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Published in:
Journal of Alloys and Compounds

DOI:
[10.1016/j.jallcom.2017.05.226](https://doi.org/10.1016/j.jallcom.2017.05.226)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Cao, H., Dong, X., Chen, S., Dutka, M., & Pei, Y. (2017). Microstructure evolutions of graded high-vanadium tool steel composite coating in-situ fabricated via atmospheric plasma beam alloying. *Journal of Alloys and Compounds*, 720(2017), 169-181. <https://doi.org/10.1016/j.jallcom.2017.05.226>

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Microstructure evolutions of graded high-vanadium tool steel composite coating in-situ fabricated via atmospheric plasma beam alloying

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ARTICLE INFO

Article history:

Received 10 October 2016

Received in revised form

8 May 2017

Accepted 20 May 2017

Available online 22 May 2017

Keywords:

Metallic composites

Plasma surface alloying

In-situ

Vanadium

Tool steel

Microhardness

ABSTRACT

A novel high-vanadium based hard composite coating was synthesized from premixed powders (V, Cr, Mo, Ti, Nb) on ductile iron (DI) substrate via atmospheric plasma beam surface alloying process. The graded coating can be divided into three distinct zones: upper alloyed zone (AZ) rich with spherical primary and eutectic submicron carbides, middle melted zone (MZ) with fine white iron structure embedded with high-carbon martensite and lower heat affected zone (HAZ) where martensite/ledenite double shells were substantially formed. Spherical or bulk-like primary carbides with diameter <1 μm in the middle AZ were formed via in-situ reactions between alloy powders and graphites in DI, presenting a refined microstructure similar to high vanadium-containing tool steel. Microstructural characterizations indicate the carbides are chiefly globular MC-type particles mixed with hard-phases such as M₂C, M₇C₃, M₂₃C₆, and martensite. EDS mappings show that MCs (M = V, Ti, Nb) form together while M₂C-type carbides tend to locate at the grain boundary or around the MC particles. Ti and Nb occur in the MC-type primary carbides besides V and TiC even features as nuclei. Though dependent upon the size, shape, type and distribution of carbides, the microhardness was obviously enhanced in both AZ and MZ.

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1. Introduction

Carbide-reinforced metal matrix composite (MMC) coatings have been widely studied for enhancing the surfaces properties of steel and iron based materials. One of the common surface treatment approaches to produce MMC coatings is hardfacing by weld overlay techniques such as laser cladding [1], plasma surface alloying (PSA) [2], gas-tungsten arc welding (GTAW) [3]. These methods can produce hard protective coatings metallurgically bonded to the substrate. This is attributed to the rapid cooling and fast non-equilibrium solidification conditions in hardfacing which help form hard alloy carbides and increase the solubility of strong carbide-forming elements in the matrix that induces solution strengthening [4]. As a result, the tribological and anti-corrosion

performances of metallic workpieces can be tremendously improved without jeopardizing the bulk properties, making the hardfacing techniques popular in surface engineering industry.

During weld hardfacing process, carbides are generally incorporated into the coating by ex-situ or in-situ synthesis [5,6]. According to earlier work [6–8], the in-situ synthesis via the reactions of extrinsic strong carbide-forming elements with carbon from the matrix is desirable to produce clean reinforcement with strong interface bond. It is also desirable to fabricate thermodynamically stable and even alloy carbides, which serve as dispersion strengthening particles to harden the metal matrix.

It is increasingly recognized that the resistance to wear of carbides reinforced composites is not only determined by the hardness of carbides, but also by their size, shape and distribution [9–11]. This explains why powder metallurgy (PM) technique, which is able to produce exceptional structural homogeneity and ultrafine microstructure, has been widely used in the production of cutting tool materials [12–14]. A majority of tool steels that are often

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subjected to extremely high load and elevated temperatures in applications are required to be highly alloyed (e.g. W, Cr, Mo, V) in order to achieve necessary wear resistance to meet the harsh service environments. However steels with high content of various alloy elements, particularly when they are manufactured in a conventional way, are not intrinsically ductile. This may cause undesired deterioration of the inherent properties such as crack resistance and toughness. Recently, steels with a large amount of vanadium (V) have proven successful in achieving excellent wear resistance and red hardness at high temperatures because vanadium promotes the formation of hard and stable MC-type carbides [15–18]. For example, commercial CPM 10 and CPM 15 (CPM-Crucible Particle Metallurgy) high-V cold work tool steels of high wear resistance are widely used in machinery industry [12,19,20]. Furthermore, an increase in vanadium content, when properly balanced with carbon, hardly affects the toughness of the composites [21]. This is because vanadium carbide (VC) has favorable wettability to iron that benefits the uniform incorporation of precipitates into ferrous matrix and the desirable spheroidal shape formed in VC can restrict stress concentration around the particles [21–25]. Arenas et al. [26] found that the roundness of the hard phase particles in the (Ti, V)C–Co cermets gains with increasing amount of VC owing to its high isotropic surface energy. Park et al. [11] concluded that the amount of MC carbides increases with rising vanadium content, while the carbides are smaller in size and uniformly distributed inside cells. In this study, a novel V-based composite powder was directly placed onto ductile iron (DI) substrate and treated with an atmospheric plasma beam. We have successfully in-situ produced an ultrafine hard-yet-tough MMC coating with graded structure by adopting an economically attractive plasma surface alloying process. It consists of a top high-vanadium alloyed layer, middle modified white iron layer and the heat-affected zone of ductile iron substrate. The morphology, size distribution, composition and formation mechanisms of the carbide phases by PSA process and the microhardness profile of the composite coating have systematically investigated. This opens a new route to produce high vanadium tool steel composite coating on inexpensive cast iron while at the same time avoids complicated process and residual sintering porosity involved in PM [13,27].

2. Experimental procedures

Ductile iron (QT-450) with a composition of Fe-3.7C-2.7Si-0.3Mn (wt. %) was used as substrate for PSA treatment. The dimensions of the DI substrate were 100 mm × 50 mm × 20 mm. The microstructure of the DI substrate consists of graphite nodules embedded in pearlite regions and a ferrite matrix, as shown in Fig. 1. The average diameter of the graphite nodules is approximately 50 μm and Fig. 1b presents a close-view of the lamellar structure of pearlite. The alloy powders (all purities ≥ 99.0%) were primarily composed of ferrovanadium (FeV50), chromium, molybdenum, titanium and ferroniobium (FeNb60) with a composition of 10V-4Cr-3Ti-3Mo-2Nb (weight ratio). No graphite powder or other carbon source was added. Powders were mechanically mixed and pre-coated onto polished DI substrate by spraying to form a layer of ~25 μm thickness. PSA process was performed by a home-made atmospheric plasma apparatus that has been detailed in elsewhere [28]. The plasma beam diameter, the current, the working distance, the scanning speed and overlapping rate were set at 4 mm, 100 A, 2 mm, 0.9–1.6 m min^{−1} and 25%, respectively. Argon was used as shielding gas to prevent oxidation of the PSA layer. After PSA treatment, cross-sectional specimens were prepared by standard mechanical grinding and polishing. Microstructural characterizations were conducted using scanning electron microscope (FEI XL30-FEG ESEM) equipped with energy

Fig. 1. SEM-SE images of substrate (a) and close-up of lamellar pearlite (b), G: graphite; α: ferrite; P: pearlite.

dispersive spectroscopy (EDS, EDAX). Both secondary electron (SE) and backscattered electron (BSE) images were used due to their respective good topological resolutions and superior chemical contrast. It should be noted that SEM observations on cross-sections of several specimens were conducted to better interpret the possible formation of alloy carbides. Transmission electron microscopy (TEM, JEOL 2010-FEG) was employed to identify MC structure and nanoscale elemental compositions (EDS, Bruker). Phase structures were identified by an X-ray diffractometer (XRD, Bruker D8 Advance) using Cu Kα radiation. The samples were scanned over a 2θ range from 20° to 90° with a step size of 0.02° and a step time of 5s. Cross-sectional microhardness was measured using Vickers hardness tester under an applied load of 100 g (HV_{0.1}) for 15s each. Thereafter, the indentation morphology was analyzed with SEM.

3. Results and discussions

3.1. Microstructure evolutions

The cross-sectional microstructure of the plasma beam surface alloyed DI specimen is shown in Fig. 2. It indicates that the PSA layer can be divided into three regions: (1) the top alloyed zone (AZ), (2) the intermediate melted zone (MZ) and (3) the heat affected zone (HAZ) of DI substrate. These three distinct zones are formed because the plasma beam simultaneously melts the pre-placed powder and the substrate surface. Besides, the alloy constituents in the melt actively participate in forming carbides, which impede the diffusion of alloys in depth. As a result, a thin alloyed

layer of $\sim 200\ \mu\text{m}$ thickness is formed on the substrate surface. Fig. 3a reveals the linear distribution of elements (V, Cr, Mo, Ti, Nb, Fe and C) versus the depth of the plasma modified layer. Though Ti has the highest content within a limited depth at the outermost surface, the content of V is higher than other four alloy elements over the whole plasma modified layer. Cr, the second highest alloy element, shares similar variation trend with V. The content of Mo and Nb hardly changes in the AZ before both drop to zero since MZ. The gradual decrease of all alloy elements content in the transition

zone between AZ and MZ (see the inset of Fig. 3a) indicates the formation of graded composition and microstructure that prevent a sharp interface. In addition, C content remains relatively low and homogeneous in both AZ and MZ. This implies that the original graphite nodules are basically dissolved in PSA and turn into carbides. EDS analysis of the whole AZ in Fig. 3b also confirms the highest amount of V (11.62 at. %) and the second highest amount of Cr (8.77 at. %) in the coating. Fig. 4a, a close view of the middle AZ in Fig. 2, shows that AZ contains a large proportion of ultrafine and spherical dark particles that are homogeneously dispersed in the matrix. To estimate the size and distribution density of these MC particles formed in AZ, Fig. 4a was analyzed with software ImageJ. It was found that the volume fraction of the MC particles could reach 31.3% and the average diameter of granular MCs was around $0.51\ \mu\text{m}$ (see Fig. 4d). This highlights that the size of the MC particles produced by PSA, if not smaller, is at the same level with that of the laser-clad CPM 15V or PTA-weld 12V commercial tool steel coating [19,29] while almost one order of magnitude smaller than that of recently reported as-cast high-vanadium high speed steel (HSS) [15,30]. Wang et al. [19] found out that in general laser processed tool steel layer, either by melting or cladding, exhibits fine

Fig. 2. Cross-sectional SEM micrograph of plasma surface alloyed DI specimen.

Fig. 3. (a) EDS line scan from the point A to point B (line not shown) in Fig. 2 showing element distributions versus depth and (b) EDS analysis of the whole AZ in Fig. 2. The inset of (a) shows a gradual decrease of alloying elements in the transition zone from AZ to MZ and also the highest content of Cr compared with other alloying elements.

Fig. 4. (a) Cross-section SEM micrograph of the middle AZ in Fig. 2; (b) close view of the corresponding area indicated by a dashed box in (a); (c) overlaid EDS elements mapping and (d) size distribution of MC micro-particles seen in (a).

Fig. 5. EDS area mapping of AZ: (a) SEM morphology; (b) overlaid element mapping; (c–i) distribution of individual elements indicated.

cellular and/or dendritic structure. However, Fig. 4 indicates that plasma alloyed high-V composite can form submicron equiaxed carbides particles while neither cellular nor dendritic structure is formed in the AZ.

According to the classical nucleation theory presented by Flemings [31], the radius r^* of a nucleus particle stable at an undercooling ΔT is given

$$r^* = \frac{2\sigma V_s T_M}{\Delta T \Delta H} \quad (1)$$

where V_s is the molar volume and T_M is the equilibrium melting point of the phase; σ is the surface energy and ΔH is the latent heat of solidification. Eq. (1) reveals that a large increase in undercooling ΔT will reduce the critical radius of a stable nucleus and thus increases nucleation sites. Thus nuclei appear both along the grain boundaries and inside the grains, making carbides homogenous [32].

It is well-known that the undercooling ΔT is positively associated with the solidification rate (S_R) [31–33]. Increasing S_R will not only decrease the radii of critical nuclei but also accelerate the rate of formation of nuclei. Luan et al. [32] reported that the size of carbides in cast HSS rolls was remarkably reduced and the volume fraction increased with rise in S_R . The nuclei can be further suppressed by the insufficient time to grow and coarsen in the case of PSA. Additionally, the cooling rate of PSA process can be roughly estimated to be around 100 °C/s according to Ref. [34] while only 0.1–5.0 °C/s happens in casting ingots. It is therefore expected that the characteristics of the high cooling and solidification rate during PSA create the possibility to form denser and more refined carbides particles, demonstrating the superior advantages offered by PSA over traditional casting techniques. Another contributing factor is that strong carbide-forming elements such as V, Ti and Nb that have limited solubility in austenite impede the growth of prior austenite grain [35], which leads to smaller resultant phase transformation products after solidification.

The submicro-sized particles in AZ are assumed to be MC-type primary carbides, especially VC, considering the extraordinarily high content of V as verified by EDS analysis, while Mo and Cr elements tend to agglomerate in bulk or strip shaped carbides. Fig. 4c displays the spherical dispersed particles are V-rich phases (colored in blue), partly doped with Ti (colored in red), elucidating that the fine VC-TiC crystals tend to grow together to form double carbide [8,26]. This is because both VC and TiC carbides share a NaCl-type face centered cubic (FCC) structure with a small crystal lattice mismatch ($a_{VC}=0.417$ nm, $a_{TiC}=0.432$ nm) and thus have good mutual compatibility [8,18,36]. Wang et al. [8] reported that VC-TiC system fulfills Hume–Rothery condition, which means that metallic atoms can be substituted or moved without impairing the stability of FCC structure such that they can randomly distribute inside the solid solution. Dobrzański et al. [37] investigated the possibility of partial substitution of Ti for V in the W-Mo-V high-speed steels. They found that though Ti induced a decrease in primary austenite grain size and determined the increase in the portion of primary carbides, Ti existed only in the MC-type primary carbides rather than in the matrix. However, Fig. 4a and the corresponding EDS mapping (Fig. 4c) show a different case in the investigated alloy. It is found that TiC can practically have various tendencies with respect to VC, such as embedded in VC (indicated by arrow 1), intersected with VC (indicated by arrow 2) and leaned against VC (indicated by arrow 3 and 4), and occasionally exist in the matrix alone (indicated by arrow 5 and 6). Closer inspection (Fig. 5) reveals that, coincident with Dobrzański [37], TiC can serve as the nucleation sites for the formation of VC, where the round TiC particles (dark area) are centered inside the VC crystals (dark gray

Fig. 6. (a) SEM-BSE micrograph showing the morphology and composition contrast of MC particles in the AZ. The inset is the enlarged view of a TiC/VC particle marked by a dashed box; (b) linear EDAX EDS analysis along the arrow marked in Fig. 6a; (c) sketch of the formation and distribution of the primary TiC/VC particles.

Table 1
Point EDS analysis of AZ shown in Fig. 6a.

Spot No.	Elements (at.%)						
	Fe	C	V	Cr	Ti	Mo	Nb
1	9.42	39.15	38.47	2.93	5.80	1.87	3.15
2	23.09	22.69	30.10	3.23	16.59	2.00	2.30
3	17.09	24.81	33.98	2.89	16.67	1.96	2.60
4	62.55	20.27	2.71	9.88	0.20	4.12	0.27
5	61.33	17.30	3.72	11.57	0.32	5.20	0.56
6	73.75	13.55	3.86	6.14	0.17	2.00	0.54

surrounding). Combined with EDS mapping shown in Fig. 5b–e, it can be concluded that the spherical particles are mostly enriched in vanadium, while at the centermost Ti substitutes some part of V

Fig. 7. Morphology of M_7C_3 carbide particles (a) and of eutectic $M_{23}C_6$ carbide (b) with the inset showing that $M_{23}C_6$ grows from blocky M_7C_3 carbide; (c) overlaid EDS elements mapping and (d) Cr element distribution of (a).

Fig. 8. (a–b) SEM images showing the distribution of eutectic M_2C -type carbides and eutectic MC; (c) overlaid EDS mapping and (d) Mo element distribution of (a).

due to the significant affinity of Ti to C [38]. This makes TiC-type carbide nuclei around which MC carbides grow containing besides V also Ti and other alloy elements such as Cr (see Fig. 5g) and Mo (see Fig. 5h). In particular the element of Mo, indicated by the arrows in Fig. 5b, either surrounds MC particles or locates at the grain boundaries. Another explanation for the replacement of V with Ti could be the higher melting temperature of TiC (3140 °C/s) than VC (2830 °C/s) [38], indicating that earlier precipitation of TiC from the melt serves as favored heterogeneous nuclei for VC and other carbides. Apart from Ti, Fig. 5f shows that Nb also presents similar distribution as V, which suggests a potential miscibility of VC-NbC crystals as well [39]. In fact, NbC also holds a FCC crystal lattice with $a = 4.4458$ nm that is comparatively close to VC, making this hypothesis reasonable. Wang et al. [27] pointed out that Nb has a higher affinity with carbon compared with V and thus can be used as a substitutional carbide-forming element to form stable carbide NbC. However, different with TiC, NbC tends not to act as the nucleating sites for VC formation and the mechanism is still uncertain. One possible reason could be that the total content of Nb in the present alloy is apparently deficient (0.73 at.% as shown in Fig. 3b). Previous studies [11,39] proposed that the predominant effect of vanadium in HSSs is to form MC-type carbides. In contrast, chromium, which has the second highest content in the alloy, almost scatters over the entire AZ instead of merely in MCs as can be seen from Fig. 5g.

Further quantitative analysis of these alloy elements are shown in Fig. 6 and point EDS analyses are listed in Table 1. The spot 1 indicates that the stoichiometric proportion of V (38.47 at.%) to C (39.15 at.%) is near 1:1, proving it being VC-type carbide. EDS of spot 2 and spot 3 on the round darker center of flower-like particles confirms a notable increase of Ti (from 5.8 at.% in VC particles to ~16.6 at.%), which manifests a TiC core in the TiC/VC double carbide. The EDS line scan shown in Fig. 6b further demonstrates the role of TiC in serving as nucleation site for VC. The formation mechanism and distribution of primary VC- and TiC-type carbides can be schematically depicted in Fig. 6c. In addition, the EDS line scan illustrates that Nb keeps in step with V though at much lower content. This finding may indicate the possible substitution of V with Nb. The spots 1–3 contain a high amount of V and certain Cr, Mo and Nb, which implies that some V atoms are partly substituted by other alloy atoms to form (V, Cr, Nb, Mo)C [40]. EDS of spot 4 and 5 suggests that the plate-like whitish phases incline to be Cr- and Mo-containing carbides, likely M_7C_3 . The highest Cr content among all alloy elements (6.14 at. %) in spot 6 confirms the highest chromium dissolution in the matrix, in line with Fig. 5g. Porter [41] reported the solubility products of carbides and nitrides in austenite as a function of temperature and concluded that chromium has highest solubility in austenite.

Despite its significant contributions to the matrix solution hardening, Cr also conditionally exists in the form of chromium carbides, generally of the M_7C_3 and $M_{23}C_6$ types. Fig. 7a and c-d confirm the coarse bulk-like carbides are Cr-rich, which can be assumed as M_7C_3 -type carbide [30]. Moreover, ultrafine carbides nucleated in the intergranular lamella (see Fig. 7b) have either a rod-like or thin platelet morphology, which are in accordance with Ref [11,17,42]. For example, Hetzner et al. [42] characterized these ultrafine globules to be $M_{23}C_6$ -type carbide by utilizing electron backscatter diffraction (EBSD) technique. M_7C_3 precipitating at grain boundaries and the consequent chromium depleting in the surroundings make provisions for the secondary $M_{23}C_6$ via either eutectic reactions or a peritectic reaction $L + M_7C_3 \rightarrow M_{23}C_6$ [43]. The inset of Fig. 7b shows that the lamellar or granular $M_{23}C_6$ carbides (indicated by yellow arrows) appear to grow from the blocky M_7C_3 (indicated by white arrows) carbides.

It is also important to note that vanadium carbides can be

divided into primary carbides and eutectic carbides. Primary VC that precipitates first from the melt can grow with less restriction in various directions [44]. This means primary VC can evolve from spheroidal (Fig. 4a) to polygonal (Fig. 7a), petal-like (Figs. 6a and 8a), which is also sketched in Fig. 6c. $L \rightarrow (\gamma + MC)$ eutectic reaction takes place with increasing V depletion when the melt arrives at the eutectic composition and temperature. Thus eutectic VC carbide is formed generally in the shape of strip, shot rod or chrysanthemum distributed along the network boundaries and inside cells (see Fig. 8a and b) [15,19,32,44]. Yan et al. [44] attributed these morphologies to the fact that during the eutectic solidification, austenite tends to form divorced eutectic and hence

Fig. 9. (a) Transition zone from AZ to MZ showing MC particles embedded into ledeburite matrix with the inset enlarging the twinned martensite; (b, c) MZ showing fragmented cementite and plate martensite accompanied with retained austenite in ledeburite matrix.

Fig. 10. Transition from AZ to MZ: (a) overview micrograph, (b–d) close view of the areas marked in (a) showing both lathy and twined martensite (M) and M_3C -cementite in MZ.

prompts the faceted VC to grow along the austenite grain boundaries. Along the boundaries between eutectic regions, there are networks of strip bands (see Fig. 8a and b), which is consistent with

laser-clad CPM 10V coating [19]. EDS analyses (Fig. 8c and d) reveal that they are strongly enriched in molybdenum and can be determined as $(\gamma + M_2C)$ eutectics. M_2C eutectic carbide may deteriorate

Fig. 11. (a) Martensite and ledeburite double shells surrounding the remaining graphite nodules in the heat affected zone (HAZ); (b) close-view of a full ledeburite nodule surrounded by needle-like martensite in (a); (c) EDS line scan indicated by the line #1–#2 in (a) showing the element variation of C and Fe; (d) sketch of microstructure development in HAZ.

the hot workability and toughness and often initiates cracks in HSS [11,45]; however, as a meta-stable phase, M_2C is also found to favorably induce secondary hardening by following the decomposition path: Matrix + $M_2C \rightarrow MC + M_6C$ [10,39], which forms smaller MC globules inside the bands.

Still, it is worth mentioning that vanadium carbides are formed preferentially during solidification process owing to the ability of carbides formation of V, Mo, Cr in a decreasing order [46]. This explains why no visible primary chromium and molybdenum carbides are observed in Fig. 4a, where abundant vanadium together with trace amounts of titanium and niobium take priority to form MCs. Consequently it leaves inadequate supply of carbon for chromium and molybdenum that are therefore forced to dissolve into the matrix to form solid solutions. In the case of Figs. 7a and 8a, due to the uneven distribution of alloy elements probably brought about by plasma convection, less vanadium concentration in these areas results in free retained carbon, and consequently makes way for the formation of carbides such as M_2C and M_7C_3 .

The subsurface remelting of DI substrate results in a structure similar to white cast iron consisting of lathy cementite and interdendritic eutectic ledeburite (Ld'), accompanied by many plate martensite (M, Z-shaped grains) and retained austenite (RA, bitty areas segregated by martensite) as shown in Fig. 9. Since no external carbon was provided from the preplaced powder, the amount of carbon that dissolves from graphite nodules of DI substrate during plasma melting can be considered as constant. Fewer strong carbide-forming alloy atoms since the bottom AZ implies relatively more carbon retained in MZ. Therefore carbon-enriched austenite transforms into martensite in rapid cooling after solidification, explaining higher volume fraction of martensite in MZ than AZ. From the transition zone between AZ and MZ in Fig. 9a, it is seen that the MCs fragment the original reticular ledeburite into segregated crystals, which helps release the high stress prevailing in the inter-connected structure [25,45]. Besides fewer globular MC particles, bulk shaped M_7C_3 carbides as indicated by arrows in Fig. 9a tend to form at this transition zone, as supported by the higher Cr content than V (see the inset EDS in Fig. 3a).

Fig. 10 shows a transition zone primarily consisting of martensite from AZ to MZ and plenty of retained austenite locate in between neighboring martensite laths. Fig. 10b and c indicates the area close to AZ has a mixture of both twinned martensite and lath martensite, while at the area close to MZ lenticular high-carbon martensite dominates in large quantities (Fig. 10d). The martensitic transformation is known as diffusionless and can only occur if the diffusion-controlled transformation of austenite is inhibited [47]. During the PSA process the cooling rate is considered rapid to suppress the transformation of austenite to ferrite or pearlite and therefore the austenite-martensite transformation is favored, though in an incomplete way leading to that retained austenite fills regions among packets of the martensite laths. Martensite is the phase that exhibits high hardness and strength but embrittles steels [45]. Therefore post heat treatments are required to promote the transformation of martensite into tempered martensite to relieve brittleness.

At the bottom of the MZ (Fig. 11), reduced plasma energy results in decreased molten time that limits austenite transformation during the solidification and produces a mixture of modified ledeburite (Ld' , residual austenite and cementite) surrounding the graphite nodules of dwindled diameters, high-carbon twinned martensite and residual austenite. A large amount of the ledeburite/martensite double shells are formed as indicated in Fig. 11a. Such shells illustrate that material surrounding the graphite nodules firstly melts. This is because greater carbon enrichment closer to the graphite nodules renders carbon content at graphite-matrix interface approaching to eutectic concentration and thus locally

lowers the melting point [48]. The line-EDS in Fig. 11c indicates that carbon content, although seldom fluctuating within the double shells, starts to decrease from the outer surface of the martensite annulus. Also, it is interesting to mention that the shells are asymmetric (see Fig. 11a and d) with larger dimensions in the direction towards the plasma modified surface. This is due to the higher temperature in the zones closer to the top surface and consequently faster carbon diffusion in a prolonged heating.

3.2. Phase transformations

XRD spectra of the DI substrate and plasma alloyed coating are shown in Fig. 12 to characterize the phases formed in the PSA coating. For the untreated DI, only diffraction peaks of α -Fe and graphite can be indexed (Fig. 12a). Several carbide phases formed in the PSA coating are identified as MC and M_2C ($M = V, Ti, Nb$ and Mo) type carbides. It should be noted that Cr in the melt favors the formation of chromium carbides rather than cementite-type carbides because Cr has a stronger affinity to form carbides than Fe [4,49]. Besides, the high cooling rate in PSA process increases the solubility of alloy elements in the matrix [5], thereby rendering excessive metallic elements into the matrix to form precipitates [50] such as $Mo_2V_4C_5$ [JCPDS No.: 65–8769] and $Ti_{0.42}V_{1.58}C$ [JCPDS No.: 65–7965]. It is also noteworthy that martensite and retained austenite were detected, as readily observed in SEM and TEM micrographs.

Along with XRD analysis, TEM was further employed to identify the VC crystals. Fig. 13a and b shows the densely distributed spherical, lumpy or polygonal carbide clusters embedded in AZ. The inserted EDS spectra indicate the bright tiny particles being V-rich phases. The selected area diffraction patterns confirm that they are primarily VC (JCPDS No.: 65–7885) crystal as shown in Fig. 13e (EDP 1) and f (EDP 2) together with some V_8C_7 (EDP3, JCPDS No.: 89–2608), consistent with [9,14,18,30,44]. The measured plane spacing in the Fourier filtering processed HRTEM (the inset in Fig. 13f) is 0.241 nm, matching perfectly to the distance of plane (111) of VC with a discrepancy of 0.054%. The V atoms are packed as face-centered cubic and carbon atoms fill in the octahedron interstice. Defect lattices in this type of compound result in some of the sites for carbon unfilled as reflected in the EDS analysis of spot 2 and spot

Fig. 12. XRD patterns of (a) ductile iron substrate and (b) the PSA coating.

Fig. 13. TEM micrographs of the upper AZ: (a, b) plan-view images of dense VC clusters formed in the coating; (c, d) close-up of corresponding areas marked by dashed boxes in (a) and (b) respectively; (e–g) corresponding selected area electron diffraction patterns (EDP) in (a), (c) and (d), respectively. The insets are EDS analyses corresponding to the areas for EDPs. M in (c) refers to martensite.

3 in Table 1. This makes the atomic ratio of C to V in the lattice <1 , explaining the formation of V_8C_7 [44,51]. The EDS of EDP2 reveals a relatively high amount of Ti, which indicates $(V, Ti)C_{1-x}$. Twined martensite in needle shape exists between MC particles as shown in Fig. 13c, which is in accord with the inset of Fig. 9a.

3.3. Mechanical properties

Fig. 14 shows the average microhardness profile measured on a cross section of the PSA coating. The hardness is determined by the characteristic features of carbides (including their type, proportion, shape, size and distribution) and the structure of the matrix. As seen in Fig. 15a–d, the indentation marks formed under 100 g load are between 16.2 μm and 19.3 μm in diagonal length corresponding to the hardness range of approximately 700–1290 $HV_{0.1}$. This measures the average deformation resistance of the composite coating reflecting the combined effect of matrix and the reinforcing

carbides with fine size of only 0.5–2 μm . It can be seen from Fig. 14 that the average microhardness of AZ varies from $\sim 620 HV_{0.1}$ to 960 $HV_{0.1}$, marginally lower than that of MZ.

Several indentation impressions in the different zones are analyzed in Fig. 15. The hardness of AZ with considerable fluctuations can be ascribed to several reasons. Firstly, due to the locally uneven composition of melt bath caused by plasma induced convection, the larger and denser spherical primary MC carbides (Fig. 15a) are generally formed in the top part of the PSA layer. They can bear higher resistance to deformation than the ever finer and sparser eutectic MC and secondary carbides or Mo–Cr carbides (indicated by yellow stroked arrows in Fig. 15b) of relatively lower hardness. Previous study by Lin et al. [52] indicated that smaller secondary carbides did not promote the micro-cutting wear resistance of steels owing to their “size effect” and distributions; they reduced the wear resistance because of the easy-spall or rolling effects. It is, however, noteworthy that smaller carbide particles of

Fig. 14. Microhardness profile of PSA coating as a function of depth.

enough volumetric fraction could enhance wear resistance via dissipating strain energy and deflecting crack propagation [25]. Consequently the indentation surface of Fig. 15b appears rather smooth and dense without obvious cracks, while breakage takes place in the relatively coarse MC carbide in Fig. 15a (indicated by red stroked arrow). Furthermore, some $(V, Ti, Nb)C_{1-x}$ particles are observed in larger crystals in Fig. 15a. It has reported [53] that addition of 0.5% Nb or 0.3% Ti increased the maximum hardness of quenched and tempered W-Mo-V HSS by some 1.5 HRC, indicating favored replacement of a proportion of V with Ti and Nb. Finally, the AZ features a matrix with ductile retained austenite [19], thus encouraging plastic flow of the matrix as a significant pile up seen at the edge of the indentation (indicated by yellow filled arrows in Fig. 15a and b). This observation is in contrary to the fact that plastic deformation is significant in the coating only with low hardness, leading to a conclusion that significant plastic deformation can occur in hard composite provided that the ultrafine alloy carbides are formed in spherical shape and as well embedded in a ductile matrix. Previous studies [54] reported that conventionally brittle ceramics could turn to ductile, permitting plastic deformations. Karch et al. [54] ascribed this ductility to the diffusional creep of

Fig. 15. Vickers indentation under a load of 100 g: (a–b) AZ with different size and density of MCs; (c) martensite-rich area between AZ and MZ; (d) MZ; (e) HAZ; and (f) DI-substrate.

atoms along the abundant intercrystalline interfaces caused by decreasing size of particles.

Fig. 15c and d indicates enhanced hardness is also obtained in the intermediate melted zone. This is because this zone contains significant amounts of martensite and cementite that impart a higher hardness, in comparison to 200 HV_{0.1} in the substrate (Fig. 15f). However, cracks including both intergranular fractures (particularly along the martensite laths) and transcrystalline fractures readily occur, indicated by red stroked arrows.

Our prior results showed that the wear resistance of alloyed samples could reach over 20 times of the substrate. Although plasma remelted surface has comparable tribological performance as PSA alloying, careful observations on the wear scars obviously revealed brittle exfoliations [25]. This suggests finely dispersed spherical MC-reinforced high-vanadium alloy composite overall combines high hardness, adequate toughness and good abrasive resistance. Furthermore, the subsurface melted zone functions like a hard buffer layer to bear higher loads and increases AZ adhesions with the substrate by metallurgical bonding (see Figs. 3a and 9). This preferably makes the graded coating thick and strong to enable a feasible long wear life.

4. Conclusions

1. A novel MC-reinforced alloy layer - modified white iron - ductile iron graded coating was synthesized in situ by plasma surface alloying process. The top alloyed zone consists of dense spheroid-like MC particles of submicrometer size. The intermediate melted zone chiefly consists of intercellular ledeburite and cementite, embedded with a large proportion of twined martensite while ledeburite/martensite shells are formed at the heat affected zone.
2. No obvious dendrites are observed in the AZ because a large amount of primary MC particles serve as heterogeneous nuclei and gain refining due to restrained growth by rapid solidification during PSA. M₂C, M₇C₃, M₂₃C₆ distribute mainly along grain boundaries while MC carbides are dispersed throughout the matrix.
3. EDS proves that Ti and Nb occur in the MC-type primary carbides besides V, and TiC even features as nuclei. While vanadium atoms in VC particles are partly substituted by other alloy atoms to form (V, Cr, Mo)C, lattice defects in NaCl-type VC also cause some carbon unfilled, explaining the formation of V₈C₇ evidenced in TEM.
4. The ultrafine MC allied with hard phases such as M₂C, M₇C₃, M₂₃C₆ and martensite is supposed to make the HVHSS coating hard-yet-tough; Hardness enhancement should be attributed to both the synergistic effects of hard alloy precipitates strengthening and solid solution hardening as well as fine-grain strengthening.
5. This research provides an economic and easy route to produce high-performance high-vanadium tool steel coating. But the wide solidification range and the complex eutectic reactions as wells as process influences such as plasma convections make possible many combinations of alloy carbides and their unexpected distributions. Further studies should focus on optimized production process and post heat treatments to yield MMC structure of desired size and uniform distribution.

Acknowledgments

The PSA specimens were prepared at the Huazhong University of Science and Technology (HUST), China and microscopy characterizations were conducted at the University of Groningen, the Netherlands. The financial support by the China Scholarship

Council (CSC) was also acknowledged.

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