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Letter

The microstructure evolution of VC coatings on AISI H13 and 9Cr18 steel by thermo-reactive deposition process

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ABSTRACT

The microstructures of VC coatings on AISI H13 and 9Cr18 steel obtained by thermo-reactive deposition at 920 °C for 4 h were studied. The coating on AISI H13 was composed of equiaxed grains with an average size of 0.27 ± 0.12 μm; the coating on 9Cr18 was composed of elongated grains. The average size was 1.56 ± 0.54 μm in the direction parallel to coating/substrate interface and 0.69 ± 0.09 μm perpendicular to coating/substrate interface. The increase in grain size of the coating formed on 9Cr18 was caused by the poor-supplying of carbon atoms for the formation reaction of vanadium carbide. These tendencies of the formation of equiaxed and elongated grains were attributed to the high and low carbon activities in the substrates, respectively.

1. Introduction

Thermo-reactive deposition/diffusion (TRD) is a technology to prepare hard, wear-resistant coatings of carbides, nitrides, or carbonitrides on steels [1–3]. TRD process involves immersion of materials in a molten borax bath that contains the relevant carbide/nitride forming element (CFE/NFE) such as V, Nb, or Cr [1]. Coatings are formed by the combination of CFE/NFE in the salt bath and the carbon/nitrogen (to obtain a nitride coating, steel is always pre-treated by nitriding prior to TRD process) diffused from substrates. The obtained coatings present excellent adhesion with the substrate, high hardness, good wear resistance, and low coefficient of friction [4].

As one of the hardest transition metal carbides [5,6], VC coating obtained by TRD process is commonly used in tribological applications. The performance of coatings is rather sensitive to the microstructures. For instance, columnar grains are anisotropic and the grain boundaries become the sites for crack initiation, resulting in premature failure of coatings; while the fine equiaxed grains throughout the coating are randomly oriented and can improve its tribological performance [7]. The different microstructures of VC coating may be induced by the significant composition difference among substrates with a carbon content of 0.3 wt.% or higher [8]. In fact, both columnar and equiaxed grains were observed in the VC coatings obtained by TRD process [9]. Therefore, it is important to study the influence of substrates on the microstructures for better understanding the properties and improving the performance of TRD coatings formed on different substrates. Unfortunately, previous studies on TRD coatings always focus on the wear behavior and growth kinetics but rarely on the relationship between the microstructures and substrates.

In the present paper, the microstructures of VC coatings prepared by TRD process were studied on two steels with different carbon activities, AISI H13 steel and 9Cr18, to indicate the influence of substrates on the grain morphology.

2. Experimental procedure

The materials used for TRD treatment were AISI H13 (0.43 wt.% C, 4.98 wt.% Cr, 1.32 wt.% Mo, 1.09 wt.% Si, 1.04 wt.% V, 0.35 wt.% Mn, Balance Fe) and 9Cr18 (0.92 wt.% C,17.69 wt.% Cr, 0.73 wt.% Si, 0.80 wt.% Mn, Balance Fe) steel. The as-received materials were sized to Φ30 mm × 10 mm with a 2 mm hole in center for hanging purposes. All the specimens were ground, polished and ultrasonically cleaned in acetone. After that, TRD experiments were performed by molten borax bath process with a commercial salt at 920 °C for 4 h, and subsequently cooled in air.

The microstructures and compositions of the coatings were analyzed with scanning electron microscopy (SEM) with an energy dispersive X-ray facility (EDX). The EDX results were used to distinguish the vanadium carbide, chromium carbide and the steel substrate semi-quantitatively. In order to make it believable, all the EDX results were measured for five times and then averaged. For the cross-section observation purpose, the specimens were polished and etched with an aqueous solution 10% KOH + 10% $K_3[Fe(CN)_6]$. The specimens for surface observation were etched without polishing.

3. Results and discussion

3.1. *Grain morphology in coatings on AISI H13and 9Cr18*

Fig. 1(a) and (b) show the etched cross-section and surface morphology of VC coating on AISI H13. It can be seen that

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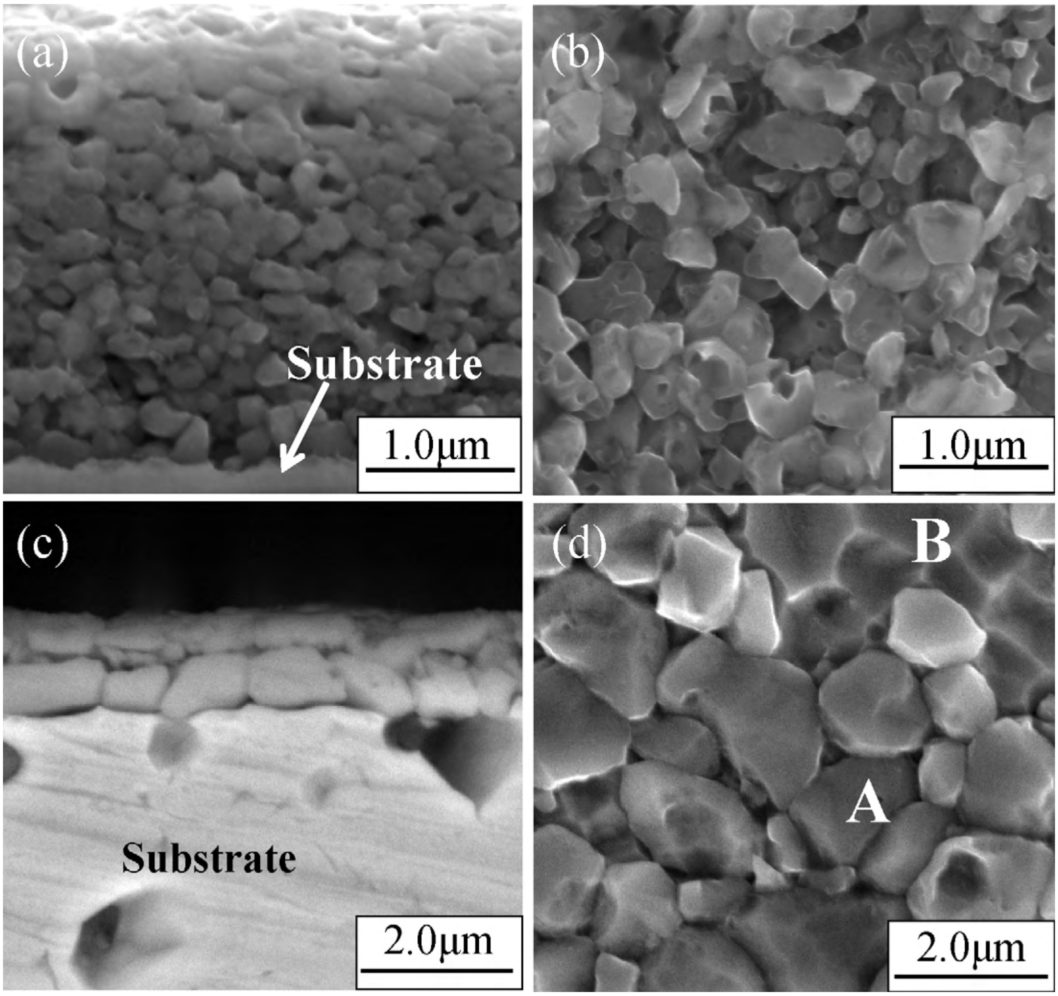

Fig. 1. SEM micrograph of (a) etched cross-section and (b) surface morphology of coating on AISI H13, and (c) etched cross-section and (d) surface morphology of coating on 9Cr18, respectively.

Table 1
The EDX results of regions A, B in Fig. 1(d) and region C in Fig. 3 (at.%).

Element	C	V	Fe	Cr
A	48.39 ± 0.43	51.61 ± 0.43	–	–
B	7.91 ± 1.49	2.77 ± 0.40	77.06 ± 1.52	11.77 ± 0.17
C	23.87 ± 0.32	3.25 ± 0.43	28.41 ± 0.73	45.14 ± 0.64

equiaxed grains are formed throughout the coating. The average grain size is 0.27 ± 0.12 μm determined by the linear intercept method. Fig. 1(c) shows the etched cross-section of coating on 9Cr18. Elongated grains in the region adjacent to substrate are observed. The size of elongated grains in the direction perpendicular to coating/substrate interface is much smaller than that parallel to coating/substrate interface. The elongated grains also can be observed in the etched surface of coating on 9Cr18 as shown in Fig. 1(d). After etching grains in outer layer of the coating spall and two distinction regions (A and B) are observed. The EDX results presented in Table 1 show that A is VC grains and B is substrate. Region B is the stamps induced by the spalled VC grains. It is suggested that the grains in Fig. 1(d) corresponds to the region adjacent to substrate in Fig. 1(c). The average size of elongated grains is 1.56 ± 0.54 μm in the direction parallel to coating/substrate interface and 0.69 ± 0.09 μm perpendicular to coating/substrate interface.

Grains in the coating on AISI H13 are finer than those on 9Cr18. The difference is probably attributed to the supplying of carbon atoms for the formation reaction [9]. Although the carbon content in 9Cr18 is higher than that in AISI H13, the carbon activity in AISI H13 is higher than that in 9Cr18 by a factor of 2–3 at 920 °C calculated according to regular solution sub-lattice theory [11], as listed in Table 2. In the reaction front, the carbon activity can be assumed to be zero [11]. Therefore, higher carbon activity in substrate induces a larger driving force for carbon diffusion from

Table 2
Carbon activity in AISI H13 and 9Cr18 substrate at 920 °C.

Substrate	AISI H13	9Cr18[a]
Carbon activity	0.122	0.044[b]–0.053[c]

[a] The equilibrium contents of chromium and carbon in austenite determined by the Fe–Cr–C ternary phase diagram [10] at 900 °C and 1000 °C were used to estimate the carbon activity because there is a large amount of undissolved chromium carbides at the treating temperature for 9Cr18.
[b] Carbon activity at 900 °C.
[c] Carbon activity at 1000 °C.

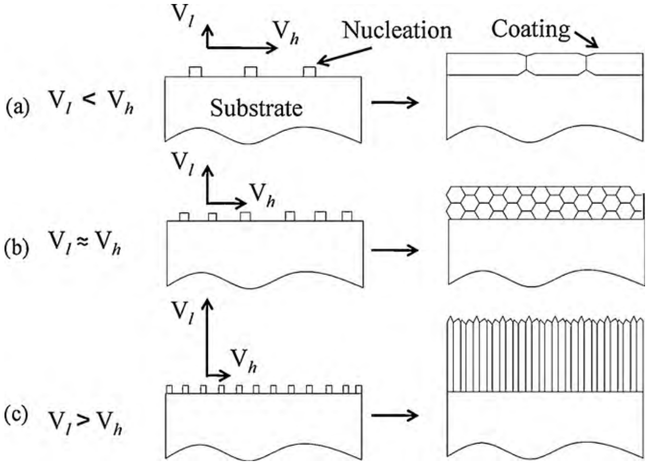

Fig. 2. Schematics of the microstructures evolution in VC coatings on substrates with (a) low carbon activity; (b) medium carbon activity and (c) high carbon activity V_h, horizontal growth rate; V_l, the longitudinal growth rate.

substrate at the initial stage of coating growth, and subsequently improves the nucleation density. The higher the nucleation density, the finer the grains generated [12].

3.2. Mechanism for grain morphology evolution

It was reported that the VC coating on W1 steel by TRD process was composed of a columnar region adjacent to the substrate and an upper equiaxed region [9]. However, no columnar grains are observed in the present work. The grain morphology in the region adjacent to substrate is probably related with the nucleation and growth behavior of VC coating. It has been pointed out that a number of sub-micron sized grains formed on the substrate surface in the initial stage of TRD process. And relatively coarse grains grew from these grains by increasing their size and number with the increasing time to form a continuous thin layer on the steel surface [9]. For substrates with relatively low carbon activity such as 9Cr18, relatively low nucleation density is induced by the small driving force for carbon atoms diffusion. It is difficult to form a continuous layer by increasing the grains number. Thus, in the initial stage of coating growth, the horizontal growth (V_h) of sub-micron sized grains in the direction parallel to substrate to cover the whole substrate surface is dominant; the longitudinal growth (V_l) perpendicular to substrate is inhibited due to the poor-supplying of carbon atoms. Therefore, the elongated grains form as illustrated in Fig. 2(a). As mentioned in Section 3.1 the calculated carbon activity in AISI H13 was much higher than that in 9Cr18. With the increase of driving force, relatively more carbon atoms can be supplied to the reaction front for the longitudinal growth as well as the horizontal growth of grains. Meanwhile, the nucleation density increases and the horizontal growth rate of grains decreases due to the grain growth competition [13]. The growth rate in both directions becomes almost uniform and equiaxed grains form, as illustrated in Fig. 2(b).

Further evidence on the mechanism for the grain evolution can be found from the grain morphology in the region adjacent to chromium carbides (region C in Fig. 3) on 9Cr18.The composition of region C determined by EDX is presented in Table 1. It can be seen that the grains formed on chromium carbides are not elongated but rather equiaxed. The average size is 0.89 ± 0.10 μm. It is generally recognized that vanadium works as a strong carbide former element [14]. The driving force for the formation of vanadium carbides is larger than that of chromium carbides. Therefore, vanadium carbide grains can directly nucleate and grow on chromium carbides [15]. The grain size in the region adjacent to chromium carbides is smaller than the elongated grains, which suggests relatively sufficient carbon atoms needed for the formation of vanadium carbide can be supplied by chromium carbides compared with the substrate. Consequently, the nucleation density is improved and equiaxed grains form.

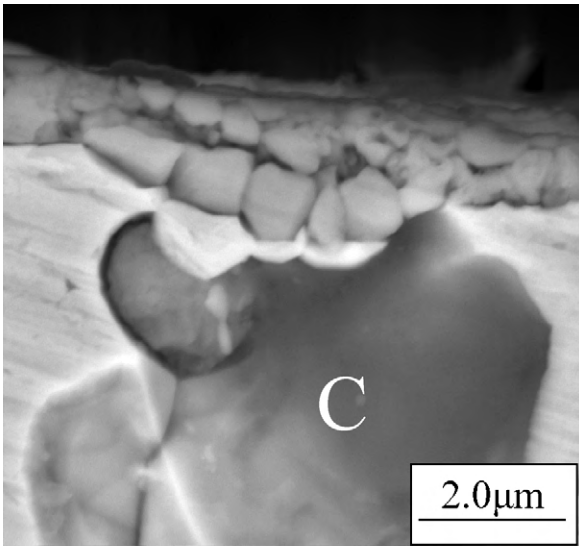

Fig. 3. The grain morphology in the region adjacent to chromium carbides in 9Cr18.

Columnar grains may be formed when the carbon activity in substrate is high enough. In this case longitudinal growth rate is higher than horizontal growth rate ($V_l > V_h$) as illustrated in Fig. 2(c). This conjecture agrees with the results reported in the literature [9]. In their study, columnar region was obtained on W1 Steel at 1183 K, and the corresponding carbon activity was approximately 0.61, greatly higher than that in the both substrates used in this study.

4. Conclusions

The microstructures and mechanisms for the grain evolution of VC coatings on AISI H13 and 9Cr18 obtained by TRD process at 920 °C for 4 h were studied. Based on those results, the following conclusions were drawn.

Coating on AISI H13 was composed of equiaxed grains and the average grain size was 0.27 ± 0.12 μm; coating on 9Cr18 was composed of elongated grains. The average size was 1.56 ± 0.54 μm in the direction parallel to coating/substrate interface and 0.69 ± 0.09 μm perpendicular to coating/substrate interface. Grain size of coatings formed on different substrates had significant distinction. The increase in grain size of coating formed on 9Cr18 was caused by the poor-supplying of carbon atoms for the formation reaction of VC.

The grains morphology in the region adjacent to the substrate was sensitive to the carbon activity in substrates and consequently nucleation density and growth rate of grains in the initial stage. With a relatively low carbon activity, elongated grains would be formed. With the increase in carbon activity, the elongated grains were replaced by equiaxed grains.

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References

[1] M. Aghaie-Khafri, F. Fazlalipour, J. Phys. Chem. Solids 69 (2008) 2465–2470.
[2] U. Sen, Mater. Chem. Phys. 86 (2004) 189–194.
[3] M. Aghaie-Khafri, F. Fazlalipour, Surf. Coat. Technol. 202 (2008) 4107–4113.
[4] C.K.N. Oliveira, R.M. Muñoz Riofano, L.C. Casteletti, Mater. Lett. 59 (2005) 1719–1722.
[5] H.L. Liu, J.C. Zhu, Y. Liu, Z.H. Lai, Mater. Lett. 62 (2008) 3084–3086.
[6] J.H. Ma, M.N. Wu, Y.H. Du, S.Q. Chen, J. Ye, L.L. Jin, Mater. Lett. 63 (2009) 905–907.
[7] Y.H. Chen, K.W. Lee, W.A. Chiou, Y.W. Chung, L.M. Keer, Surf. Coat. Technol. 146–147 (2001) 209–214.
[8] C.K.N. Oliveira, C.L. Benassi, L.C. Casteletti, Surf. Coat. Technol. 201 (2006) 1880–1885.
[9] T. Arai, S. Moriyana, Thin Solid Films 249 (1994) 54–61.
[10] G.V. Raynor, V.G. Rivlin, in: Hugh Baker (Ed.), Alloy Phase Diagrams, vol. 3, ASM Handbook, 1992, pp. 1563–1566.
[11] X.J. Liu, H.C. Wang, D.W. Li, Y.X. Wu, Surf. Coat. Technol. 201 (2006) 2414–2418.
[12] H. Itoh, T. Osaki, H. Iwahara, J. Mater. Sci. 26 (1991) 3763–3768.
[13] C.X. Liu, Y.Q. Yang, R.J. Zhang, X. Luo, Comput. Mater. Sci. 44 (2009) 1281–1285.
[14] D. Nam, J. Do, S. Lee, Scripta Mater. 60 (2009) 695–698.
[15] T. Arai, Thin Solid Films 229 (1993) 171–179.