Materials

Investigation on laser cladding of MoSi₂ powder on steel

Laigi Zhang¹⁾, Guangnan Chen²⁾, and Zuqing Sun¹⁾

 State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China
Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China (Received 2004-10-15)

Abstract: The feasibility of the fabrication of coatings for elevated-temperature structural applications by laser cladding $MoSi_2$ powder on steel was investigated. A dense and crack-free fine coating, well-bonded with the substrate has been obtained by this technique. This coating consists of FeMoSi, Fe₂Si and a small amount of Mo_5Si_3 due to dilution of the substrate in the coating. The microstructure of the coating is characterized of typical fine dendrites. The dendrites are composed of FeMoSi primary phase, and the interdendritic areas are two eutectic phases of FeMoSi and Fe₂Si. The hardness of the coating reaches 845 Hv_{0.5}, 3.7 times larger than that of the steel substrate (180 Hv_{0.5}).

Key words: laser cladding; molybdenum silicide powder; coating; microstructure

[This work was financially supported by the National Natural Science Foundation of China (No.59836220), the Major Science Research Foundation of the Chinese Academy of Science (No.KY951-A1-601-03), and the Science Research Foundation of the University of Science and Technology Beijing (No.20041004790).]

1 Introduction

The intermetallic compound MoSi₂ possesses an interesting combination of high melting point (2030°C), lower density (6.24 g/mm³), and excellent high-temperature oxidation resistance. More importantly above all, this compound is as almost brittle as ceramics at room temperature, however it displays a brittle-ductile transition (BDT) behavior at around 1000°C. Above the BDT temperature, the strength is governed by plastic flow, and it will has more reliability than ceramics at service temperature. Therefore, MoSi₂ is an attractive candidate for elevatedtemperature structural applications [1-3]. However, the poor low-temperature fracture toughness and modest high-temperature strength and creep resistance have hampered efforts to develop and apply MoSi₂ as a massive material.

On the other hand, $MoSi_2$ was applied as a high temperature corrosive-protective coating material for ductile metals as early as in 1907, because of its excellent oxidation behavior and the fact that it is brittle in nature [1,4]. Commonly, these coatings are fabricated mostly by fused slurry siliciding, pack cementation process, chemical vapor deposition and lower pressure plasma spraying [4-7]. The objective of laser cladding is to produce a dense material in the form of fine coatings where the adhesion is obtained by surface melting of substrates. Laser processing offers many advantages such as flexibility of the process, localization of the elaboration, high energy density, high solidification rate that induces a fine microstructure after processing, and high temperature gradients in the liquid pool which enhance convection movements and therefore favor mixing of the different elements [8-9].

The purpose of this work is to attempt to manufacture the coatings for high temperature structural applications on an ordinary steel substrate by cladding $MoSi_2$ powders using the laser beam as the energy resource, which are expected to improve certain properties of resistance to high temperature.

2 Experimental

Commercial 45 steel was used as the substrate. $MoSi_2$ powder with a tetragonal structure was used as the coating material. The purity is 99.5% and the particles have an average size of 8.3 µm, with size distribution ranging from 1.0 to 30 µm. $MoSi_2$ and polyethylene glycol were used to obtain a pasty mixture. The paste was pre-coated onto the specimen surface by brushing to a thickness of about 1.0 mm. Pre-

Corresponding author: Laiqi Zhang, E-mail: zhanglq@skl.ustb.edu.cn

coated samples with dimensions of 10 mm×60 mm×100 mm were preheated to about 200°C before laser processing.

A 5 kW continuous wave CO_2 laser was employed to produce coatings. The varied parameters were laser power, beam size and beam scanning speed. The processing parameters were established after a few trial runs. The criteria for determining the optimum quality of coatings were based on a compromise of the highest hardness, the best homogeneity and the lowest occurrence of cracks. On the basis of these criteria, the best processing conditions were determined to be as follows: traverse speed for 50 mm/min, beam diameter for 4.5 mm, and laser power for 4.0 kW. An argon atmosphere was used to protect the molten pool from air.

Phase identifications were conducted on the top surface of coatings by a Rigaku D-max X-ray diffractometer (XRD) using a Cu K_{α} radiation source. The microstructures of coatings were examined by scanning electron microscopy (SEM, Cambridge S-250 and S-360) with back scattered electron (BSE) imaging, equipped with energy dispersive spectroscopy (EDS). Microhardness measurements were performed on sample cross-sections with a Leitz Minil Oadz Vickers hardness tester using a load of 4.9 N and a dwell time of 15 s.

3 Results and discussion

3.1 Phase constitution of the laser-clad coating

The clad coating with good quality, which was free from macro-cracks and -pores, and well-bonded to a substrate can be obtained by the irradiation for the $MoSi_2$ powder pre-placed on the 45 steel with laser beam under the conditions of foregoing parameters.

Figure 1 presents the X-ray diffraction patterns of this coating. The strong diffraction peaks of both FeMoSi and Fe₂Si were present, and their standard d values from JCPDS data were in good accordance with experimental ones. Consequently, it may be concluded that the coating is mainly composed of FeMoSi and Fe₂Si. In addition, it has been found from figure 1 that the clad coating has also a small amount of Mo₅Si₃.

The existence of element Fe in the obtained coating only comes from the steel substrate because the coating material ($MoSi_2$ powder) does not contain element Fe at all, showing that the substrate has a significant dilution to the coating material. In fact, $MoSi_2$ powder is melted and also the substrate is locally melted, Fe is uniformly mixed with Mo and Si in the laser molten pool by convection movement during laser cladding, therefore the obtained coating is an Mo-Si-Fe ternary alloy composed of both $MoSi_2$ powder and Fe of the 45 steel substrate. The work by Ignat *et al.* [10] also found that a higher dilution rate considerably reduced the crack risks. Therefore, from this point of view, a higher dilution can be considered an advantage.

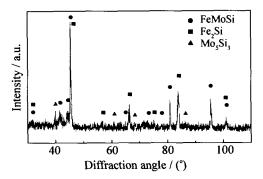


Figure 1 XRD patterns of the laser-clad coating.

3.2 Microstructure of the laser-clad coating

The SEM-BSE micrographs of the laser-clad coating in figure 2 reveal that there is no pores and cracks in the microstructure. However, the MoSi₂ coating cladded with laser beam on a steel by Hidouci et al. [9] contained a large number of cracks. Figure 2 shows that the microstructure of the laser-clad coating is characterized of typical fine dendrites, where the primary solidification phase is with the dendritic growth morphology, and a eutectic is with the interdendritic. It can be also observed from figure 2 that the dendrites in the outer coating are finer than in the inner (Figure 2(a), and a white band with a width of about 8 μ m, referred as a bonded zone (BZ) in the interface between the coating and the substrate is visible (figure 2(b)). Additionally, near the bonded zone, only eutectic microstructure can be observed, while the primary solidification phase with the dendritic growth morphology can not. This reason is possibly that the contents of Mo and Si are relatively very small in the melt pool bottom, which may lead to the compositional ratio of Mo, Si and Fe within this clad zone identical to ternary eutectic composition.

The composition line scanning analyses of the cladcoating were performed by SEM-EDS, as shown in **figure 3**. The results demonstrate that Mo distribution within the whole coating fluctuates very much, while Si and Fe distributions hardly do, but Fe content gradually increases from the outer to the inner. All composition distributions of Mo, Si and Fe in the interfaces between the coating and the substrate change gradually, illustrating that the elements of the coating and the substrate diffuse each other by pool convection and atomic diffusion and thus the coating and the

J. Univ. Sci. Technol. Beijing, Vol.12, No.5, Oct 2005

substrate are bonded metallurgically. The chemical composition results by EDS confirm that some black spheroids in micrographs in figure 3 are not pores at

all, and Mo-poor and Si-rich. As for its phase identification, it might be very difficult.

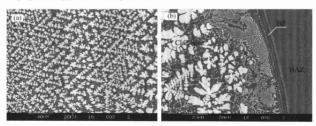


Figure 2 BSE images of the coating (a) and the coating-substrate interface (b). HAZ represents the heat affected zone, and BZ does the bonded zone.

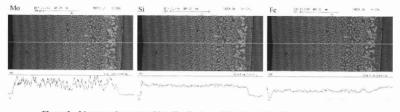


Figure 3 Line scanning composition distributions of Mo, Si and Fe of the laser-clad coating.

EDS results of dendrites and interdendritic areas (as shown in **table 1**), together with X-ray diffraction analysis results reveal that the dendrites are composed of FeMoSi primary phase, and the interdendritic areas are two eutectic phases of FeMoSi and Fe₂Si. Mo₅Si₃ phase measured by XRD hardly can be observed very distinctly in the microstructure because of its amount is very small, possibly within FeMoSi dendrites.

Area	Mo/wt%	Si/wt%	Fe/wt%	Mo/at%	Si/at%	Fe/at%
Dendrites	48.503	8.768	42.723	31.944	19.722	48.334
Interdendritic areas (black)	2.091	10.366	87.558	1.113	18.841	80.046
Interdendritic areas (white)	28.436	9.931	61.628	16.904	20.163	62.933

Table 1 EDS results of dendrites and interdendritic areas of the laser-clad coating

3.3 Microhardness of the laser-clad coating

The hardness of the laser-clad coating, the heat affected zone (HAZ) and the substrate is 845, 400-450 and 180 Hv_{0.5}, respectively. The hardness of the coating is 3.7 times larger than that of the steel substrate.

Although the hardness of the laser-clad coating obtained by this work is lower than MoSi₂ (the level of hardness reached for this compound was about 1000 Hv), the toughness of this coating is higher than MoSi₂, and thus the coating is not fragile. Moreover, it is fortunate that this coating would be a promising candidate for protective coatings of steels for elevated-temperature structural applications.

4 Conclusions

The feasibility has been shown in this study that the high-temperature resistant structural coating, with good quality, can be manufactured by laser cladding MoSi₂ powder on a steel. This coating consists of FeMoSi, Fe₂Si and a small amount of Mo_3Si_3 due to dilution of the substrate in the coating.

The microstructure of the coating is characterized of typical fine dendrites. The dendrites are composed of FeMoSi primary phase, and the interdendritic areas are two eutectic phases of FeMoSi and Fe₂Si. There are no pores and cracks in the microstructures. All composition distributions of line seanning of Mo, Si and Fe in the interfaces between the coating and the substrate change gradually, the elements of the coating and the substrate diffuse each other by pool convection and atomic diffusion, the coating and the substrate are bonded metallurgically. The hardness of the coating reaches 845 Hv_{0.5}, 3.7 times larger than that of the steel substrate (180 Hv_{0.5}).

References

- A.K. Vasudévan and J.J. Petrovic, A comparative overview of molybdenum disilicide composites, *Mater. Sci. Eng.*, A155(1992), p.1.
- [2] Y.L. Jeng and E.J. Lavernia, Processing of molybdenum disilicide, J. Mater. Sci., 29(1994), No.10, p.2557.
- [3] L.Q. Zhang, Z.Q. Sun, Y. Zhang, et al., Microstructure and mechanical properties of in situ SiC particulates reinforced MoSi₂ matrix composite, Acta Metall. Sin. (in Chinese), 37(2001), No.3, p.325.
- [4] J. Schlichting, Molybdenum disilicide as a component in modern high-temperature solid solutions, *High Temp*.

High Pressures, 10(1978), No.3, p.241.

- [5] T.A. Kircher and E.L. Courtright, Engineering limitations of MoSi₂ coatings, *Mater. Sci. Eng.*, A155(1992), p.67.
- [6] A. Mueller, G. Wang, R.A. Rapp, et al., Oxidation behavior of tungsten and germanium-alloyed molybdenum disilicide coatings, *Mater. Sci. Eng.*, A155(1992), p.199.
- [7] C.M. Packer and R.A. Perkins, Development of a fused slurry silicide coating for the protection of tantalum alloys, *J. Less-common Met.*, 37(1974), No.2, p.361.
- [8] J.M. Pelletier, M.C. Sahour, M. Pilloz, et al., Influence of processing conditions on geometrical features of laser claddings obtained by powder injection, J. Mater. Sci., 28(1993), No.19, p.5184.
- [9] A. Hidouci and J.M. Pelletier, Microstructure and mechanical properties of MoSi₂ coatings produced by laser processing, *Mater. Sci. Eng.*, A252(1998), p.17.
- [10] S. Ignat, P. Sallamand, A. Nichici, et al., MoSi₂ laser cladding—elaboration, characterization and addition of non-stabilized ZrO₂ powder particles, *Intermetallics*, 11(2003), p.931.