Carbide reinforced Ni–Cr–B–Si–C composite coating on 4Cr5MoSiV1 steel by comprehensive plasma melt injection method

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Abstract

The present work deals with fabricating a carbide reinforced nickel matrix composite coating on 4Cr5MoSiV1 steel. Electroless nickel coated silicon carbide particles (Ni/SiCp) were injected into plasma generated nickel alloy melt pool using plasma melt injection (PMI) method and plasma transfer arc (PTA) process simultaneously. The appropriate injection angle (θ) in this comprehensive PMI method (PTA + PMI) was calculated to satisfy the specific requirement of injection position for reducing the gasification of SiC particles (SiCp). The effects of the PTA + PMI method and electroless nickel coating (ENC) on SiCp were identified in a comprehensive manner by comparing the microstructural aspects of the coatings. The results show that the appropriate value of θ ranges from 57° to 64° in the present study. The deposition of ENC on SiCp is found to be very effective in retarding the gasification of SiCp during the PTA + PMI process. Meanwhile, the improved wettability of SiCp by the ENC decreased the necessary minimal vertical velocity of SiCp which consequently promoted the impregnation of SiCp in the PTA + PMI process. The nickel matrix composite coating reinforced by Ni/SiCp (SS) using the PTA + PMI method mainly consists of large amount of in situ chromium-rich carbides (M6C) together with nickel silicide (Ni3Si) in a nickel iron solid solution (γ-Ni(Fe)). Microhardness and tribological tests reveal considerable improvement in surface microhardness and wear resistance properties of 4Cr5MoSiV1 steel.

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1. Introduction

Silicon carbide (SiC) is commonly used as an important semiconductor material due to its superior device performance [1]. It is featured by perfect high temperature capability as a result of large bandgap, high physical and chemical stability. Therefore, it has aroused significant interest in developing the advanced material for applications in harsh environment [2,3]. In recent years, SiC has also attracted much attention as reinforcing material not only in metal matrix composites (MMCs) [4–7], but also in ceramic matrix composites [8,9]. In these composites, SiC is generally in the form of particle, whisker or fiber. Compared to continuous fiber, composites reinforced by particles or whiskers are easier to fabricate, cost-effective and capable of improving isotropic property. Up to now, there are many applications for SiC particle (SiCp) or whisker reinforced MMCs, i.e. SiCp reinforced copper matrix composites are widely used as electronic packaging [5] and heat sink materials [4], while SiCp reinforced aluminum matrix composites are applied in automotive [6] and marine industries [7].

The Ni–Cr–B–Si group is the primary composition of nickel-based alloys with good wear and corrosion resistance [10,11]. In order to meet severe environmental requirements of the engineering machinery parts, appropriate levels of SiCp can be added to nickel alloys for the fabrication of surface coatings on these parts. This can produce significant improvement on surface hardness and wear resistance [12]. However, utilization of SiCp as filler in iron, nickel and cobalt matrices is limited due to the fact that iron prefers to form stable compounds with both silicon and carbon, while nickel and cobalt prefers to form stable compounds with silicon. In other words, SiCp could readily be dissolved or dissociated in liquid iron, nickel and cobalt alloys [13–18]. Moreover, an inherent difficulty encountered for the wide applications of SiCp in MMCs is its poor wettability with metal, which deteriorates the mechanical properties of composites [19,20]. Many efforts were devoted to solve these problems. The attempts include thermal oxidation method [13,21], precoating method [4,19,20,22–25] and in situ protection method [13,26]. These methods aim at protecting the SiCp from direct contact with the metal. Among them, thermal oxidation process focuses on generating a passive silica (SiO2) layer around SiCp as a diffusion.
2. Experimental details

2.1. Sample preparation

Plain hot-work tool steel 4Cr5MoSiV1 was used as a substrate. Hot-forged bars of 4Cr5MoSiV1 die steel were cut into small blocks of nominal size 230 × 90 × 16 mm³. The edges were rounded off to remove or reduce the stress rising points, and samples were then subjected to a heat treatment cycle with a final hardness value of 45 ± 5 HRC (microhardness of 450 ± 20 HV0.5). Nickel based alloy powder (Ni60A) and SiCp (98.5 wt.%) were used as the cladding materials. The sizes of clad powders were ranging from 44 to 104 μm and from 180 to 250 μm for Ni60A and SiCp, respectively. The nominal chemical composition of type 4Cr5MoSiV1 substrate steel and Ni60A is given in Table 1. In this study, Ni/SiCp was obtained by repetitious electronless plating in order to obtain a thick coating with a thickness of about 6 μm. The experimental setup of deposition of ENC on SiCp was documented in detail in Ref. [44]. The PTA + PMI experiments were carried out with a 10 kW commercial plasma cladding machine (LU-F400-D400-CNC). The schematic illustration of this process is shown in Fig. 1. In the process, the Ni60A powder is fed to the interior of plasma arc by a coaxial powder feeding system using Ar as carrier gas. Consequently, the Ni60A powders are melted in the plasma arc and then deposited on the surface of the substrate metal (label 1 in Fig. 1). In order to produce a uniform ceramic reinforced coating over the entire plasma cladding track, a cyclone where the major gas flow escapes through an upper outlet while the powder is fed into the outer powder injection nozzle is used (label 2 in Fig. 1). The SiCp is fed to the cyclone by an SF-3 outer powder feeding machine (label 3 in Fig. 1) using Ar as carrier gas (label 4 in Fig. 1). Subsequently, the SiCp is injected into the nickel alloy melt pool by the nozzle at an injection angle of 0° with respect to the surface (label 5 in Fig. 1). In addition, Ar is also used as plasma gas and shielding gas in PTA. The deposition conditions of the PTA and PMI processes are listed in Table 2. Five coating tracks (denoted as S1–S5) with each thickness value of 3 mm were deposited onto 4Cr5MoSiV1 steel using the PTA or PTA + PMI process. Table 3 summarizes the characteristics of these samples. In Table 3, the mixed powders were mechanically blended and the weight fraction of SiCp, including nickel coated or uncoated ones in the mixed powders was 10 wt.%. 

2.2. Sample characterization

The as-deposited specimens for metallographic examination were first cut perpendicular to the coating surface with a wire cut machine. Then the top surface of the coatings was wet ground with Al₂O₃ emery paper until removal of 0.5 mm defect layers followed by polishing with diamond suspensions to a 0.5 μm roughness. Finally, the specimens were degreased with acetone in an ultrasonic bath, and were prepared by conventional metallographic procedures for metallog graphical examination. Microstructural observations were conducted with an Axio Scope A1 (Carl Zeiss Jena) optical microscope (OM). In particular, FEI Nova400Nano SEM attached with an Energy Dispersive Spectrometer (EDS) was used for the microstructural and microchemical examination of S5. An X-ray diffraction meter (XRD) (Model D/MAX-RR, Rigaku, Japan) was adopted to identify the phase composition of S5 with Cu Kα X-ray source (λ = 1.54056 Å, step of 0.02° and scanning angle 2θ = 20°–80°). The microhardness profile on the top-surface of all the samples was measured using a HV-1000 machine loaded at 0.5 kgf. Sliding wear resistance was evaluated on a ball-on-disk sliding wear machine (HT–1000, China) at room temperature. The 4Cr5MoSiV1 steel, S1 and S5 samples were in the form of disk, while the Al₂O₃ ball with a diameter of 6 mm was used as a counterbody. The S1 and S5 were also ground until the removal of 0.5 mm defect layers. Subsequently, the disks were polished to get a smooth surface (Ra ≤ 0.5 μm). The wear test conditions were given as 22 N normal load, 955 rpm rotating velocity.
of the disk, 2 mm rotating radius and total sliding time of 20 min (about 0.2 m/s relative sliding speed). The friction coefficient was continuously recorded during the test. The wear tracks were also examined using SEM and EDS. In this study, the mass wear rate (g·m⁻¹) and volume wear rate (mm³·m⁻¹) were calculated by dividing total mass wear loss or volume wear loss with the total sliding distance, respectively. Mass loss was measured by Sartorius BSA 124S to within 0.1 mg, and the average value for each specimen is calculated using three data. The specific wear volume for coatings is calculated using the following Eq. (1) [45]:

$$V_{wear} = \frac{D^2L}{8} \left[ 2 \sin^{-1} \frac{b}{D} - \sin \left( 2 \sin^{-1} \frac{b}{D} \right) \right]$$

where \(D\) is the diameter of ball (mm), \(b\) the average scar width (mm) and \(L\) the circumference of the wear track formed on the disk after wear test. The value of \(b\) was obtained by OM method.

3. Results and discussion

3.1. The injection angle (\(\theta\)) of plasma melt injection process

Kloosterman [34] found that the highest temperature of the substrate affected by laser beam was situated behind the middle of the laser beam and the melt pool was extended behind the laser beam. They proposed that the dissolution of the particles could be controlled by the positioning of the powder flow. From this viewpoint, the direction of the particle flow with respect to the normal direction of substrate surface, the injection position of the particles, and the interaction time between SiCₚ and the laser are important. In this study, the so-called “over-hill” direction named by Vreeling et al. [35] was used as shown in Fig. 1. In order to find out the appropriate injection position of the SiCₚ, the temperature distribution of the plasma arc contacting region on substrate (melt pool) was estimated by examining the morphology of substrate steel affected directly under plasma beam for one second. Fig. 2 shows that three distinct areas named heat affect zone (HAZ), transfer arc zone (TAZ) and non-transfer arc zone (NTAZ) can be identified on the surface of plasma treated substrate steel. The NTAZ exhibits a heavy melting pit as illustrated in the inset in Fig. 2, which implies a high temperature of the melt pool in this area. This phenomenon is attributed to the self-compressed behavior of the plasma arc, which leads to a current constriction. Consequently, the central zone of the plasma arc possesses the highest energy density and hence a heavy melting pit in NTAZ. The experimental result suggests that the powder flow of SiCₚ should not cross the central zone of the plasma arc, which might result in an undesirable overheating. Thus, the injection position is controlled within the region of TAZ subtracted by NTAZ. It should be noted that this injection position is slightly different from that proposed by Kloosterman [34]. Since their analytical mode used for estimating the shape of melt pool in the direction of the laser did not incorporate either melting or convection, it may be not suitable for PMI due to the intense agitation occurring in the PTA generated melt pool. Therefore, in this study, there is no attempt to extend the plasma melt pool backwards behind the plasma beam as far as possible, which will provide the necessary space for particles to inject without touching the plasma beam. Notably the geometric positional relationship among the plasma gun, outer powder injection nozzle and substrate in the PMI process is illustrated in Fig. 3. The distance between the outer powder injection nozzle and the substrate is defined as \(h_1\), while the distance between the plasma gun and the substrate is defined as \(h_2\). The distance between the outer powder injection nozzle and the plasma gun is \(b_1\), while the distance between the injection location of particles and the plasma

Table 1

<table>
<thead>
<tr>
<th>Element (wt.%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>V</th>
<th>Mo</th>
<th>B</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Cr5MoSiV1</td>
<td>0.32</td>
<td>0.93</td>
<td>0.32</td>
<td>0.03</td>
<td>0.006</td>
<td>4.70</td>
<td>0.12</td>
<td>0.09</td>
<td>0.35</td>
<td>1.21</td>
<td>18</td>
<td>.bal</td>
</tr>
<tr>
<td>Ni60A</td>
<td>0.6</td>
<td>4.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>18</td>
<td>.bal</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.0</td>
<td>4</td>
</tr>
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</table>

Fig. 1. Schematic picture of the plasma melt injection process. The particles are injected in the so-called “over-hill” direction.
3.2. Microstructure of the coatings

Fig. 4 shows the optical micrographs of the surface sections of the obtained coatings including S1, S2 and S3. Fig. 4(a) and (d) show that the structure of the Ni60A coating (S1) mainly consists of γ-Ni matrix, irregular eutectics and precipitates which were mainly identified as chromium carbides or chromium borides [46,47]. In comparison with the S1, no distinct discrepancies are found in the micromorphologies of SiCp or Ni/SiCp by coaxial feeding method in the PTA process. Furthermore, it is observed that a large amount of visible flue gas generated during the preparations of S2 and S3.

In order to better understand the experimental results, it is essential to consider the experiences of the feeding powders during the PTA process using the coaxial powder feeding method. The PTA processes can be divided into two parts: the powders are melted in the interior of plasma arc in coaxial feeding mode all together accelerated the gasification reactions of SiCp in the part P1. Consequently, this inhomogeneity led to the fact that the individual SiCp was surrounded with insufficient Ni60A alloy powders in P1 part. Therefore, the solid–gas reactions (gasification reactions) of SiCp in the interior area of plasma arc were exacerbated. The presence of special physical and chemical properties of SiC, inhomogeneity of the mixed powders, and the directly heat exchange between SiCp and plasma arc in coaxial feeding mode all together accelerated the gasification of SiCp, in the part P1. Consequently, only a small amount of residual SiCp resulting from incomplete gasification in part P1 were deposited on the surface of the substrate metal. Subsequently, these residual particles were partially dissolved or dissociated by Ni60A matrix in part P2, which will be proven by the latter microhardness result of the coatings. Nevertheless, the burning loss of most SiCp in part P1 is responsible for the similarity in the microstructure of the S1, S2 and S3 coatings. In addition, it is predictable that the residual SiCp would accompany with the light phases tend to float on the top surface of melt pool in part P2 due to their low densities. Xuan [51] mentioned that the ceramic particles tended to accumulate more density near the top surface of the laser nickel matrix coating due to the much smaller density and higher melting point. Actually, in the welding process, the light phases floating upon the surface of melt pool are regarded as the slag which takes advantage of deoxidizing and protecting the welding layer. However, this slag layer is also regarded as the defect layer and should be removed prior to engineering applications. In this case, about 0.5 mm thickness of the top section was removed in each coating. Therefore, the absence of SiC particles in S2 and S3 coatings can be attributed to the main burning loss of SiC particles in part P1, partial dissolution or dissociation of SiC particles in part P2 and probably the removal of the slag layer during sample preparation.

Fig. 5 shows the OM micrographs of the S4 and S5. In general, the morphologies of these coatings (Fig. 5(a) and (b)) are distinctly different from the PTA coatings including S2 and S3. In the higher magnification micrograph of S4 (Fig. 5(c)), a typical structure with primary nickel matrix dendrites surrounded by a network of interdendritic eutectics and precipitates is observed. In addition, the volume fraction of eutectics and precipitates decreases in S4 compared to that of S2 and S3. On the other hand, it is clearly visible that a large amount of new precipitates can be found in S5 as shown in the areas circled by the red dashed line in higher magnification OM image (Fig. 5(d)).

Fig. 6 presents the SEM micrographs of the intermediate layer in the cross section of S5. From Fig. 6(a) it may be noted that a large amount of new phases with granular morphology are uniformly distributed in S5. These new phases with size of about 10 μm are clearly seen in Fig. 6(b). And the new phase (label 1 in Fig. 6b) is well bonded by the nickel matrix and locates directly in the matrix rather than in the grain boundary of the matrix. The SEM-EDS spectra of the corresponding areas circled in Fig. 6(b) indicate that the new phase in area 1 is rich in chromium (Fig. 6(c)), while the phase in area 2 is rich in nickel

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Experimental conditions for PTA and PMI process.</th>
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<tr>
<td>M1/g·min</td>
<td>M2/g·min</td>
</tr>
<tr>
<td>PTA</td>
<td>7</td>
</tr>
<tr>
<td>PMI</td>
<td>7</td>
</tr>
</tbody>
</table>

M1 — nickel alloy powder feed rate (coaxial feed method), M2 — SiCp feed rate (PMI method), Q1 — carrier gas flow rate, Q2 — plasma gas flow rate, Q3 — shielding gas flow rate. H — Torch gap, λ — oscillation width, γ — oscillation rate. V — travel speed of the plasma gun, U — transferred arc voltage. I — transferred arc current.
and silicon (Fig. 6(d)). It is also noted that the nickel matrix as circled in area 3 is rich in silicon (see Fig. 6(e)). In the EDS measurements, the appearance of a moderate Fe signal in all samples indicates that there could be an acceptable dilution of coatings resulting from the element diffusion of the substrate.

XRD analysis reveals a possible phase of S5 due to the complexity of the coating (Fig. 7). In fact, the proximity between the Ni, Cr, and Fe in the periodic table of chemical elements makes it difficult to find the real structure of this coating. Finally, some compositions consistent with the EDS data are suggested. Indeed, the XRD patterns of the S5 reveal that the microstructure of the coating consists mainly of nickel iron solid solution (γ-Ni(Fe)) consistent with Refs. [52–54], M7C3 carbides (M represents Cr and Fe), silicides (Ni3Si) and borides (Fe2B, Ni2B). Based on the XRD and EDS analyses, the phases highlighted in Fig. 6(b) can be recognized as: Cr-rich M7C3 (label 1), the main phase of Ni3Si (label 2) and possibly the mixture phase of γ-Ni(Fe) and Ni3Si (label 3).

The differences in the microstructural aspects between the PTA and the PTA + PMI coatings can be attributed to their different powder feeding modes. In PTA + PMI, SiCp travels over the Ni60A coating towards the center of the melt pool without directly contacting the high temperature region (interior) of plasma arc. This is beneficial to reduce the interaction time and the amount of heat exchange between the plasma arc and SiCp, which are important for reducing the burning loss of SiCp. In addition, the heat absorption and the following deviation of partial SiCp from the injection position as a result of the inevitable collision between SiCp and Ni60A powders in the complex gas flow were the facts which resulted in heat loss and material loss of the melt pool in the PTA + PMI process. In order to minimize the influence of the mass loss of SiCp, the weight percent of SiCp used in PTA + PMI (30 wt.%) was higher than that in the PTA process (10 wt.%). However, the additional PMI process could inevitably affect the actual situation of the PTA + PMI process. Therefore, the energy, momentum, and mass transport in the melt pool of the PTA + PMI process in the PTA + PMI process were changed by the powder flow of SiCp, leading to a distinct difference in solidified microstructure between the PTA + PMI coatings (S4, S5) and the PTA coatings (S2, S3).

It is surprising that the microstructure of S5 is remarkably different from the S4. The fabricating process parameters of PTA + PMI in each case are the same and therefore the differences are mainly dependent on Ni/SiCp. In the PTA + PMI process, there was also a very obvious tell-tale sign of gasification of SiCp during S4 preparation, i.e. plenty of visible flue gases were generated. However, the generation of flue gases was not obvious during S5 preparation. These experimental results indicate that the gasification reaction of SiCp in the PMI process is obstructed by applying ENC on SiCp. Obviously, the ENC surrounded on SiCp could melt quickly during the PTA + PMI process due to the high temperature of plasma arc. Consequently, the strong heat exchange between plasma arc and SiCp is prevented and the direct contact between oxygen and SiCp is avoided by the surrounded liquid nickel, and hence the gasification is minimized. The similar protective efficacy of the ENC was reported by Li and Ding [55]. They claimed that the molten liquid nickel covering the would-be solidifying chromium carbides resulted in a decrease in the decarbonization of the carbides in plasma spray process.

Furthermore, Vreeling et al. [35] proposed that the energy of the powder used to overcome the molten surface barrier and to propagate further into the melt pool is its kinetic energy. They assumed that the powder is in a spherical shape with a radius R and a vertical component of velocity Vo. Thus, the kinetic energy of the powder is:

$$ E_{kin} = \frac{2}{3} \pi R^3 \rho_{\text{bac}} V_0^2 $$

where $\rho_{\text{bac}}$ is the density of SiC.
The energy of the surface barrier \( \Delta G_{\text{barrier}} \) can be estimated by the equation:

\[
\Delta G_{\text{barrier}} = \left( \frac{\sigma_l + \sigma_{lp} - \sigma_{pv}}{\sigma_l} \right)^2 \pi R^2
\]

(5)

where \( \sigma \) is the interface energy (tension) between the phases indicated by the indices \( l \) (liquid metal), \( p \) (solid SiC particle) and \( v \) (vapor). Combining Eqs. (4) and (5), the minimal vertical velocity of the particle \( V_{\text{min}} \) needed to overcome the melt surface barrier can be obtained:

\[
V_{\text{min}} = \sqrt{\frac{3}{2 \sigma_l R_p \rho_{\text{liq}}}} \left( \sigma_{lp} + \sigma_{pl} - \sigma_{pv} \right).
\]

(6)

Eq. (6) indicates that if the initial particle velocity is higher than \( V_{\text{min}} \), the powder overcomes the surface barrier and may propagate further into the melt. Considering the Young equation for the case, when a liquid droplet is situated on the planar solid interface, the equilibrium contact angle \( \Theta \) between the phases can be written as:

\[
\sigma_{pv} - \sigma_{pl} = \sigma_{lv} \cos \Theta.
\]

(7)

Hence the liquid–particle interfacial energy \( \sigma_{pv} \) in Eq. (6) can be replaced by the contact angle \( \Theta \) using in Eq. (7), after rearrangements we have:

\[
V_{\text{min}} = \sqrt{\frac{3}{2 \sigma_{lv} R_p \rho_{\text{liq}}}} \left( 1 - \cos \Theta \right) \sigma_{lv}.
\]

(8)

From Eq. (8), it can be seen that the \( V_{\text{min}} \) decreases with a decreasing \( \Theta \). In other words, perfect wetting is required in order to easily inject a particle into the melt pool. However, the rejection of the ceramic phase such as SiCp by the liquid metal due to the poor wettability is a well-known truth [56]. Unfortunately, it has not been reported yet whether the contact angle between SiCp and Ni60A alloy would decrease after the pretreatment of SiCp with ENC. However, it can be expected from the experimental results by many researchers. For example, Ip [57] reported that the contact angle between the aluminum and CVD nickel-coated graphite was only 4° while the contact angle between the aluminum and graphite was 140°. Leon [19] reported that the reached contact angles with aluminum were 12° for Ni-coated SiC and 11.6° for Ni-coated Al2O3. Both of these studies indicated that the wettability between ceramic and metal was improved by applying ENC on the surfaces of non-metallic materials. In addition, the wettability between Ni/SiCp and Ni60A alloy metal could be promoted by the high mutual affinity of the same major constituent (nickel element). Therefore, it is concluded that the wettability of SiCp by Ni60A metal pool was improved by ENC, leading to a decreased \( V_{\text{min}} \) of SiCp. Consequently, the Ni/SiCp was easily injected into the Ni60A alloy melt pool in PTA + PMI.

It is well known that strong solid state interfacial reactions could occur between SiC and Ni at elevated temperature [15]. Nickel could enter into the SiC by decomposing it into a thermodynamically more favorable silicide phase, leaving carbon black behind. It is pertinent to mention that Y. T. Pei [12] fabricated a composite coating using the mixture of Ni alloy and SiCp by pre-placed method in LSE. They found that the complete dissolution of SiCp took place during laser melting, leading to a microstructural evolution of the coatings associated with the SiCp content. M2X3 or M23X6-type carboborides, silicide (Ni3Si2) and Ni-based solid solution were found as the main microstructural constituents of the clad layer. The ablation and decomposition of SiCp were also reported by B.Y. Lou [58] who used the pre-placed mixture of Ni60A alloy powders with SiCp in LSE. The dissolution and dissociation of SiCp during laser alloying could also been found in Refs. [59–61]. The results in these literatures clearly support the view point that SiCp reacts with nickel alloy in metal pool resulting in dissolution or dissociation, and consequently lose its original characteristics in SS. Obviously, this is mainly responsible for the absence of SiCp in SS, with the substituting Cr-rich M7C3 phases with granular morphology in the coating. It may be pointed out that this situation is distinct from, for example, the use of laser processing for the formation of a metal matrix composite coating (MMCC) on the substrate by incorporating ceramic powders. In the latter case, the injected particles do not dissolve in the molten substrate, but remain embedded in the matrix of the substrate to yield MMCCs, which are also extremely promising [30–33]. However, the dissociation of SiCp in present study results in another type of enhanced coating by promoting the formation of carbides, silicides and nickel solid solution in NMCCs. A similar enhanced mechanism was...
reported in a variety of literatures involving addition of SiC by pre-placed method [59–61]. It is pertinent to emphasize that the interfacial reactions (in situ reactions) dominate the dissociation of Ni/SiC in PTA + PMI because of the dynamic character of injected SiC in melt pool. This could provide the system with many homogeneous Cr-rich M7C3 phases still acted as nucleation sites, their size was increased.

Fig. 5. Optical micrographs of the surface sections of the PTA + PMI coatings: (a) S4 and (b) (S5) while (c) and (d) are the higher magnification micrographs of S4 and S5, respectively.

Fig. 6. The SEM and EDS cross-sectional analysis of S5, (a) and (b) are the intermediate layer of S5 at different magnifications. (c), (d) and (e) are EDS results of the corresponding dotted line circled areas including 1, 2 and 3 in (b), respectively.
substantially. Consequently, large quantities of granular M₇C₃ phases were distributed uniformly in S5 (Fig. 6(a)). The absence of the granular Cr-rich M₇C₃ carbides in S4 indicates that SiCₚ could be hardly injected into the nickel alloy melt pool without precoating with ENC. This phenomenon could be attributed to the following three reasons: (1) low density of SiCₚ, (2) poor wettability between SiCₚ and metal melt pool, and (3) lack of protective ENC. The first one makes the SiCₚ float upon the top surface of melt pool, the second increases the difficulty of impregnation of SiCₚ, and the last favors the gasification of SiCₚ.

3.3. Microhardness of the as-received coatings

The microhardness of the surface section of as-received coatings is given in Fig. 8. The microhardnesses of S1, S2, S3, S4 and S5 are about 507±14 Hv₀.₅, 546±20 Hv₀.₅, 546±25 Hv₀.₅, 505±12 Hv₀.₅ and 787±44 Hv₀.₅, respectively. It is obvious that the surface hardness of Ni₆₀A is increased considerably by injecting Ni/SiCₚ into Ni₆₀A melt pool using PTA + PMI.

The hardness of S2 is very close to that of S3, and a little higher than that of S1. This result confirms the dissolution or dissociation of small amounts of SiCₚ in S2 and S3, and hence slight improvement on microhardness. The relative lower microhardness of S4 is attributed to its solidified microstructure which has primary nickel matrix dendrites accompanied with lower volume fraction of eutectics and precipitates (Fig. 5(b)). The above experimental results indicate that using the mixture of SiCₚ and Ni₆₀A alloy by coaxial powder feeding mode in PTA process or using uncoated SiCₚ using PTA + PMI process makes little positive contribution on microhardness of Ni₆₀A. However, an increase of 380 Hv₀.₅ in hardness is obtained in S5 than in S1 (Fig. 8). The significant increase in surface microhardness is largely attributed to the formation of a large amount of in situ Cr-rich M₇C₃ carbides, nickel silicide (Ni₃Si) and the nickel solid solution (γ-Ni(Fe)) in S5. For example, the hardness of Cr-rich M₇C₃ carbides and Ni₃Si has hardness values of approximately 1200 and 644 Hv, respectively [62,63]. Nevertheless, the contribution of the nickel solid solution to the overall hardness of S5 coating should not be ignored [64]. In addition, the large fluctuation in microhardness of S5 normally happens in ceramic reinforced composite coatings because of different hardness values of matrix and reinforcement phases.

3.4. Wear performance

Fig. 9 shows the wear rate of the 4Cr₅MoSiV₁ substrate steel, S1 and S5 based on mass wear rate and volume wear rate. The mass wear rate of the 4Cr₅MoSiV₁ substrate steel, S1 and S5 decreases in turn. The same trend is evident in the volume wear rate of these coatings. The results in Fig. 9 indicate that the wear resistance of the 4Cr₅MoSiV₁ substrate steel is enhanced considerably by S5.

Fig. 10 shows the friction coefficient (COF) of the 4Cr₅MoSiV₁ substrate steel, S1 and S5. We can find that the 4Cr₅MoSiV₁ steel exhibits the highest average friction coefficient of about 0.85. For the Ni₆₀A coating, the COF is about 0.45. However, for S5, the COF exhibits the lowest value of about 0.35 and is much more stable than the 4Cr₅MoSiV₁ substrate steel and S1 despite the gradual increase of the instantaneous friction coefficient with the increase of sliding time.

The difference in the wear behavior of the 4Cr₅MoSiV₁ substrate steel, S1 and S5 can be further verified by the worn surface morphologies as shown in Figs. 11–13. The worn surface of the 4Cr₅MoSiV₁ substrate steel in Fig. 11(a) is characterized as the grooves and adhesive layers, an indication of abrasive and adhesion wear. At the higher magnified image, as shown in Fig. 11(c), the substrate steel clearly behaves in a more ductile manner so that many adhesive layers with severe plastic deformation are seen. In addition, large amounts of white debris are found on the worn surface. EDS analysis indicates that the white debris (area 2 in Fig. 11(b)) is mainly composed of iron and oxygen (Fig. 11(e)), while the adhesive layer (area 1 in Fig. 11(b)) is mainly composed of iron (Fig. 11(d)). These results reflect that the 4Cr₅MoSiV₁ steel shows much more intricate wear patterns, including abrasion, oxidation and plastic deformation. And it is considered to be responsible for its highest coefficient of friction and the highest disk wear loss. Khan [65] also reported that the plastically dominated wear mechanism existed in AISI H13 (equivalent to 4Cr₅MoSiV₁) using diamond pin-on-plate wear sliding test. In our study a higher wear sliding speed of about 0.2 m·s⁻¹ was adopted compared to the sliding speed of about 0.012 m·s⁻¹ in the report of Khan. Hence, the high frictional heat resulting from high speed sliding was adequate for oxidation of the disk. On the other hand, since the adhesion existed between the 4Cr₅MoSiV₁ disk and Al₂O₃ ball, it is not surprising that the fluctuation of the COF would happen during sliding wear test [Fig. 10]. Liu et al. [42] also observed the similar fluctuation of the COF accompanied with the severe adhesion between the ceramic ball and steel disk. It is worthy to note that no Ni element was detected in the debris, which means that most debris generated from the disk (4Cr₅MoSiV₁ steel). This is because the hardness of the Al₂O₃ ball was about 1670 Hv, which makes abrasive wear of the ceramic ball not likely to happen.

The worn surface of the Ni₆₀A coating shows both grooves and a severely adhesive layer (Fig. 12(a)). Moreover, there are deep grooves with evidence of parallel scratches and brittle detachments of the
wear fragment on the Ni60A coating (Fig. 12(c)). These results allow us to state that the abrasive wear and adhesive wear could be the most important wear mechanisms in the Ni60A coating pairing with Al2O3 ball. The EDS analysis reveals the existence of nickel, chromium and silicon (Fig. 12(d)) in grooves (area 1 in Fig. 12(b)). Aluminum and oxygen are detected (Fig. 12(e)) in the adhesive layer (area 2 in Fig. 12(b)). These results indicate that adhesive layers result from physical interactions or tribochemical reactions involving material transferred from the ball due to the abrasion of the ball. In fact, strong adhesion between steel and alumina is well-known and sliding contact leads to extensive transfer and back transfer of material between the two surfaces [66, 67]. The enhanced wear resistance of 4Cr5MoSiV1 steel by S1 satisfies the Archard’s relationship which inversely relates the wear loss with the hardness [68]. Furthermore, one plausible factor for the comparable wear resistance of the 4Cr5MoSiV1 substrate steel and S1 is their comparable chromium contents. The higher chromium content of the Ni60A coating (18 wt.%) in comparison with 4Cr5MoSiV1 steel (4.7 wt.%) results in different microstructures between the Ni60A coating and the 4Cr5MoSiV1 substrate steel, especially in the types and volume fraction of chromium-rich carbides. The chromium-rich carbides in the Ni60A coating are mainly Cr23C6 with a hardness of 1650 HV or Cr7C3 with a hardness of 2200 HV, respectively [69]. Since the hardness of the Cr7C3 is higher than the Al2O3 ball (1670 HV), it possibly led to some abrasive wear of the Al2O3 ball during the sliding wear test. Ming [70] also reported that the wear resistance of nickel clad metal depended more on the type and amount of the main hard phase present rather than the average microhardness of the clad layer. And the fact is also reported by Wallstable [69] who found that in case of abrasion as main wear mechanism, not only hardness but also the microstructure has a major influence on abrasive wear. Another possible reason responsible for the improved wear resistance of the Ni60A coating compared to the 4Cr5MoSiV1 steel is the generation of the severely adhesive layers on the coating surface. Scratch marks observed on the adherent layers as shown in the inset of Fig. 12(b) indicates that these layers prevent wear surfaces from direct contact with the ball or the abrasive particles and consequently reduce the wear loss. Stott et al. [71] and Kesavan et al. [46] described the role of tribo-layers on sliding surfaces which can temporarily protect the surfaces from further contact damage. These protective glaze layers are continually replenished during sliding and wear of previous layer. The progression of formation, wear off, and reformattting result in a variation in friction coefficient of the Ni60A coating as can be seen from Fig. 10.

By comparing the low magnified images in Figs. 11–13(a), it can be found that the S5 exhibits less abrasive width and depth as well as less deformation. The micro-abrasion as the dominant wear mechanism with evidence of relatively smooth scar, and the slight plastic deformation with the evidence of micro-ploughing action, were also observed at higher magnified image (Fig. 13(c)). EDS analysis of the random regions circled as areas 1 and 2 in Fig. 13(b) indicates that the elements in the center and the edge of the scar are mainly composed by Ni, Cr, Si, Cr, and Fe, which come from the coating itself. The appearance of moderate oxygen signal in all regions indicates that a slight oxidation of the worn surface results from the frictional heat. The larger amounts of Cr-rich M7C3 carbides generated are mainly responsible for the much superior wear resistance of the S5. In a microstructure consisting of a mixture of Cr-rich M7C3 carbides in a soft nickel matrix, the hard carbide particles provide the resistance to abrasion, whereas the tough matrix plays the role of binding the relatively brittle carbides. It is known that the wear resistance and other mechanical properties of MMCs depend on the amount and size of the dispersed phase, apart from the mechanical characteristics of the matrix, particles and interfaces. Since the size of Cr-rich M7C3 carbides in S5 is about 10 μm, the particle-strengthening reinforcing mechanism occurs, which can significantly improve the wear resistance [43,72,73]. It should be also noted that strengthening of S5 is achieved by the particles of Cr-rich M7C3 itself, solid solution.

Fig. 9. Wear loss of the specimens of 4Cr5MoSiV1 substrate, S1 and S5.

Fig. 10. Typical friction coefficient curves of the specimens of 4Cr5MoSiV1 substrate steel, S1 and S5.
strengthening of the $\gamma$-Ni(Fe) matrix phase and matrix deformation restrained by the mechanical constraint of Cr-rich M7C3 particles. Meanwhile, the smooth wear surface of S5 is formed by the dominating contact micro-abrasion mechanism, which has a polishing effect resulting from the activity of the small debris rolling in the contact region between the ball and the sample [67, 74]. In addition, the polishing effect is responsible for the gradual increase in friction coefficient of S5, because the ball and the disk would progress into self-mating stage, causing more intimate contact of clean interfacial area between the ball and the disk even though the contact surface roughness would decrease. Thus, the frictional force as well as the friction coefficient increased.

4. Conclusions

On the basis of the above experimental results of the study concerning the investigation of the carbide reinforced NMCCs using Ni/SiC$_p$ by the comprehensive PMI method, the following conclusions can be summarized:

1. The in situ M$_7$C$_3$ carbide particulate reinforced NMCC is produced by the proposed PTA + PMI process. The injection position of the SiC$_p$ is controlled within the region of TAZ subtracted by NTAZ through a special angular range of injection angle, i.e. the value of $\theta$ is in the range of 57°–64° according to the special geometric positional
relationship among the plasma gun, outer powder injection nozzle and substrate in this study.

2. Application of Ni/SiCp instead of SiCp yields substantial enhancement in mechanical properties of NMCC by the comprehensive PMI method. The gasification of SiCp is retarded by the ENC. Meanwhile, the necessary minimal vertical velocity of SiCp in the PTA + PMI process is decreased, which results from the improved wettability of SiCp by ENC. Consequently, the impregnation of SiCp into NMCC is promoted.

3. It is interesting to note that the dissolution or dissociation of the injected Ni/SiCp in nickel alloy melt pool results in a remarkable change in microstructure of the coating, leading to the formation of homogeneously distributed in situ chromium-rich carbides (M7C3), nickel silicides (Ni3Si) as well as the solid solution of nickel matrix (γ-Ni(Fe)) in the coating.

4. The micro-hardness and wear resistance of the 4Cr5MoSiV1 can be significantly increased due to the carbide reinforced Ni/SiCp in PTA + PMI. The presence of in situ Cr-rich M7C3 carbides and the nickel solid solution in the as-received surface layer is mainly responsible for the increased wear resistance as well as the micro-hardness.

This work shows the potential of the comprehensive PMI method in fabricating the carbide reinforced MMCCs for surface layer hardening of steels. Moreover, the application of ENC on the surface of ceramic in the comprehensive PMI method can guarantee efficient use of SiCp in PTASE, thus substantially enhanced MMCCs.

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