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ARTICLE

XPS and EDS Analysis of VC Coatings Prepared by TD Process

Kong Dejun[1, 2], **Wang Jinchun**[1], **Guo Haoyuan**[1]

[1]Changzhou University, Changzhou 213164, China; [2]Jiangsu Key Laboratory of Materials Surface Science and Technology, Changzhou 213164, China

Abstract: VC (vanadium carbide) coating was prepared on the substrate surface of Cr12MoV cold worked die steel by TD (thermal diffusion) process using anhydrous borate, FeV50, FeSi45 as main materials. The structures and the chemical element distributions of the coating were characterized with SEM (scanning electron microscope), XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy) and EDS (energy dispersive spectrometer), respectively. The chemical element distributions of VC coating surface and interface were analyzed with plane scan of EDS, and the mechanism of interfacial metallurgical bonding was discussed. The results show that the VC coating is a compound, consisting of C and V elements, and the concentration of V atom is twice as large as that of C atom. The VC coating is single VC phase, where the electron binding energy of V element is located at 512.8 eV, and that of C element is located at 282.2 eV. The diffusion between V, C and Fe elements occur at the coating interface and a layer of interface diffusion is formed, and the interface of VC coating-substrate is combined with the metallurgical bonding.

Key words: VC coating; TD (thermal diffusion) process; bonding interface

VC coating is one of the highest hardness transition metal carbon compounds and also a stoichiometrical compound [1,2]. It has a face-centred cubic structure with high melting point, high hardness and high chemical stability, etc.[3] Therefore it is widely used in materials modification. There are many methods of preparing VC coating, such as direct carbonization, in situ burning form, and TD (thermal diffusion) processing[2-4]. VC coating can be formed in the mold surface by TD process, which is one of surface treatment methods of solving surface pulled damage of forming die[4]. At present, TD surface strengthening process is widely used for moulds in Japan, Korea and America. However, the researches on TD process are still at experimental stage, and used rarely in the actual production, which somewhat restrict the application of TD process in industries. The investigations about TD process mainly focused on growth mechanism, structure, abrasion performance of VC coating[5-8]. The related chemical element distributions in VC coating showed that C concentration had a slight increase in coating interface, while C content first slightly increased to the maximum capacity, presenting a decreasing trend [9]. But there was little report about the chemical element plane distributions of VC coating interface and metallurgical bonding formed by interface diffusion. In the present investigation the VC coating was prepared on the Cr12MoV cold worked die surface by TD process. The structures and the chemical element distributions were analyzed with SEM, EDS, XRD and XPS, respectively, and the metallurgical bonding mechanism of the coating interface was analyzed to provide the basic experiments for actual applications.

1 Experiment

The substrate material was Cr12MoV steel, and the equipment was a TD salt bath furnace with the highest heating temperature of 1300 ℃ and automatic control

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Corresponding author: Kong Dejun, Ph. D., Professor, College of Mechanical Engineering, Changzhou University, Changzhou 213164, P. R. China, Tel: 0086-519-83290205, E-mail: kong-dejun@163.com

temperature accuracy of ±5 ℃. The raw materials were composed of the following powders: (1) no-water borax salt, the particle morphology is shown in Fig.1a, and the average size was 20~30 μm; (2) reducing agent FeSi45, its particle morphology is shown in Fig.1b, and the average size was 10~15 μm; (3) vanadium agent FeV50, its particle morphology is shown in Fig.1c, and the average size was 20~25 μm. The XRD patterns of raw materials are shown in Fig.2.

When the salt bath was prepared, first of all, the salt furnace was started by base salt. Then the vanadium agent of FeV50 and reducing agent of FeSi45 were mixed evenly into salt bath, and finally the activator of NaF was put in to increase the liquidity of salt bath. After full melting, Cr12MoV cold worked die steel was soaked in salt bath at the temperature of 1200 ℃ for 12 h, afterward quenched in oil at the tempering of 180 ℃ for 2 h, and then the required sample was obtained. The surface-interface morphologies and chemical element distributions were observed and tested with JSM-6360 LA typed SEM and the electronic energy equipment. The phase of VC coating and the XPS map were analyzed by D/max2500PC type XRD and ESCALA 250 type XPS, respectively.

2 Analysis of Experimental Results

2.1 Surface morphology, EDS and XRD analysis

The coating surface is smooth and dense, as shown in Fig.3a. The distribution of grain and particle size is uniform with certain porosity. EDS analysis of the surface is shown in Fig.3b. The coating is composed of V and C elements without other impurities, and the mass fraction is V=89.45%, C=10.55%, and the atomic fraction is V=66.66%, C=33.34%, which is the main reasons for that VC coating has a high hardness. The microhardnesses of coating surface and substrate surface are 30500~32000 MPa and 5000~5500 MPa under the loading of 2 N for 15 s, respectively, measured by HXD-1000 type micro hardness tester, forming the function hardness gradient that improved effectively the surface resistance strain capacity and the surface quality of forming die.

The phase structure was analyzed with D/max2500PC type X-ray diffraction, the test parameters were: Cu target Kα radiation (λ=0.15418 nm), pipe voltage of 40 kV, current of 100 mA. The results are shown in Fig.4, and there is single VC phase with a little amount of V_8C_7 and C atoms, no brittle α-FeV phase, which is the same result as energy spectrum analysis.

2.2 XPS analysis of the surface

XPS energy spectrum analysis was conducted with Thermo ESCALAB 250 type X-ray photoelectron spectroscopy instrument. The test parameters were: monochrome Al Kα (*hv*=1486.6 eV), power of 150 W, X-ray beam spot of 500 μm, and fixing through analyzed energy of 30 eV. The surface elements of XPS full spectrum are shown in Fig.5a, where V 3p, V 3s, C 1s, V 2p and V 2s signals are detected. The existence form of the surface elements shows that the surface is mainly composed of V and C, which is the same as the EDS result.

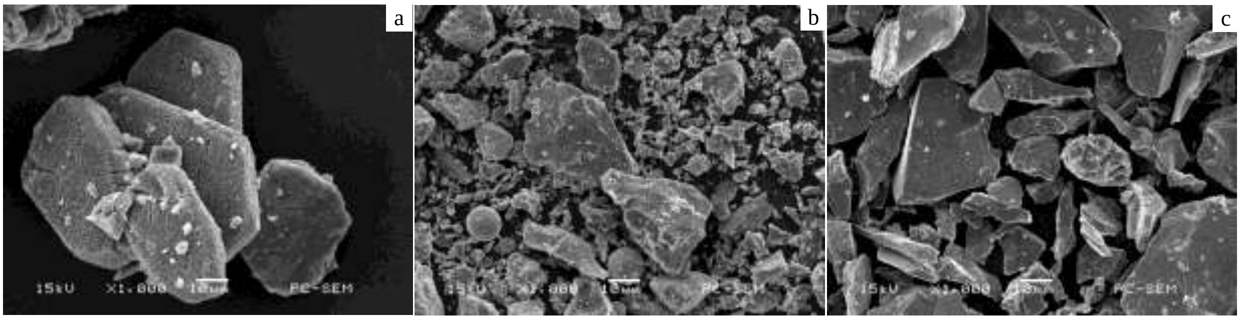

Fig.1 Surface morphologies of the salt raw materials: (a) borax, (b) silicon iron powder, and (c) vanadium iron powder

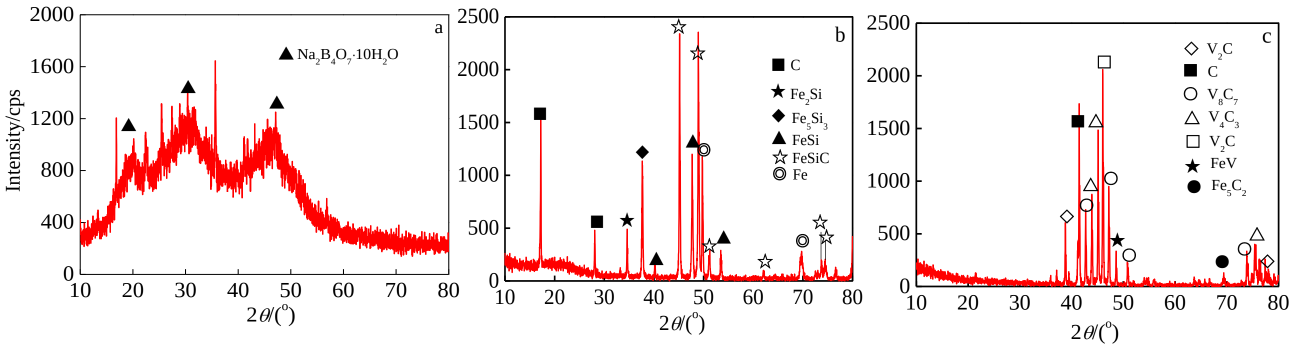

Fig.2 XRD patterns of the raw materials: (a) borax, (b) silicon iron powder, and (c) vanadium iron powder

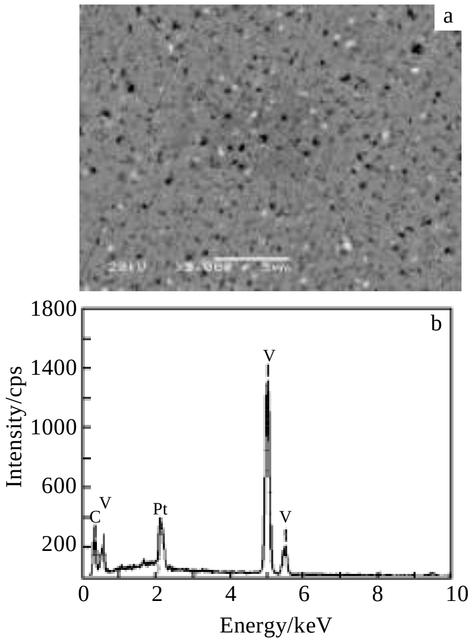

Fig.3 Surface morphology (a) and EDS analysis (b) of VC coating

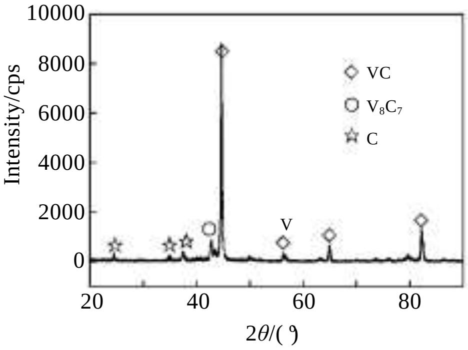

Fig.4 XRD analysis of VC coating

The electron binding energy of V is 512.8 eV (Fig.5b), V $2_{p3/2}$ peak appears in 512.8 eV, and the full width at half maximum (FWHM) is 1.6 eV. Besides, another 520.4 eV also appears in V $2_{p1/2}$ peak place, corresponding to V^{4+} and V^{5+}. Element V comes from the salt bath furnace FeV, and the wide cavitation phenomenon of V core level does not happen obviously [10]. C 1s peak appears in 282.2, 283.31 and 285.12 eV (Fig.5c), and the full widths at half maximum (FWHM) are 0.82, 1.62 and 1.44 eV, respectively, while the peak of 282.2 eV is C, coming from the Cr12MoV whose C content is 1.45%~1.70% with mass fraction corresponding to the VC coating in Ref[11], and there is no other element, showing the coating is made of V and C whose existence form is VC, not the forming of clearance atoms with V solid solution.

2.3 Plane scans of the surface

The plane scans of V and C are shown in Fig.6a and 6b, The surface is rich in V and C. Because the lattice constant of VC coating is 0.4160 nm, while that of Cr12MoV is 0.35 797 nm, there is a relatively small difference and good compatibility. Therefore, during the diffusion process it is easy to grow through combination attachment, forming the VC carbide structure. The result of plane scan is shown in Fig.6c, and the atomic fraction is V 35.52 as well as C 64.48, where the content of C is about twice as large as that of V element. The composition of the coating is uniform and there are no sudden element changes. Combining with Fig.3a, it can be seen that V and C are mainly distributed with the particles in Fig.6a and 6b, which ensures that VC compound is composed of V and C particles.

2.4 Plane scans of the interface

The coating is rich in V while the substrate is rich in Fe, which leads to the formation of diffused layer near the bonding interface. Therefore, the metallurgical bonding is realized. The different elements play different roles in the transition layer of interface. In this system, the activity of chemical elements is: C＞Si＞V＞Cr＞Fe＞Mo. In the salt bath, the replacement reaction of V in salt bath with C occurs, the C in the substrate diffuses to the substrate surface, and it reacts with V atoms in salt at 770 ℃ to form VC, and FeV + C = VC + α-Fe [3]. When the temperature is up to 1200 ℃, the rest V will continue to finish the unfinished carbonization reaction, the solid solution VC is formed from VC, and its grain is bulky. From Table 1, it can be seen that Fe has certain diffusion ability because of its

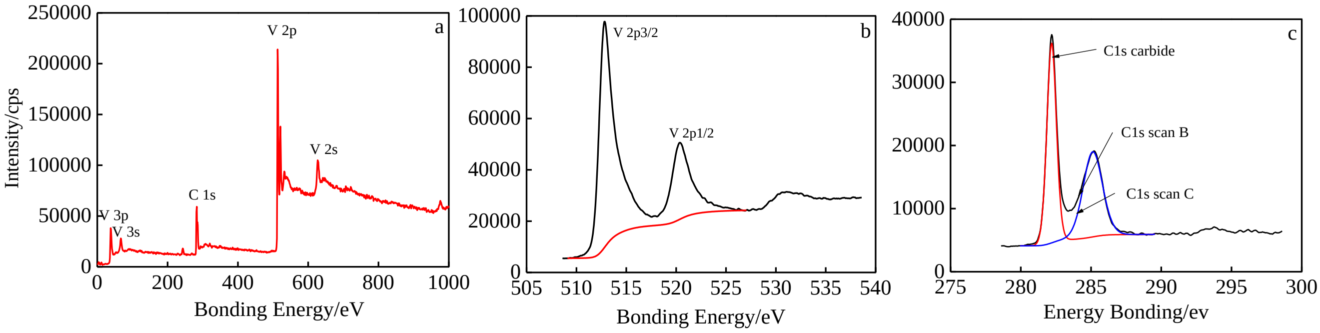

Fig.5 XPS spectra of VC coating surface: (a) full spectrum, (b) spectrum of V element, and (c) spectrum of C element

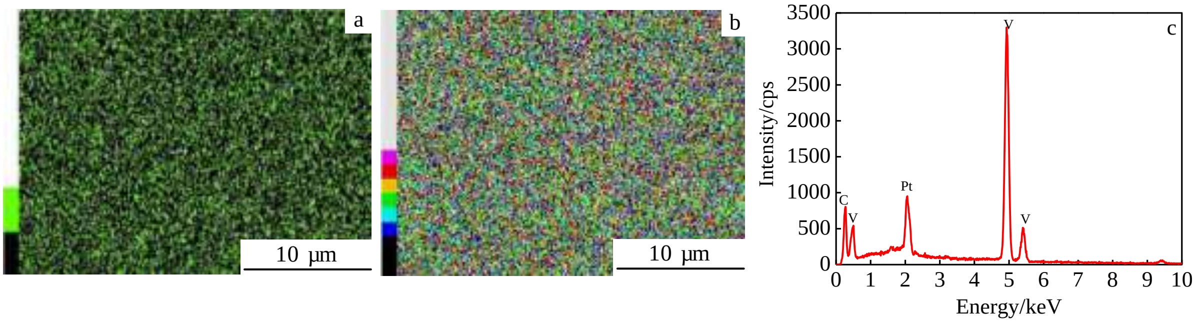

Fig.6 Plane scans of VC coating surface C (a), V (b), and EDS spectrum (c)

smaller atomic radius, and a metallurgical bonding is formed in interface diffusion layer[12]. As the chemical activity of V is greater than that of Fe, the diffusion of Fe in VC is limited, at the same time, the radius of C atom is much smaller than that of V, which makes C atom successfully diffuse to the coating, and it is the source of the generation element. The radii of Cr, Mo and Si atoms are exactly the same as that of V atom, because its diffusion coefficient is small, and it is difficult to diffuse in the coating. Therefore, in the interface of VC there exists mainly the diffusion among C, V and Fe, which is the main mechanism of forming metallurgical bonding at VC coating interface.

During the thermal diffusion, the mutual diffusion between V and C happens, and VC coating is formed in the substrate surface. Fig.7a shows the morphology of VC coating interface with the thickness of about 5 μm, whose density and continuity are very well to form a completely covered layer. The diffusion between the coating and the substrate is significant, indicating that the coating interface is metallurgical combination mode. The plane scans of energy spectrum are shown in Figs.7b and 7c. In the VC coating, V and C are uniformly distributed, and mainly concentrated on the coating, and some V in the coating spread to the substrate side in the interface diffusion layer. Fe in the substrate diffuses to the interface diffusion layer. The solid-phase reaction is increased significantly when the temperature is up to 870 ℃ and Cr in the interface begins to diffuse and a reaction takes place in interface[13]. As it is fully spread to present the continuous distribution pattern in the interface and promote the gradient distribution of chemical composition, a gradient change of structure and performance occurs[14]. Cr is uniformly distributed near the interface, which is beneficial to realize the metallurgical bonding. In the process of diffusion, Cr is body centered

Table 1 Atom radii and coefficients of thermal expansion

Chemical elements	Atom radius/nm	Coefficients of thermal diffusion
Fe	0.126	11.8
V	0.192	8.4
C	0.077	7.1
Cr	0.185	4.9
Mo	0.201	4.8
Si	0.117	2.6

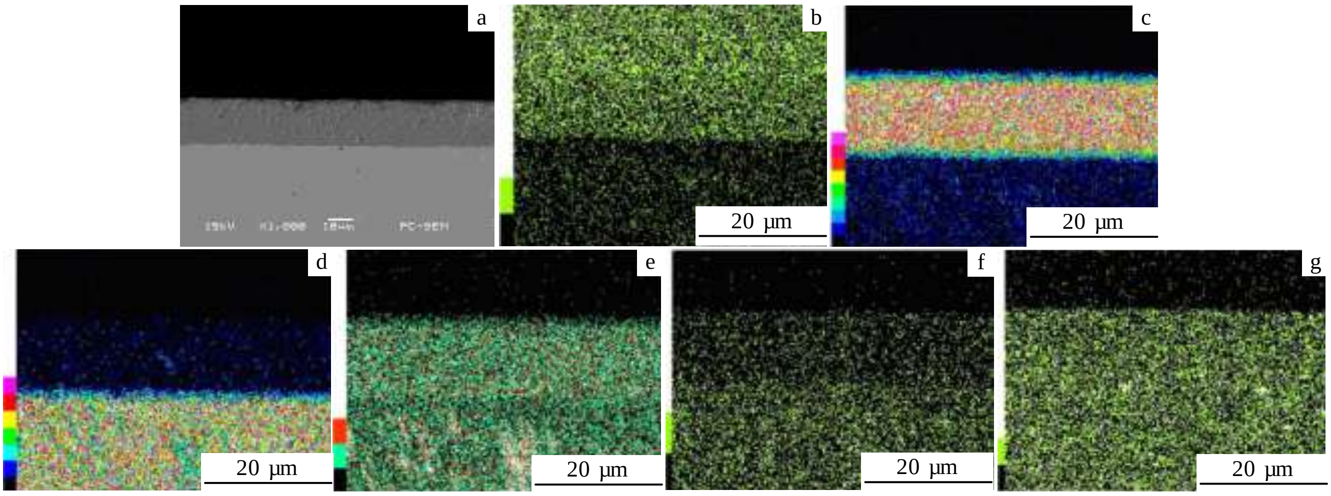

Fig.7 morphology of VC coating interface (a), and EDS plane scans of VC coating interface: (b) C, (c) V, (d) Fe, (e) Cr, (f) Mo, and (g) Si

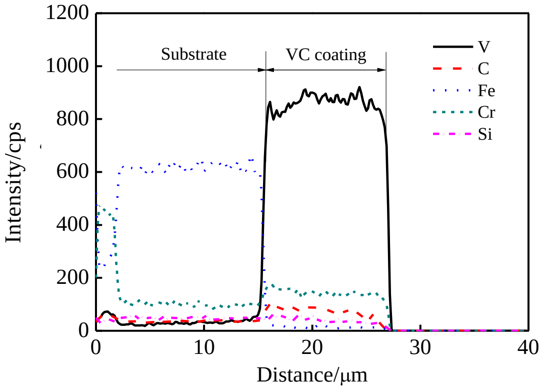

Fig.8 Line scans of VC coating interface

cubic dot matrix and hard to form the substitutional solid solution with Fe, and it is relatively difficult to diffuse in the substrate [15]. Fe and Cr have an obvious boundary, shown in Figs.7d and 7e. V and Fe atoms in the interface change sharply and smoothly between the coating and the substrate. In the interface layer, V and Fe generate Fe-V intermetallic. From Fe-V phase diagram[16], it is known that FeV would dissolve in α-Fe at about 1373 K, forming the interstitial solid solution (α-Fe, V) [17]. The Mo and Si atoms in the substrate are mainly distributed in the substrate which are out of the coating, Mo and Si almost do not diffuse relatively to the V atoms in coating, as shown in Fig.7f and 7g, and there is no apparent diffusion.

2.5 Line scan of the interface

As shown in Fig.8, V is concentrated in one side of interface and V content presents a continuous belt gradient distribution in coating interface diffusion layer while it is evenly distributed both in the coating and in the substrate. The contents of V and Fe change greatly in the bonding interface, while V and C form VC phase. Fe is riched in the substrate, the diffusion layer of interface appears corresponding concentration gradient step, while the other elements have the more even distributions.

3 Conclusions

1) VC coating prepared by TD process is composed of V and C which is a single VC phase, and the surface microhardness reaches 30500~32000 MPa.

2) V atomic electrons energy is 512.8 eV, exists in V^{4+} and V^{5+}, while C atomic electrons energy is 282.2 eV, without any other element existence.

3) VC coating interface is an interface diffusion layer formed by mutual diffusion among V, C and Fe, which is the main mechanism of metallurgical combination at VC coating interface.

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TD 处理制备的 VC 涂层 XPS 谱与 EDS 面扫描分析

孔德军[1, 2]，王进春[1]，郭皓元[1]

(1. 常州大学，常州 213164)

(2. 江苏省材料表面科学与技术重点实验室，常州 213164)

摘　要：以无水硼砂、FeV50和FeSi45为主要原料，通过TD和扩散处理在Cr12MoV基体表面制备了VC涂层。利用扫描电镜(SEM)、X射线衍射(XRD)、X射线光电子能谱(XPS)和能谱分析(EDS)等手段对VC的组织结构和化学元素分布进行了表征。用能谱面扫描分析了VC涂层表面和界面化学元素分布，对其界面冶金结合机理进行了探讨。结果表明，VC涂层为C和V两元素组成的化合物，其中V原子浓度大约是C原子的2倍；VC涂层为单一的VC相，V元素电子结合能位于512.8 eV，C元素电子结合能位于282.2 eV；V、C和Fe等元素在涂层界面处发生了相互扩散，形成了界面扩散层，涂层-基体结合界面为冶金结合方式。

关键词：VC 涂层; TD 处理; 结合界面

作者简介：孔德军，男，1966年生，博士，教授，常州大学机械工程学院，江苏 常州 213164，电话：0519-83290205，E-mail: kong-dejun@163.com