Rare Metal Materials and Engineering
Volume 47, Issue 3, March 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(3): 0759-0765.

ARTICLE

Surface Metallization of SiC Ceramic by Mo-Ni-Si Coatings for Improving Its Wettability by Molten Ag

Zhao Santuan[1,4], **Zhang Xiangzhao**[2], **Liu Guiwu**[2], **Valenza Fabrizio**[3],
Muolo MariaLuigia[3], **Qiao Guanjun**[1,2], **Passerone Alberto**[3]

[1] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China; [2] Jiangsu University, Zhenjiang 212013, China; [3] Institute for Energetics and Interphases, IENI-CNR, Via De Marini 6, 16149 Genoa, Italy; [4]Henan University of Science and Technology, Luoyang 471003, China

Abstract: Three kinds of Mo-Ni-Si metallized coatings with various chemical compositions were deposited on SiC ceramic substrates by vacuum fusion sintering process, and the phase compositions of the coatings and their interface microstructures were analyzed. The wetting and spreading properties of molten Ag on the coated SiC ceramic substrates were investigated by the sessile drop technique, and the interfacial behavior of the Ag/coated SiC systems was analyzed. The results show that the coatings are mainly composed of Mo_5Si_3, $MoSi_2$, Ni_2Si, $NiSi_2$ and MoNiSi. The tetragonal $MoSi_2$ grains on the coating surface disappear gradually with the concentration of Mo increasing from 20 at% to 40 at%. The final contact angles of Ag/coated SiC systems at 1000 ºC for holding 30 min are 45º, 79º and 85º for the coating compositions of Mo20-Ni32-Si48, Mo30-Ni28-Si42 and Mo40-Ni24-Si36, respectively. This result could be closely related to the interactions between the Ag drop and the microstructures of the three Mo-Ni-Si coatings. No obvious reaction layers are found at all the coating/substrate interfaces before and after the wetting tests.

Key words: surface metallization; Mo-Ni-Si coating; SiC ceramic; wetting; interface

An essential consideration in the brazing of ceramic to metal or to itself is to promote the wetting of the ceramic surfaces by the brazing filler metals[1-4]. However, the wettability of metals on ceramic surface is not always good. At present, to add active alloying elements (such as Ti, Zr, and Cr) into brazing filler and to metallize the ceramic surface with metallic coating are the two main technological methods for improving the wettability of metal/ceramic system. For the former, a case in point is to add 3%~5% Ti into Ag-Cu alloys for brazing ceramics[5]. For the latter, the metallic coatings on the ceramic substrates can be fabricated by physical vapor deposition (such as sputtering[6,7] and evaporation[8]), chemical vapor deposition[9,10], plating (electroless plating or electroplating)[11,12], molten salt reaction[13], spraying[14], shot peening[15], ion implantation[16] and metal powder sintering[17-19], etc. However, the most commonly used method is the "molybdenum-manganese" process which forms a metallic coating on the surface of ceramic (especially alumina) by sintering a mixture of Mo, Mn or its oxide (such as MnO and MnO_2) and glass powders[18,19]. Although the molybdenum-manganese metallization process is successfully adopted in oxide ceramics, it is not commonly suitable for SiC ceramics because the SiC ceramics widely used in industry are fabricated by a solid-state sintering process where no glassy phases form, resulting in a poor bonding due to no chemical reaction and glass migration between the molybdenum-manganese metallization coating and the SiC ceramic matrix.

In order to improve the wettability of metals on the SiC ceramic, there are a few investigations focused on surface modification of SiC by formation of an additional layer on

---

Received date: March 15, 2017
Foundation item: National Natural Science Foundation of China (51572112, 511172177); the Natural Science Foundation of Jiangsu Province (BK20151340); the Six Talent Peaks Project of Jiangsu Province (2014-XL-002); the Post Doctorial Science Foundation of China (2014M551512); the Innovation/Entrepreneurship Program of Jiangsu Province ([2013]477, [2015]26)
Corresponding author: Liu Guiwu, Ph. D., Professor, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, P. R. China, Tel: 0086-511-88791947, E-mail: gwliu76@ ujs.edu.cn

the SiC ceramic substrate by ion implantation[16], electroless plating[20,21] and plasma pulses[22]. For instance, C. A. Leon et al[20] investigated the wettability of molten Al on plain and Ni-coated SiC ceramics, and found that the corresponding contact angle at 800 °C decreased sharply from 87.3° to 12.2°; however, the interface bonding of Ni coating/SiC substrate by electroless plating is relatively poor. In order to improve simultaneously the wettability of metals on the SiC substrate and the interface bonding between coating and the SiC substrate, we recently fabricated the Co-Si(-Mo) coatings on the SiC ceramic by vacuum fusion sintering process and found that excellent wettability with final contact angles of 0°~27° can be obtained in the molten Cu/coated SiC system[23]. In the present study, the results of alternative Mo-Ni-Si coatings with higher Mo concentrations (20 at%~40 at%) on the SiC ceramics are reported, together with the analyses of the phase compositions of coatings and of the interface microstructures. In particular, the wetting of molten Ag on the Mo-Ni-Si coated SiC, performed by sessile drop tests, is discussed, followed by microstructural and microchemical analyses.

1 Experiment

The SiC ceramic substrate was prepared by mould pressing and solid-phase sintering at 2150 °C for 1 h. The density of sintered SiC ceramic was 3.1 g/cm^3. The SiC ceramic pieces of Φ20 mm × 6 mm were abraded and polished to the roughness of ~1 μm before applying the coating.

A certain content of Mo powder (particle size of 2~4 μm, 99% purity), Ni powder (particle size of 1~3 μm, 99% purity), and Si powder (particle size 1~3 μm, 99.9% purity) were ball-milled together in ethyl alcohol for 24 h, and then dried at 80 °C. The resulting mixture powder was mixed with an organic medium at a ratio of 1:1 of the mass ratio to form a paste. The organic medium was composed of 10 vol% ethyl cellulose and 90 vol% terpinol. The as-prepared paste was screen-printed on the polished surface of SiC ceramic substrates using an 80 mesh screen, and then dried at 80 °C. Three coatings with nominal compositions of Mo20-NiSi (Mo20-Ni32-Si48, at%, similarly hereinafter), Mo30-NiSi (Mo30-Ni28-Si42) and Mo40-NiSi (Mo40-Ni24-Si36) on the SiC ceramic samples were fabricated by vacuum sintering at 1350 °C for 10 min in a vacuum of about 4×10^{-2} Pa. Here, the relatively short sintering time is to avoid the volatilization of the melt.

The wetting and spreading kinetics were evaluated by a high temperature contact angle measuring instrument (OCA15LHT-SV, Dataphysics, Germany). The dimensions of Ag (99.9 purity) for the metallic drop were Φ2 mm × 2 mm. The wetting experiments of the Ag on the coated SiC samples were conducted at 1000 °C for 30 min in a vacuum of less than 4×10^{-4} Pa. The heating rate was 5 °C/min. The solidified sessile drop/substrate couples were cross-sectioned, polished and observed to investigate the interfacial behavior by a scanning electron microscope (SEM, Quanta600, FEI) coupled with an energy dispersive spectrometer (EDS). To identify the phase compositions of the three coatings, X-ray diffractometry (XRD-7000, Shimadzu Limited) and grazing incidence X-ray diffractometry (GIXRD) analyses were performed. The angle of X-ray incidence was fixed at 2°. The surface morphologies of the as-sintered coatings were measured by a 3D laser color microscope (KEYENCE, VK-9700).

2 Results and Discussion

2.1 Metallizing coating

Fig.1 shows the macrographs of uncoated and coated SiC ceramic pieces (Fig.1a) and the optical photographs of the three Mo-Ni-Si coated SiC samples (Fig.1b~1d). The color of original SiC substrate is black, while the coated SiC ceramic samples present a silvery metallic luster. Grains with a tetragonal aspect, with dimensions of around 20 μm × 20 μm, are observed on the surfaces of 20MoNiSi and 30MoNiSi coatings (Fig.1b and 1c): they have been identified as tetragonal $MoSi_2$ by EDS and XRD patterns. However, almost no similar tetragonal grains are found on the surface of Mo40NiSi coating (Fig.1d).

Fig.2 shows the isothermal section of the Mo-Ni-Si system at 950 °C which is close to the temperature of wetting experiments[24,25]. The three Mo-Ni-Si systems (Mo20-Ni32-Si48, Mo30-Ni28-Si42 and Mo40-Ni24-Si36) are situated on this isothermal section. According to this isothermal section, the presence of several binary phases (δ' = Ni_2Si, π= $MoSi_2$, T= Mo_5Si_3) and a ternary phases Γ is foreseen in the three Mo-Ni-Si systems. Table 1 lists the related binary and ternary phases of the Mo-Ni-Si system[24,25].

Fig.3 shows the GIXRD patterns of the three coatings on the SiC ceramic substrate. The surface layers of three coatings are mainly composed of Mo_5Si_3, $MoSi_2$, Ni_2Si, $NiSi_2$ and MoNiSi phases, which is only partially consistent with the isothermal section of the Mo-Ni-Si system at 950 °C. This could be attributed to the sintering procedure (sintering at 1350 °C for 10 min) that cannot lead to an equilibrium structure due to the too short sintering time. Actually, the coating microstructure could evolve during the wetting tests at 1000 °C, resulting in formation of unusual phases, such as the MoNiSi phase. Moreover, the contents of $MoSi_2$ and MoNiSi phases decrease and increase, respectively, with increasing the Mo content. In addition, the phase compositions of the three coatings on the SiC ceramic substrate are also detected by XRD, showing almost identical results to those obtained by GIXRD.

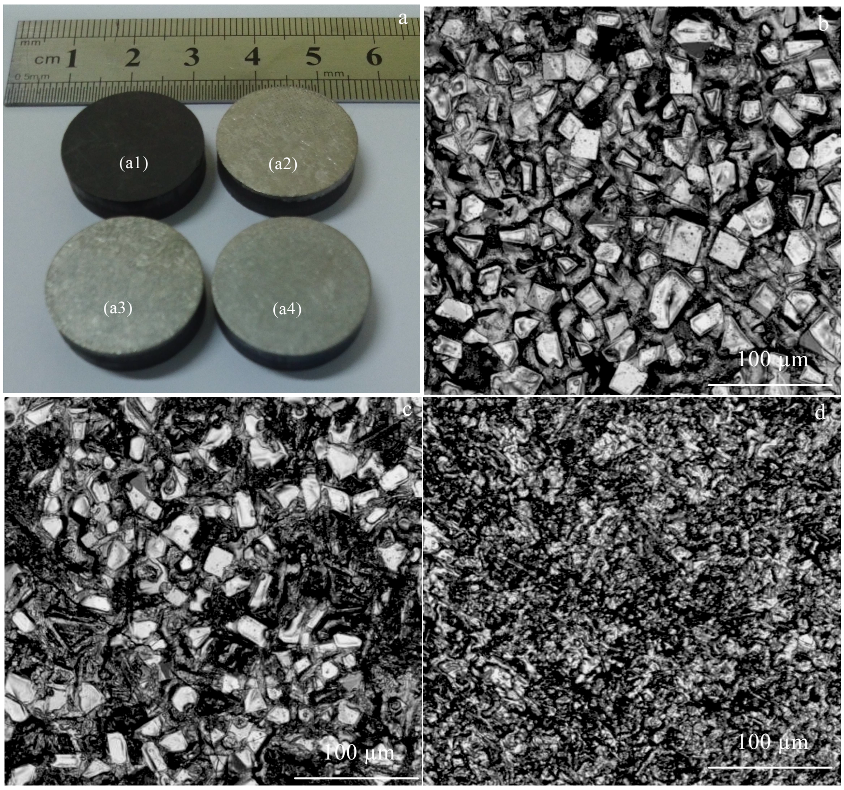

Fig.1 Macrographs and optical photographs of the uncoated and coated SiC samples: (a1~a4) the uncoated, 20MoNiSi, 30MoNiSi and 40MoNiSi coated SiC samples; (b~d) the optical photographs of 20MoNiSi, 30MoNiSi and 40MoNiSi coated SiC surfaces

Fig.4 shows the cross-sectional SEM images of the Mo-Ni-Si/SiC interfaces, indicating that the thicknesses of three coatings are 20~30 μm. According to the EDS results, the Mo20-NiSi coating is composed of $MoSi_2$, $NiSi_2$, and a mixed zone containing Mo, Ni and Si (here termed as Mo-Ni-Si zone) (Fig.4b), while the Mo30-NiSi coating consists only of $NiSi_2$ and the Mo-Ni-Si zone (Fig.4d). Surprisingly, only this Mo-Ni-Si zone could be detected in the Mo40-NiSi coating (Fig.4f). By comparison with the EDS and XRD results of Mo40-NiSi coating, the Mo-Ni-Si zone seems to be mainly composed of Mo_5Si_3, $MoSi_2$, Ni_2Si, $NiSi_2$ and MoNiSi phases. The presence of all these phases is in partial agreement with the phase diagram (Fig.2), as shown in Table 1. In the case of Mo20-NiSi coating, its phase composition of $MoSi_2$, $NiSi_2$ and Mo-Ni-Si zone is in good agreement with the phase diagram. However, the only Mo-Ni-Si zone in the Mo40-NiSi coating is not in agreement with the phase diagram.

Furthermore, all the coating/substrate interfaces are smooth and clean without visible precipitates (Fig.4), indicating that no macroscopic dissolution of the ceramic substrate occurs, although the pure Ni can strongly react with SiC[26]: Ni + SiC→Silicides + C. The addition of Si can suppress this reaction, and the Ni-Si alloys still wet the ceramic substrate well if the Si content is higher than the critical value of about 37 at% at 1350 °C[27]. Some other binary silicon alloys, such as Co-Si[28], Cu-Si[29], Fe-Si[30],

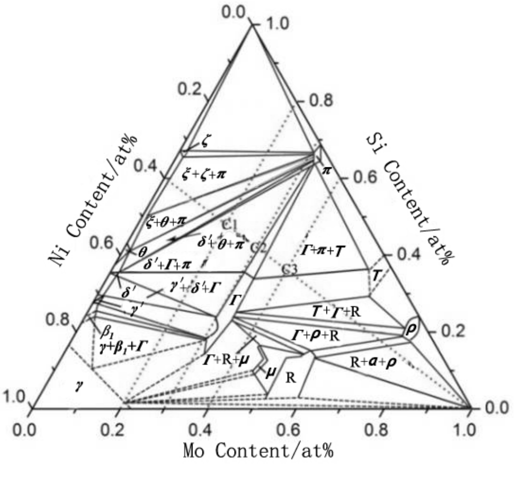

Fig.2 Isothermal section of the Mo-Ni-Si system at 950 °C[24,25] (the three intersection points of four red dotted lines correspond to the nominal compositions of Mo20-NiSi (C1), Mo30-NiSi (C2) and Mo40-NiSi (C3) coatings, respectively)

Table 1 Related binary and ternary phases of the Mo-Ni-Si system[24,25]

Phase designation	Composition
δ	MoNi
δ'	Ni_2Si
Γ	Ternary Mo-Ni-Si
π	α $MoSi_2$
π'	β $MoSi_2$
T	Mo_5Si_3
ζ	$NiSi_2$
ζ'	$NiSi_2$

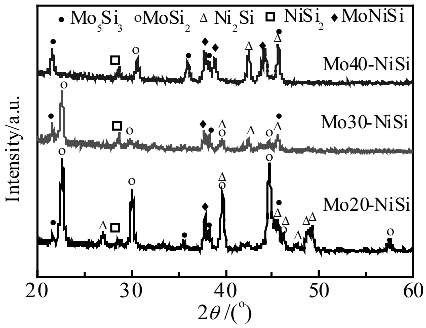

Fig.3 GIXRD patterns of the three Mo-Ni-Si coatings on the SiC ceramic

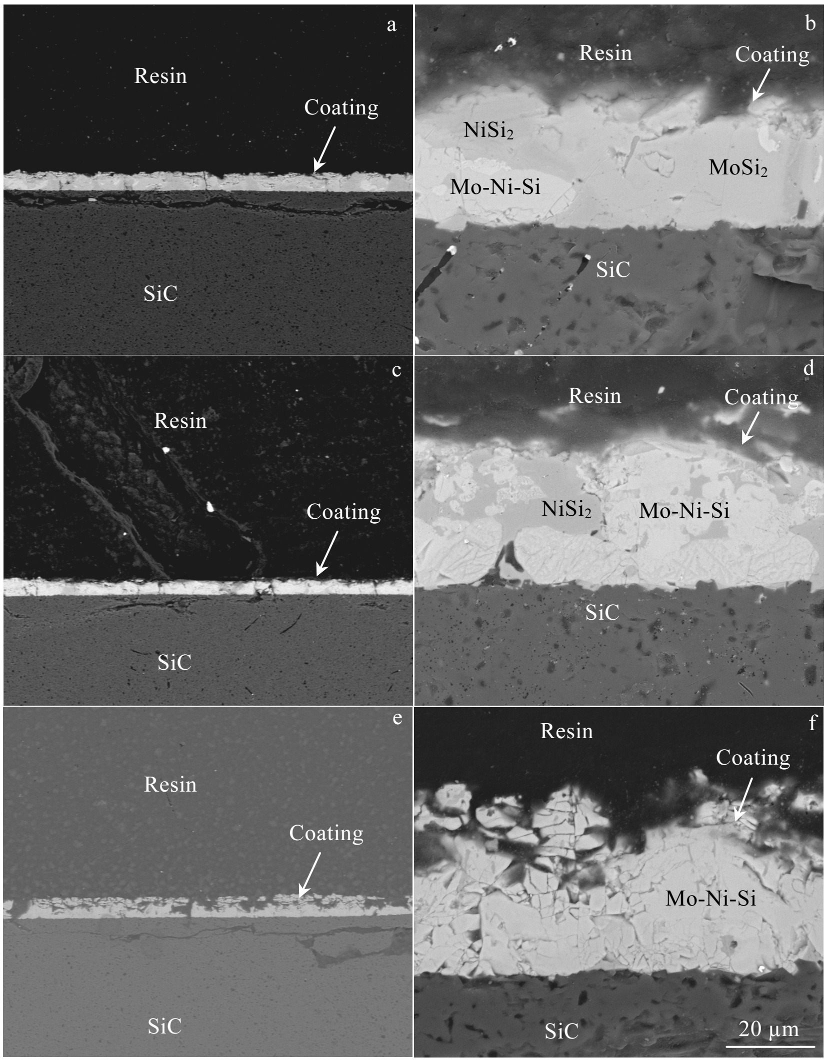

Fig.4 Cross-sectional SEM images of three Mo-Ni-Si coated SiC samples: (a, b) Mo20-NiSi coating and Mo20-NiSi/SiC interface; (c, d) Mo30-NiSi coating and Mo30-NiSi/SiC interface; (e, f) Mo40-NiSi coating and Mo40-NiSi/SiC interface

Ag-Si[31] and Au-Si[32], have not been shown to have interfacial reactions with SiC ceramic substrates. In the present study, it is found that the non-reactive wetting characteristic of the binary Ni-Si alloy/SiC system is retained at all the ternary Mo-Ni-Si alloy coating/SiC interfaces. Indeed, in order to obtain a good interfacial bonding during the surface metallization of SiC ceramic, low reactivity between the coating and the SiC ceramic matrix is required because the interface reaction products between liquid metals and SiC can give rise to brittle compounds, such as carbides, silicides and even ternary X-Si-C compounds, which have a deleterious effect on the final mechanical properties of the metal-ceramic couple[26].

2.2 Wetting and interface behavior of Ag/coated SiC

Fig.5 shows the spreading curves of molten Ag on the three Mo-Ni-Si coated SiC ceramic substrates. Previous investigations had shown that Ag cannot wet the SiC ceramic well, with the equilibrium contact angle of Ag on uncoated SiC being θ=110 ° ~140 ° at different experimental conditions[33,34]. Indeed, the final contact angles of molten Ag on the Mo20-NiSi, Mo30-NiSi and Mo40-NiSi coated SiC ceramic substrates are about 45°, 79° and 85°, respectively. This trend can be closely related with the phase compositions of three coatings, where the contents of $MoSi_2$ and MoNiSi phases vary with the increase of the concentration of Mo (Fig.3). Thus, the three coatings have a favorable effect on the improvement of the wettability of Ag/SiC system, the best results corresponding to the coating with the lowest Mo content.

Moreover, the melting temperature (T_m) of Ag on the Mo40-NiSi coating is very close to its true T_m. On the contrary, in other coatings, the presence of Ni-compounds should have favoured contact interactions with Ag, making them melt well before 960 °C (contact melting).

Fig.6 shows the cross-sectional SEM images of the Ag/Mo-Ni-Si coated SiC couples. For the Ag/Mo20-NiSi

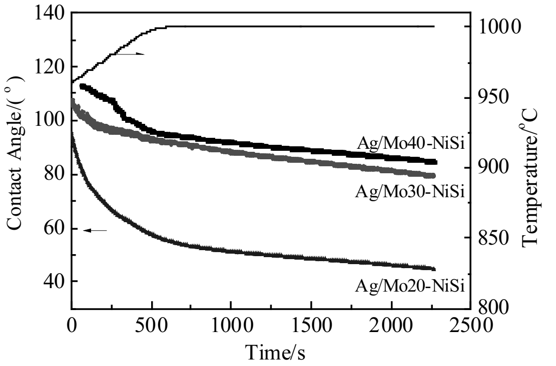

Fig.5 Contact angle as a function of time of the Ag/Mo-Ni-Si coated SiC systems

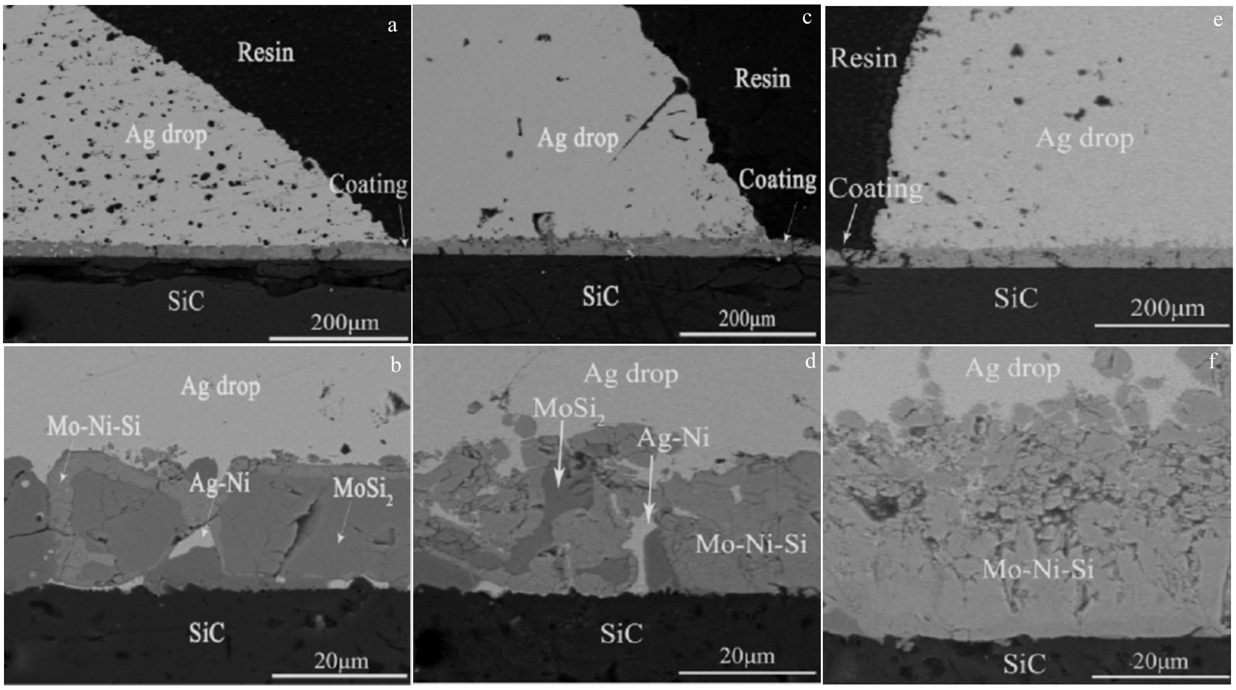

Fig.6 Cross-sectional SEM images of Ag/Mo-Ni-Si coated SiC systems: (a, b) Ag/20Mo-NiSi coated SiC system; (c, d) Ag/30Mo-NiSi coated SiC system; (e, f) Ag/40Mo-NiSi coated SiC system

and Mo30-NiSi coated SiC systems, both the Mo20-NiSi and Mo30-NiSi coatings are not dissolved in the Ag drop after wetting. However, the Ag drop penetrates into and interacts with the two coatings, resulting in the formation of an Ag alloy (Ag-2.5at%Ni), indicating that there is a small amount of elemental Ni or Ni-containing phase in the two coatings. For the Ag/Mo40-NiSi coated SiC system, the Ag drop only enters into the loose coating surface layer and could not penetrate into the Mo-Ni-Si zone to contact the ceramic substrate, due to the "dense" structure with fine grains of the Mo40-NiSi coating (Fig.1d). In short, the wettability of Ag/Mo-Ni-Si coated SiC systems can be closely related with the interactions (chemical reactions and penetration) between the Ag drop and the three Mo-Ni-Si coatings. These interactions giving rise to differences in phase composition and coating microstructure, contribute in a decisive way to promoting the wettability of the SiC-coated substrate by the molten Ag.

3 Conclusions

1) The Mo-Ni-Si coatings with nominal chemical compositions of Mo20-Ni32-Si48, Mo30-Ni28-Si42 and Mo40-Ni24-Si36 are fabricated on the SiC ceramic by vacuum fusion sintering process. The three Mo-Ni-Si coatings are mainly composed of Mo_5Si_3, Ni_2Si, $MoSi_2$ and MoNiSi. No obvious reaction layers are observed at the three Mo-Ni-Si/SiC interfaces.

2) The molten Ag can penetrate into and react with the Mo20-NiSi and Mo30-NiSi coatings, resulting in the formation of the Ag-2.5Ni alloy, while the molten Ag hardly penetrates into the Mo40-NiSi coating to contact the SiC ceramic substrate.

3) The final contact angle of molten Ag on the coated SiC ceramics at 1000 ºC for holding 10 min decreases from 85º, 79º to 45º with the concentration of Mo in the coatings decreasing from 40%, 30% to 20%. This behavior is closely related to the interactions (such as chemical reactions and penetration) of the Ag drop and the three Mo-Ni-Si coatings giving rise to differences in phase composition and coating microstructure, which in turn promotes the wettability.

References

1 Zhuravlev V S, Gab I I, Kostyuk B D *et al*. *Journal of the European Ceramic Society*[J], 2008, 28(4): 717

2 Asthana R, Singh M. Sekulic D P eds. *Advances in Brazing: Science, Technology and Applications*[M]. Cambridge, UK: Woodhead Publishing, 2013: 323

3 Fernie J A, Drew R A L, Knowles K M. *International Materials Reviews*[J], 2009, 54(5): 283

4 Kim J Y, Hardy J S, Scott Weil K. *Journal of the American Ceramic Society*[J], 2005, 88(9): 2521

5 Muolo M L, Ferrera E, Morbelli L *et al. Scripta Materialia*[J], 2004, 50(3): 325

6 Yang H, Peng T H, Wang W J *et al. Applied Surface Science*[J], 2008, 255(5): 3121

7 Jang W L, Chiu T C, Lin K L. *Thin Solid Films*[J], 2011, 519(16): 5539

8 Machac P, Barda B, Maixner J. *Applied Surface Science*[J], 2008, 254(6): 1691

9 Rong C, Zhang J Z, Liu C Z *et al*. *Applied Surface Science*[J], 2002, 200(1): 104

10 Wang Y G, Liu Q M, Zhang L T *et al. Journal of Coatings Technology and Research*[J], 2009, 6(3): 413

11 Leinenbach C, Weyrich N, Elsener H R *et al. International Journal of Applied Ceramic Technology*[J], 2012, 9(4): 751

12 Ma H F, Liu Z B, Wu L *et al. Thin Solid Films*[J], 2011, 519(22): 7860

13 Li J Q, Pan W, Yuan Z F *et al. Applied Surface Science*[J], 2008, 254(15): 4584

14 Donner K R, Gaertner F, Klassen T. *Journal of Thermal Spray Technology*[J], 2011, 20(1-2): 299

15 Komarov S V, Romankov S E. *Journal of the European Ceramic Society*[J], 2014, 34(2): 391

16 Zhao S T, Valenza F, Liu G W *et al. Ceramics International*[J], 2014, 40(5): 7227

17 Zheng Z Q, Zhang Y, Yi F C *et al. Ceramics International*[J], 2014, 40(8): 12 709

18 Ghosh S, Sengupta A, Pal K S *et al. Metallurgical and Materials Transactions A*[J], 2012, 43(3): 912

19 Liu G W, Qiao G J, Wang H J *et al. Journal of Materials Engineering and Performance*[J], 2011, 20(9): 1563

20 Leon C A, Drew R A L. *Composites Part A: Applied Science and Manufacturing*[J], 2002, 33(10): 1429

21 Tekmen C, Saday F, Cocen U *et al. Journal of Composite Materials*[J], 2008, 42(16): 1671

22 Barlak M, Piekoszewski J, Werner Z *et al. Surface and Coatings Technology*[J], 2009, 203(17): 2536

23 Zhao S T, Zhang X Z, Liu G W *et al. Ceramics International*[J], 2015, 41(10): 13 493

24 Virkar G A V, Raman A. *Zeitschrift fur Metallkunde*[J], 1969, 60: 594

25 Gupta K P. *Journal of Phase Equilibria and Diffusion*[J], 2005, 26(4): 379

26 Liu G W, Muolo M L, Valenza F *et al. Ceramics International*[J], 2010, 36(4): 1177

27 Rado C, Kalogeropoulou S, Eustathopoulos N. *Acta Materialia*[J], 1999, 47(2): 461

28 Mailliart O, Hodaj F, Chaumat V *et al. Materials Science and Engineering A*[J], 2008, 495(1): 174

29 Dezellus O, Hodaj F, Rado C *et al. Acta Materialia*[J], 2002, 50(5): 979

30 Kalogeropoulou S, Baud L, Eustathopoulos N. *Acta Metallurgica et Materialia*[J], 1995, 43(3): 907

31 Li J G. *Materials Letters*[J], 1994, 18(5): 291

32 Naidich Y V, Zhuravlev V, Krasovskaya N. *Materials Science and Engineering A*[J], 1998, 245(2): 293

33 Nogi K, Ogino K. *Transactions of the Japan Institute of Metals*[J], 1988, 29(9): 742

34 Rado C, Kalogeropoulou S, Eustathopoulos N. *Materials Science and Engineering A*[J], 2000, 276(1): 195

SiC陶瓷表面Mo-Ni-Si金属化及其与Ag的润湿性研究

赵三团 [1,4]，张相召 [2]，刘桂武 [2]，Valenza Fabrizio[3]，Muolo Maria Luigia[3]，乔冠军 [1,2], Passerone Alberto[3]

(1. 西安交通大学 金属材料强度国家重点实验室，陕西 西安 710049)

(2. 江苏大学，江苏 镇江 212013)

(3. Institute for Energetics and Interphases, IENI-CNR, Genoa 16149, Italy)

(4. 河南科技大学，河南 洛阳 471003)

摘 要：采用真空熔烧工艺在SiC陶瓷表面制备了3种化学成分的Mo-Ni-Si金属化涂层，研究了涂层的相组成和涂层/SiC陶瓷界面的微结构。通过座滴法实验考察了纯Ag在SiC陶瓷涂层上的润湿与铺展特性，分析和讨论了Ag/金属化SiC陶瓷体系的界面行为。结果表明，该金属化涂层主要由Mo_5Si_3、$MoSi_2$、Ni_2Si、$NiSi_2$和MoNiSi组成，同时随着涂层中Mo金属由20%增加至40% (摩尔分数)，位于涂层表面的具有四方结构的$MoSi_2$晶粒逐渐消失。Ag对Mo20-Ni32-Si48、Mo30-Ni28-Si42、Mo40-Ni24-Si36金属化SiC陶瓷在1000 ℃保温30 min后对应的最终接触角分别为45º, 79º 和 85º，该结果与Ag滴和3种Mo-Ni-Si涂层之间的相互作用密切相关。同时，在润湿试验前后，在Mo-Ni-Si涂层/SiC衬底界面没有发现明显的反应层。

关键词：表面金属化；Mo-Ni-Si涂层；SiC陶瓷；润湿；界面

作者简介：赵三团，男，1979 年生，博士生，西安交通大学金属材料强度国家重点实验室，陕西 西安 710049，E-mail: 709629147@qq.com