the main spraying parameters. Spraying was carried out in a low pressure argon atmosphere.

Before the ignition of the plasma arc, the spray chamber was evacuated to a pressure lower than 133 Pa. After the chamber pressure had reached a pressure of $2.6 \times 10^4$ Pa by the charge of argon gas, the plasma arc was ignited. The spraying of silicides was started after the chamber pressure was adjusted to $1.3 \times 10^5$ Pa. In order to investigate the effect of spray parameters on the structure of silicide coatings, the coatings were also deposited by changing the H$_2$ flow rate from $0.4 \times 10^4$ to $0.4 \times 10^4$ m$^3$/s and the chamber pressure from $1.3 \times 10^5$ Pa to $9.1 \times 10^3$ Pa.

In order to examine the stability of the structure of silicide coating, the coatings were heat-treated under a vacuum of $1.3 \times 10^2$ Pa and at different temperatures and under ambient atmosphere as well.

2.3 Characterization of coating structure

The structure of the silicide coatings was characterized using X-ray diffraction. The microstructure of the coating was examined by scanning electron microscopy and optical microscopy.

3. Results and discussion

3.1 The structure of plasma-sprayed MoSi$_2$ and TiSi$_2$ coatings

Figure 1 illustrates the microstructure of cross-sections of low pressure plasma sprayed MoSi$_2$ coating (a) and TiSi$_2$ coating (b) deposited by the spray conditions shown in Table 1. X-ray diffraction analysis of spray powders, as illustrated in Fig. 2, showed that both MoSi$_2$ and TiSi$_2$ powders consist of stable phases of tetragonal MoSi$_2$ and stable orthorhombic face-centered phase (C54) TiSi$_2$, respectively. However, X-ray analysis revealed that the additional quasi-stable phases appeared in the deposited coatings besides the original stable phase as starting powder, as shown in Fig. 3. Regarding MoSi$_2$ coating, both hexagonal and tetragonal phases are formed in the coating. On the other hand, TiSi$_2$ coating consists of both stable C54 and meta-stable C49 TiSi$_2$. Therefore, both MoSi$_2$ and TiSi$_2$ coatings consist of both meta-stable phases and stable phases.

The investigation into the effect of spraying parameters such as plasma power, chamber pressure and flow of secondary gas in plasma revealed that the structure of both MoSi$_2$ and TiSi$_2$ coatings was not significantly influenced by spray conditions.

![Microstructures of cross-sections of low pressure plasma sprayed MoSi$_2$ coating (a) and TiSi$_2$ coating (b)](image-url)
3.2 The effect of annealing treatment on the structure of plasma-sprayed MoSi$_2$ and TiSi$_2$ coatings

Figure 4 shows the X-ray diffraction patterns of MoSi$_2$ coatings annealed at different temperatures from 873K to 1673K in vacuum for 2 hours. It was found that the X-ray diffraction pattern of the coating annealed at 873K is similar to that of the as-sprayed one. However, the intensity of hexagonal MoSi$_2$ in the coating annealed at 1073K $\times$ 2hrs. was significantly decreased compared with that of the sprayed one. This fact implies that the phase transformation from hexagonal MoSi$_2$ to tetragonal MoSi$_2$ occurred at the temperature of 1073K. With an increase in annealing temperature to over 1273K, it was found that all hexagonal MoSi$_2$ was completely transformed into tetragonal MoSi$_2$, and no further change occurred with further increase in annealing temperature.

Such post annealing treatments of plasma-sprayed MoSi$_2$ coatings suggest that the transformation from hexagonal MoSi$_2$ to tetragonal MoSi$_2$ begins at a temperature from 873K to 1073K. DTA analysis of sprayed MoSi$_2$ coatings confirmed that the transformation from hexagonal MoSi$_2$ to tetragonal MoSi$_2$ occurs at a peak temperature of 1218K.

Figure 5 illustrates the X-ray diffraction patterns of plasma-sprayed TiSi$_2$ coatings annealed at different temperatures from 873K to 1273K under vacuum for 2hr. It can be recognized that the coating annealed at 873K shows a similar structure to that of the as-sprayed coating. However, the X-ray diffraction pattern of the coating annealed at 973K clearly shows that the annealed coating consists only of the C54 type of TiSi$_2$. With a further increase of annealing temperature the coating shows no change of structure, although a trace of Ti$_3$Si$_2$ was recognized from X-ray diffraction pattern. The results shown in Fig.5 suggest that the transformation from C49 TiSi$_2$ to stable C54 TiSi$_2$ begins at a temperature from 873K to 973K.

3.3 The effect of annealing treatment in air on the microstructure of silicide coatings

Figure 6 illustrates X-ray diffraction pattern of TiSi$_2$ coatings annealed at a temperature of 1273K under ambient atmosphere for 2hrs. It is evident that the metastable C49 phase disappeared after the annealing treatment. On the other hand, it was found that a fraction of TiSi$_2$ had been oxidized to TiO$_2$ and SiO$_2$. In addition, the formation of Ti$_2$Si$_3$ was also recognized in the coating. It was confirmed that TiO$_2$, SiO$_2$ and Ti$_2$Si$_3$ were formed throughout the coating after annealing.

Figure 7 shows the microstructures of the annealed TiSi$_2$ coatings sprayed on 316L stainless steel. Compared with the as-sprayed one, it is evident that the coating becomes dense after annealing in ambient
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Fig. 4 X-ray diffraction patterns of low pressure plasma sprayed MoSi₂ coatings annealed at different temperatures for 7.2 ks under vacuum: (a) 873K, (b) 1073K, (c) 1273K, (d) 1673K

Fig. 5 X-ray diffraction patterns of low pressure plasma sprayed TiSi₂ coatings annealed at different temperatures for 7.2 ks under vacuum: (a) 873K, (b) 973K, (c) 1073K, (d) 1273K

On the other hand, it was also recognized that there existed a diffusion layer between substrate and coating after annealing treatments at high temperature. Figure 8 illustrates the EPMA line analysis result for Si, Fe, Cr and Ni across the interface between substrate and coating. It is clear that a diffusion layer of about 5 μm in thickness was formed through annealing in an ambient atmosphere.

4. Discussion

The present results revealed that a meta-stable phase is consistently formed in the low pressure plasma-sprayed MoSi₂ and TiSi₂ coatings. In the case of MoSi₂, the hexagonal MoSi₂ phase was formed in the coating along with the same tetragonal MoSi₂ as in the starting powder. While in the TiSi₂ coating, both C49 and C54 are formed in the coating despite the single phase of C54.
in the starting powder. The formation of such meta-stable phases in the coating results from the rapid cooling characteristics which are intrinsic to the thermal spray process.

The annealing treatment clearly revealed that the meta-stable phases formed in as-sprayed silicide coatings transform to stable phases at temperatures from 873K to 1073K. After the annealing treatment, meta-stable hexagonal MoSi₂ in sprayed MoSi₂ coatings transforms to tetragonal MoSi₂. On the other hand, in the case of TiSi₂ coating, meta-stable C49 phase transforms to C54 phase. Therefore, the annealing treatment of sprayed silicide coating leads to the transformation of meta-stable phases to thermally stable phases at high temperature.

When the annealing treatment is carried out in ambient atmospheres, SiO₂ protective films can be formed to prevent the further oxidation of the coating.

Owing to the porous characteristic of sprayed coatings, the oxidation of the coating occurs inside the coating and along open pores. The oxides of TiO₂ and SiO₂ formed from the oxidation of the coating fill up the pores in the as-sprayed coating, and protect the coating and substrate from further oxidation. With such characteristics, silicide can be expected to be applied as bond-coating for thermal barrier purposes. Figure 9 illustrates the microstructures of cross-sections of as-sprayed TiSi₂/ZrO₂ two layer coating (a) compared with that exposed in ambient atmosphere at 1273K for 6.5hr (b). It can be seen that after exposure in air at high temperature the silicide coating becomes dense and no spalling occurs.

From Fig.8, it can be concluded that the heat treatment of silicide coating leads to the diffusion of silicon towards the substrate to form a diffusion layer. It can be considered that the formation of this diffusion

Fig.7 Typical microstructures of cross sections of low pressure plasma sprayed TiSi₂ coatings annealed in ambient atmospheres at the temperature of 1273K for 7.2 ks

Fig.8 EDAX analysis results across the interface between TiSi₂ coating and SUS316L stainless steel substrate after annealing in an ambient atmosphere at the temperature of 1273K for 7.2 ks
Characterization of the Structure of Plasma-Sprayed Metallic Silicide Coatings

MoSi₂ and TiSi₂ coatings were deposited using a low pressure plasma spraying process and the structure of both MoSi₂ and TiSi₂ coatings were characterized, and the effect of annealing treatment on the structure of silicide coatings was examined.

It was found that both MoSi₂ and TiSi₂ coatings consisted of both meta-stable and stable phases. The MoSi₂ coating was constituted from meta-stable hexagonal MoSi₂ and stable tetragonal MoSi₂, while the TiSi₂ coating consisted of meta-stable orthorhombic base centered phase (C49) and stable orthorhombic face-centered phase (C54). The annealing of both silicide coatings at temperatures from 873K to 1073K leads to the phase transformation from meta-stable silicide to stable silicide. The annealing of TiSi₂ at ambient atmosphere and high temperature results in the oxidation of silicide and formation of TiO₂ and SiO₂, which then fills up the pores in the coating and leads to the densification of coating. The annealing treatment also causes the diffusion of silicon towards substrate to form a strong bond between coating and substrate. However, the diffusion of silicon will deplete the silicon and may reduce the instability of the silicide coating.

References


Fig.9 Typical microstructure of cross sections of low pressure plasma sprayed ZrO2/TiSi₂ two layer coating heat-treated under ambient atmosphere at the temperature of 1273K for different holding times. (a) as-sprayed; (b) 7.2ks; (c) 36ks

layer will improve the adhesion between coating and substrate. On the other hand, the diffusion will deplete the silicon in the coating. Annealing treatments of sprayed MoSi₂ coatings of about 150 µm thick adhered on mild steel substrate surface at 1773K under vacuum for 2hrs. revealed that the main phases in the molybdenum disilicide coating became Mo₂Si₃ and Mo₃Si. Therefore, regarding the stability of coatings used at high temperature, the growth of the diffusion layer should be limited by measures to prevent the diffusion of silicon from coating to substrate.

5. Conclusions