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

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

Abstract

$MoSi_2$ and $TiSi_2$ 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 $MoSi_2$ coating is consisted of a meta-stable hexagonal $MoSi_2$ and a stable tetragonal $MoSi_2$, while $TiSi_2$ 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 $TiSi_2$ coating at ambient atmospheres results in the oxidation of silicide and formation of TiO_2 and SiO_2, 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, $MoSi_2$ is expected to be most promising of those materials[1]. Many investigations have aimed at the improvement of fracture toughness and resistance to creep at high temperature[1,2]. 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 $MoSi_2$ as a high temperature structural material, titanium silicides are mainly creating interest as electronic materials[3]. 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 Ti_5Si_3 (upto 2403K)[4] 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 deposited as a coating by the thermal spray process. Therefore, the deposition of $MoSi_2$ coating has been attempted by plasma spraying processes[5-8]. Main interests have been concerned with the mechanical properties of sprayed $MoSi_2$ 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 structure[9]. 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, $MoSi_2$ and $TiSi_2$ 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 10μm 63μm. $MoSi_2$ has a nominal composition of 62.5mass%Mo-37.5mass%Si, while the nominal composition of $TiSi_2$ was 47.6mass%Ti-52.4mass%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 133Pa. After the chamber pressure had reached a pressure of 2.6×10^4 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 1.3×10^4 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 0.4×10^{-4} to 0.4×10^{-4} m^3/s and the chamber pressure from 1.3×10^4 Pa to 9.1×10^4 Pa.

In order to examine the stability of the structure of silicide coating, the coatings were heat-treated under a vacuum of 1.3×10^{-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.

Table 1 Low pressure plasma spray conditions

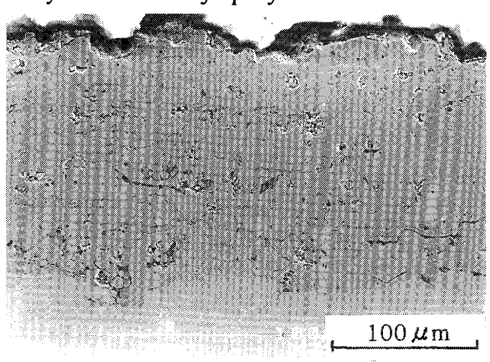
Primary plasma gas (Ar) Pressure (MPa) Flow rate (m^3/s)	 0.7 9.3×10^{-4}
Secondary plasma gas (H_2) Pressure (MPa) Flow rate (m^3/s)	 0.4 2×10^{-4}
Plasma power (kW)	32.4
Arc current (A)	600
Spray distance (mm)	300
Chamber pressure (Pa)	1.3×10^4

3. Results and discussion

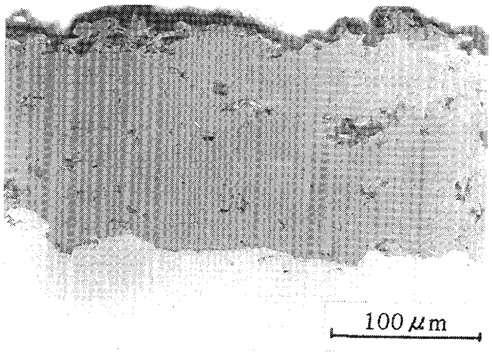
3.1 The structure of plasma-sprayed $MoSi_2$ and $TiSi_2$ coatings

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.



(a)



(b)

Fig.1 Microstructures of cross sections of low pressure plasma sprayed $MoSi_2$ coating (a) and $TiSi_2$ coating (b)

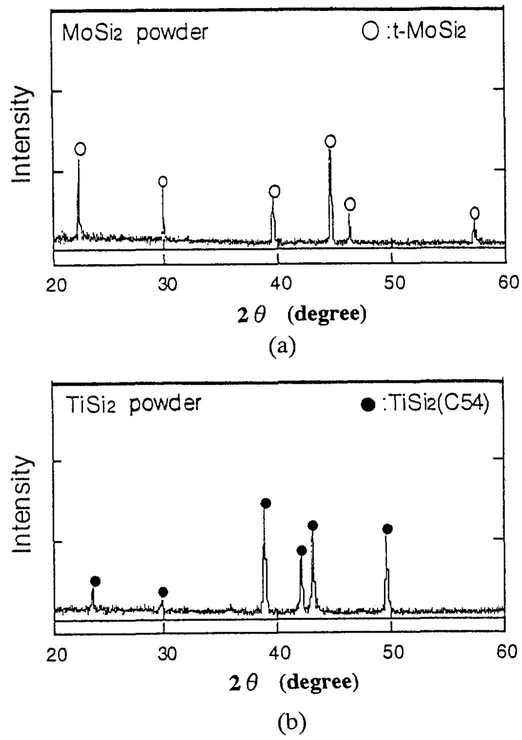


Fig.2 X-ray diffraction patterns of $MoSi_2$ powder (a) and $TiSi_2$ powder (b)

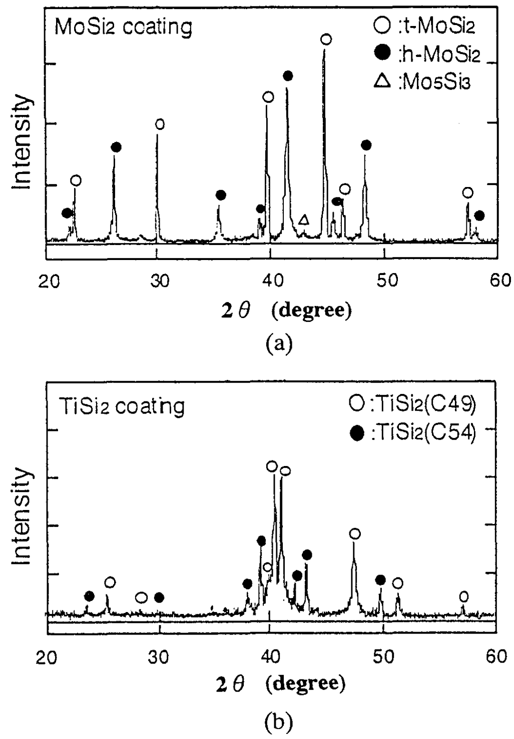


Fig.3 X-ray diffraction patterns of low pressure plasma sprayed $MoSi_2$ coating (a) and $TiSi_2$ coating (b)

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×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_5Si_3 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 meta-stable 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_5Si_3 was also recognized in the coating. It was confirmed that TiO_2, SiO_2 and Ti_5Si_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

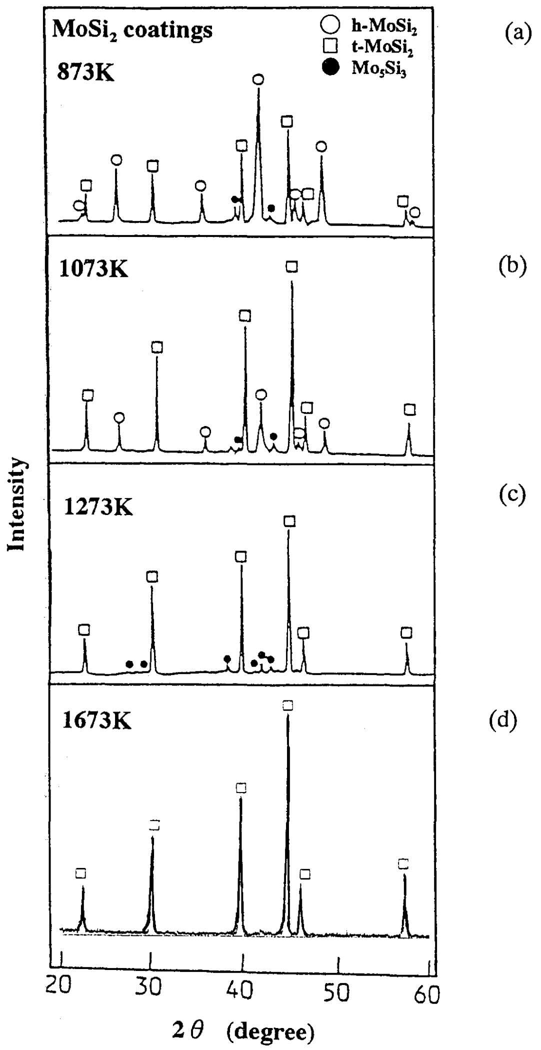


Fig.4 X-ray diffraction patterns of low pressure plasma sprayed $MoSi_2$ coatings annealed at different temperatures for 7.2ks under vacuum: (a) 873K, (b) 1073K, (c) 1273K, (d) 1673K

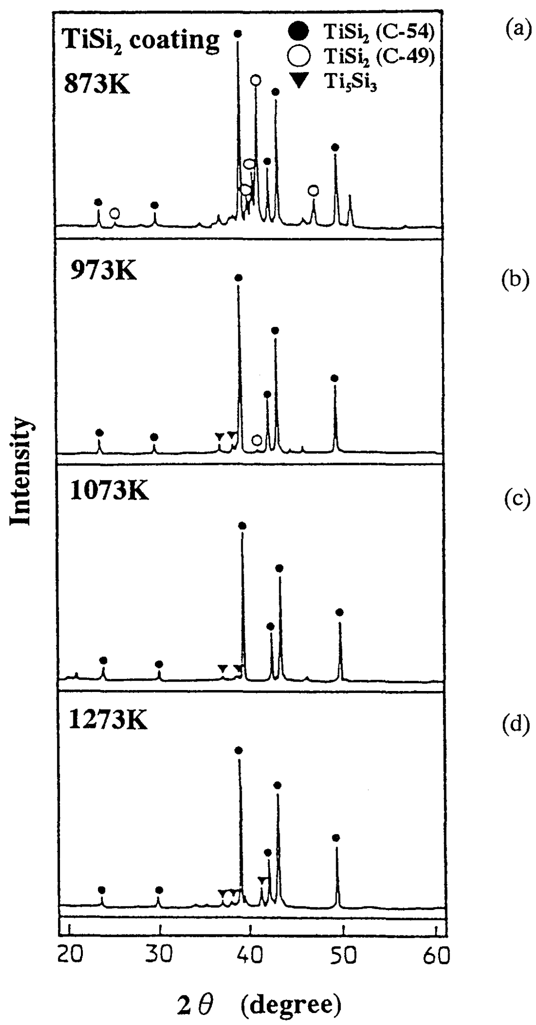


Fig.5 X-ray diffraction patterns of low pressure plasma sprayed $TiSi_2$ coatings annealed at different temperatures for 7.2 ks under vacuum: (a) 873K, (b) 973K, (c) 1073K, (d) 1273K

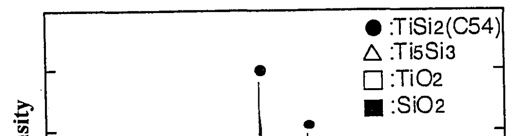


Fig.6 X-ray diffraction patterns of low pressure plasma sprayed $TiSi_2$ coatings annealed under ambient atmosphere at the temperature of 1273K for 7.2 ks

atmospheres. It is considered that this is because the oxidation of $TiSi_2$ forms oxides of TiO_2 and SiO_2 that fill up the pores in the as-sprayed coating, and this leads to the densification of the coating.

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.

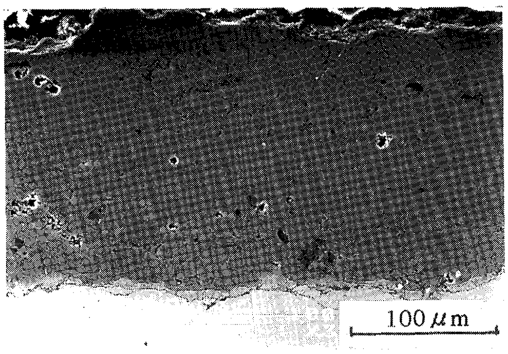
4. Discussion

The present results revealed that a meta-stable phase is consistently formed in the low pressure plasma-sprayed $MoSi_2$ and $TiSi_2$ coatings. In the case of $MoSi_2$, the hexagonal $MoSi_2$ phase was formed in the coating along with the same tetragonal $MoSi_2$ as in the starting powder. While in the $TiSi_2$ 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.

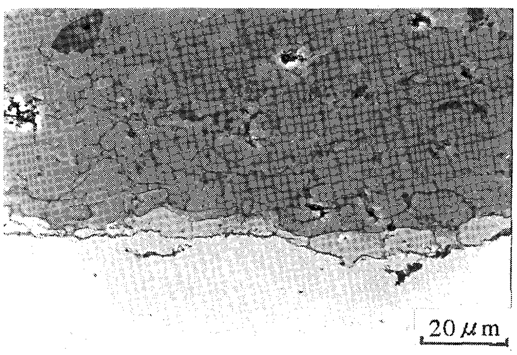
The annealing treatment clearly revealed that the meta-stable phases formed in as-sprayed silicide coatings transform to stable phases at temperatures from 873K to 1073K. After the annealing treatment, meta-stable hexagonal $MoSi_2$ in sprayed $MoSi_2$ coatings transforms to tetragonal $MoSi_2$. On the other hand, in the case of $TiSi_2$ 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, SiO_2 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 TiO_2 and SiO_2 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 $TiSi_2/ZiO_2$ 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



(a)



(b)

Fig.7 Typical microstructures of cross sections of low pressure plasma sprayed $TiSi_2$ coatings annealed in ambient atmospheres at the temperature of 1273K for 7.2 ks

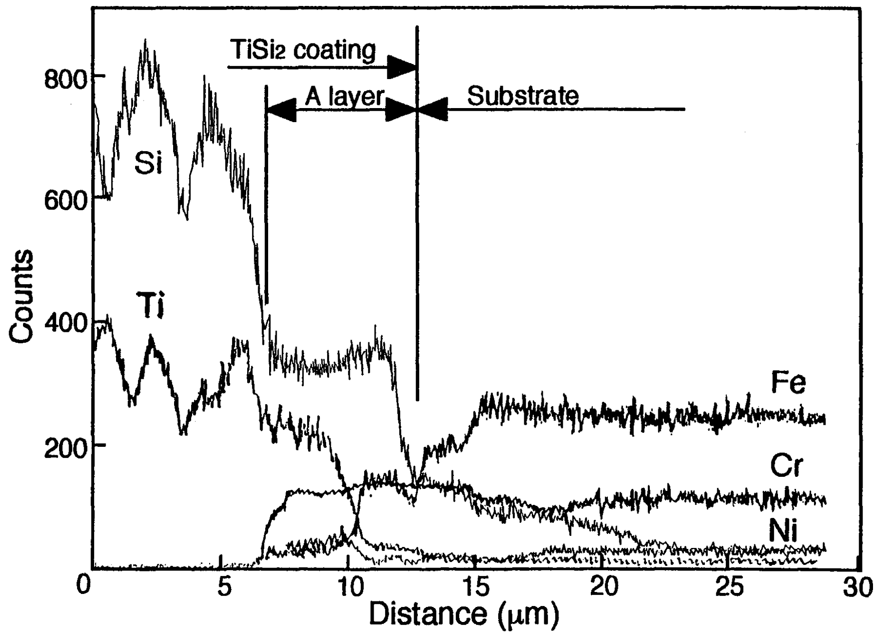


Fig.8 EDAX analysis results across the interface between $TiSi_2$ coating and SUS316L stainless steel substrate after annealing in an ambient atmosphere at the temperature of 1273K for 7.2 ks

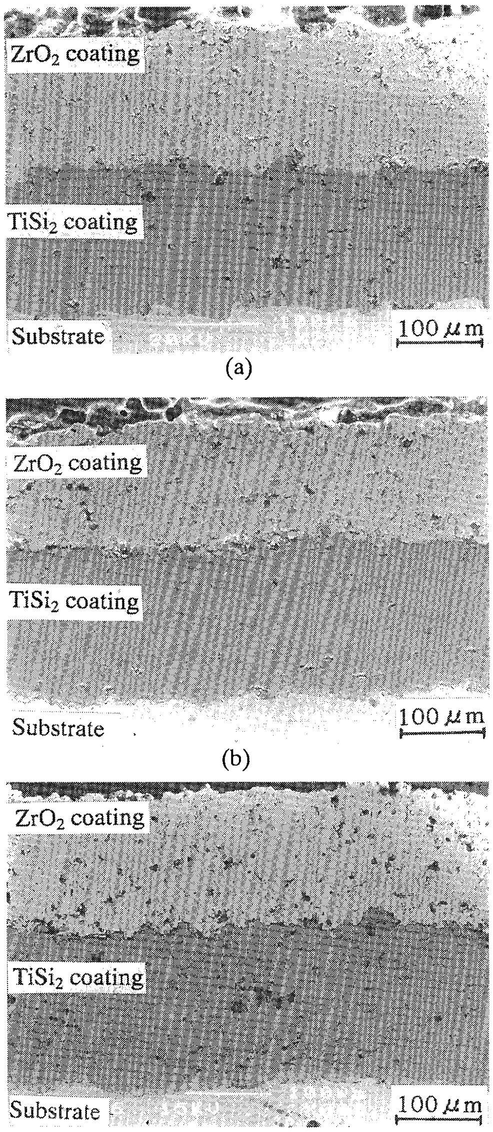


Fig.9 Typical microstructure of cross sections of low pressure plasma sprayed ZrO2/$TiSi_2$ two layer coating heat-treated under ambient atmosphere at the temperature of 1273K for different holding times. (a) as-sprayed; (b) 7.2ks; (c) 36ks

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 $MoSi_2$ 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 Mo_5Si_3 and Mo_5Si. 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

$MoSi_2$ and $TiSi_2$ coatings were deposited using a low pressure plasma spraying process 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 examined.

It was found that both $MoSi_2$ and $TiSi_2$ coatings consisted of both meta-stable and stable phases. The $MoSi_2$ coating was constituted from meta-stable hexagonal $MoSi_2$ and stable tetragonal $MoSi_2$, while the $TiSi_2$ 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 $TiSi_2$ at ambient atmosphere and high temperature results in the oxidation of silicide and formation of TiO_2 and SiO_2, 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

1) A.K.Vasudevan and J.J. Petrovic, A comparative overview of molybdenum disilicide composites, Materials Science and Engineering, A155 (1992)19-31
2) Y.-L. Jeng and E.J. Lavernia, Processing of molybdenum disilicide, J. Mater. Sci., 29(1994)2557-2571.
3) A.Ohmori, Z.Zhou and C.J. Li, Characterization of graded Ti silicide coating formed by thermal diffusion treatment of low pressure plasma sprayed silicon coaing, Proceedings of 15th International Thermal Spraying Conference, ed. C.Coddet, ASM International, 1998, p.605-610.
4) D.M.Shah, D.Berczik, D.L. Anton and R.Hecht, Appraisal of other silicides as structural materials, Materials Science and Engineering, A155 (1992)45-57
5) D.E. Alman, K.G.Shaw, N.S. Stoloff and K.Rajan, Facbrication, structure and properties of MoSi2-based composites, Materials Science and Engineering, A155 (1992)85-93
6) J. Wolfenstine, Y.-L. Jeng and E.J. Lavernia, Elevated-temperature mechanical behavior of plasma sprayed MoSi2-SiC, Materials Science and Engineering, A189 (1994)257-266
7) R. G. Castro, R.W. Smith, A.D. Rollett and P.W. Stanek, Toughness of dense MoSi2 and MoSi2/Tantalum composites produced by low pressure plasma deposition, Scripta Metallurgica et Materialia, 26(1992)207-212
8) Y.-L. Jeng , J. Wolfenstine, E.J. Lavernia, D.E.Bailey and A. Sickinger, Creep behavior of plasma-sprayed SiC-reinforced MoSi2, Scripta Metallurgica et Materialia, 29(1993)107-111
9) R.McPherson, The microstructure of thermally sprayed coatings, Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coating, Osaka, 13-15 May, 1988, High Temperature Society of Japan, 1988, p.25-30.