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Effects of surface roughness of substrate on properties of Ti/TiN/Zr/ZrN multilayer coatings

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Abstract: Ti/TiN/Zr/ZrN multilayer coatings were deposited on $Cr_{17}Ni_2$ steel substrates with different surface roughnesses by vacuum cathodic arc deposition method. Microstructure, micro-hardness, adhesion strength and cross-sectional morphology of the obtained multilayer coatings were investigated. The results show that the Vickers hardness of Ti/TiN/Zr/ZrN multilayer coating, with a film thickness of 11.37 μm, is 29.36 GPa. The erosion and salt spray resistance performance of $Cr_{17}Ni_2$ steel substrates can be evidently improved by Ti/TiN/Zr/ZrN multilayer coating. The surface roughness of $Cr_{17}Ni_2$ steel substrates plays an important role in determining the mechanical and erosion performances of Ti/TiN/Zr/ZrN multilayer coatings. Overall, a low value of the surface roughness of substrates corresponds to an improved performance of erosion and salt spray resistance of multilayer coatings. The optimized performance of Ti/TiN/Zr/ZrN multilayer coatings can be achieved provided that the surface roughness of $Cr_{17}Ni_2$ steel substrates is lower than 0.4 μm.
Key words: Ti/TiN/Zr/ZrN multilayer coatings; surface roughness; sand erosion resistance; corrosion resistance; vacuum cathodic arc deposition; TiN; ZrN

1 Introduction

Due to the outstanding properties such as high hardness, superior wear resistance and excellent heat stability [1,2], metallic nitride coatings deposited by physical vapor deposition (PVD) technique have been broadly applied to industrial fields, especially for cutting tools and anti-wear die tools. For such kinds of coatings, one challenging issue is that voids cannot be ruled out during the deposition of columnar TiN and other similar metallic nitride coatings. This can lead to poor corrosion resistances of these coatings. Furthermore, inherent high hardness and internal stress can result in the fracture of these coatings during the process of sand erosion. All these issues together limit the potential applications of TiN and other binary nitrides in industries [3,4].

In recent years, extensive studies have been focused on how to improve the adhesion and erosion performances of TiN coatings. In general, hard coatings usually have poor erosion resistance because of their high fragilities. One way to balance the fragility is to design multilayer coatings. For example, ZHANG and LIU [5] demonstrated that TiN/Ti multilayer coatings can be used to improve the fretting fatigue resistance of the titanium alloy at elevated temperature. KIM et al [6] studied the effect of the Ti buffer layer that was inserted in the middle of TiN film. Their results showed that the ductile Ti buffer layer can absorb impact energy and improve the adhesion performance of TiN coating. ULRICH et al [7] found that superb corrosion resistance and erosion resistance of composite coatings can be obtained by adjusting the thickness of TiN/ZrN multilayer coating and the interlayer structure. SONG et al [8] studied the influence of the modulation period of Ti/TiN multilayers on their structure and corrosion properties. The corrosive resistance of multilayer can be improved by short modulation period. In addition, gradient structures [9,10] can also effectively eliminate the sharp interface, thus improve the

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strength, toughness and adhesion of coatings.

In general, previous studies usually focused on the preparation of multilayer coatings from the perspective of basic scientific research. Therefore, they were far from actual industrial applications. In addition, few work focused on the effect of the surface roughness of substrates. However, the surface roughness of substrates plays a key role in determining the physical properties of multilayer coatings. Therefore, a deep insight into the relation between surface roughness and physical properties should be conducted. In this work, Ti/TiN/Zr/ZrN multi-composition and multilayer coatings with alternant soft and hard structure were prepared by vacuum cathodic arc deposition method, and the relation between surface roughness of substrate and corrosion properties of multilayer coatings was examined.

2 Experimental

2.1 Sample preparation

Rectangular blocks of $Cr_{17}Ni_2$ stainless steel with a size of 50 mm × 25 mm × 5 mm were used as substrates. To evaluate the influence of the surface roughness of substrate, substrates with surface roughness (R_a) of 1.348, 0.435, 0.326 and 0.037 μm were used. They were ultrasonically cleaned with 5% (volume fraction) metal cleaning agent, deionized water and then dried by dehydrogenation drying equipment in sequence. Ti/TiN/Zr/ZrN multilayer coatings were prepared by auto-control vacuum cathodic arc deposition equipment using AS700DTX. There are total 12 circular targets in the chamber, in which 8 targets are titanium (99.9%, mass fraction) and other 4 targets are zirconium (99.9%, mass fraction). Before deposition, substrates were cleaned by plasma using a high bias voltage of −1000 V for 25 min. A mixture of high purity (99.999%, volume fraction) Ar and N_2 gases were introduced into the chamber as working gas. Titanium and zirconium targets worked alternately which were controlled by computer. Ti/TiN/Zr/ZrN coatings with seven cycles were obtained. The deposition current was 80 A for titanium targets and 100 A for zirconium targets. A negative bias voltage of 100−150 V was applied to the substrates and the deposition temperature was 300 °C. The flow rates of nitrogen gas were 500 and 700 mL/min for ZrN and TiN layers, respectively. For the preparation of metal layers, argon gas with a flow of 300 mL/min was applied.

2.2 Structural characterization

The cross-sectional morphology of the deposited multilayer coatings was examined by scanning electron microscopy (SEM) using JEOL JSM-5910. Microstructures of these multilayer coatings were characterized by Philips X’pert MPD diffractometer. The MD-5 hardness tester was employed to measure the Vickers micro-hardness under a load of 0.245 N for 15 s. The adhesion strength was tested by HH-3000 scratch tester. During scratch measurement, a maximum load of 100 N, loading speed of 100 N/min and scratching speed of 5 mm/min were applied. Erosion test was conducted under self-designed AS600 sandblast tester following the ASTM standard G76-07. Alumina (Al_2O_3) powder with an average size of 50 μm was employed as abrasive particles. A particle velocity of (30±2) m/s, and an average particle feed rate of (2±0.5) g/min were used in each test. The impingement angle of particle-air stream towards the coated specimens was set at (30±2)°. The depth of erosion pits was measured by BMT Expert 3D profilometer. Corrosion test was carried out following the Chinese National Standard GB/T 10125—1997 by MC-952C salt spray tester in a neutral salt mist solution. The surface roughness of substrates was measured by TR200 hand roughness instrument.

3 Results and discussion

3.1 Microstructure and properties of coatings

The XRD pattern of the deposited multilayer coatings is shown in Fig. 1. The coating is mainly composed of Ti, TiN, Zr and ZrN. Impurity phases are not observed. As a top layer, the strongest peak corresponds to the (111) plane of ZrN with a FCC structure. The sub-strongest peak is indexed to the (111) plane of TiN, confirming the formation of layered structures. The results agree with the previous works [11].

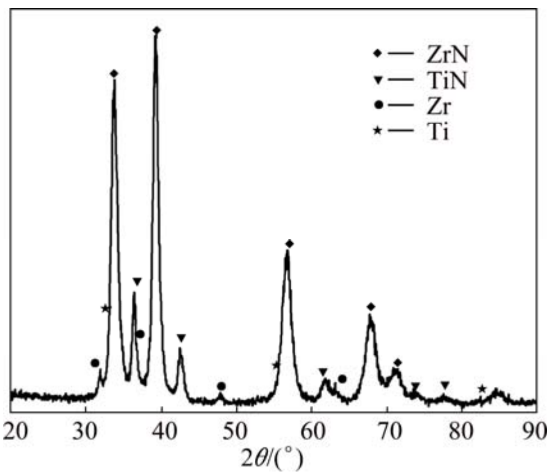

Fig. 1 XRD pattern of Ti/TiN/Zr/ZrN multilayered coatings

Figure 2 shows the cross-sectional morphologies of Ti/TiN/Zr/ZrN multilayer coatings on $Cr_{17}Ni_2$ steel substrates with different surface roughnesses. Uniform and dense morphologies can be observed without

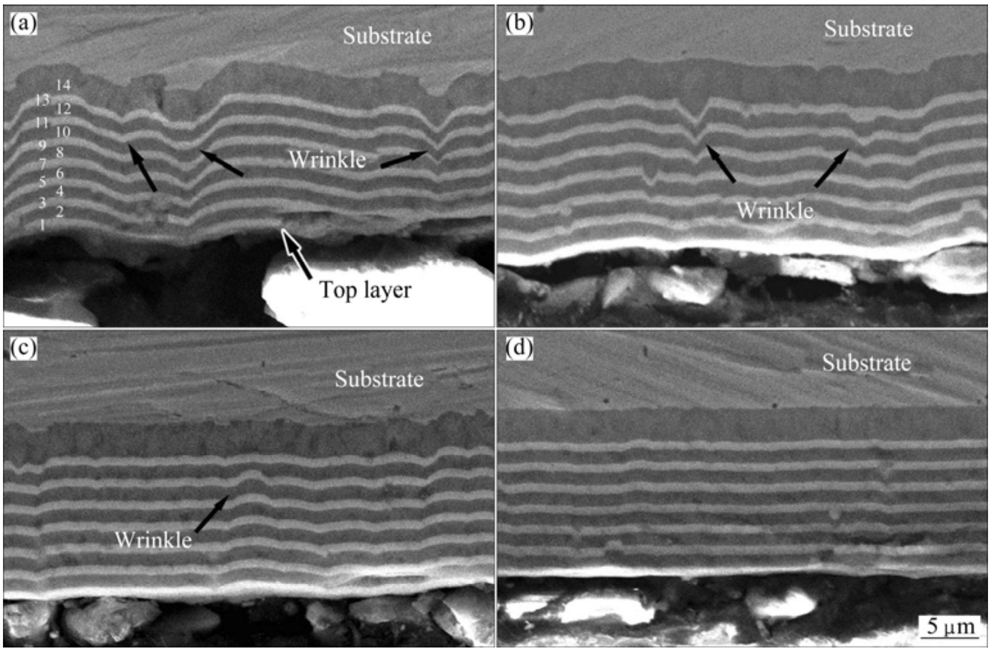

Fig. 2 Cross-sectional SEM images of Ti/TiN/Zr/ZrN multilayered coatings prepared on different surface roughness substrates: (a) R_a=1.348 μm; (b) R_a=0.435 μm; (c) R_a=0.326 μm; (d) R_a=0.037 μm

columnar structure. The alternative dark and bright layers correspond to Ti/TiN and Zr/ZrN, respectively. Ti/TiN/Zr/ZrN layers with seven periods can be clearly seen, in which the thickness of the Ti/TiN or Zr/ZrN layer is ~1.4 μm. The corresponding layers are numbered in Fig. 2(a). The cross-sectional morphology becomes more uniform and integrity as the substrate roughness decreases. When the substrate roughness is higher than 0.4 μm, the obvious wrinkles and waves can be observed as indicated by arrows in Figs. 2(a) and (b). The boundary between Ti/TiN and Zr/ZrN layers is straight and parallels with each other when the substrate roughness is lower than 0.4 μm as shown in Figs. 2(c) and (d). The volume fraction of metal in nitride layer is approximately 44% estimated from SEM images. Thin and plastic metal layers are generally used to release the impact force cumulated on hard nitride layers [12].

SEM image of Ti/TiN/Zr/ZrN multilayer coatings with high magnification indicates that columnar growth is inhibited and multilayer coatings become fine and dense as shown in Fig. 3. This can be explained as follows. The columnar structure is easily formed in single layer coatings of TiN (or ZrN). However, the columnar grains can be re-grown with the composition conversion of Ti/TiN/Zr/ZrN multilayer structure. As a result, the columnar grain growth is significantly inhibited and coatings become fine and dense. The thicknesses of metal and nitride layers are approximately 71 nm and 145 nm, respectively. Generally, droplets are hardly avoided during the deposition of Ti/TiN coatings using the vacuum cathodic arc technique. However, the

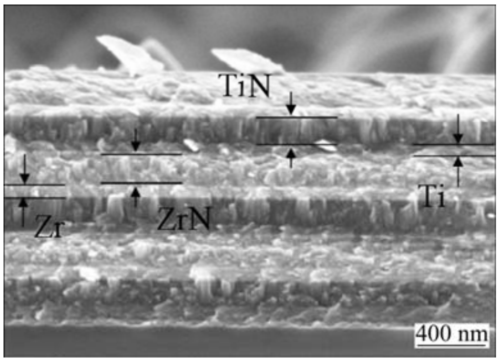

Fig. 3 High magnification SEM image of Ti/TiN/Zr/ZrN multilayer coatings

SEM images indicate that there are only several droplets in multilayer coatings. The absence of droplets should be in favor of the good corrosion resistance [13].

Different from bare $Cr_{17}Ni_2$ steels with the roughness of 1.348 μm, 0.435 μm, 0.326 μm and 0.037 μm, coated $Cr_{17}Ni_2$ steel substrates are very smooth, and the corresponding surface roughnesses (R_a) are 0.5, 0.38, 0.35 and 0.25 μm, respectively. The similar values indicate that thick coatings can repair the substrate surface and have a relatively smooth surface. In addition, the micro-hardness of these Ti/TiN/Zr/ZrN multilayers is about 29.36 GPa, showing good mechanical properties.

3.2 Impact of surface roughness of substrate on adhesion strength

The scratch testing was carried out to estimate the adhesion strength of Ti/TiN/Zr/ZrN multilayer coatings.

The adhesion properties of the multilayer coatings are usually characterized by L_{C1} and L_{C2}. L_{C1} is associated with the start of chevron cracking, indicating cohesive failure in the coating. L_{C2} is related to the initiation of chipping failure extending from the arc tensile cracks, indicating adhesive failure between coatings and substrates. Therefore, L_{C2} can be used to evaluate the adhesion strength of coatings. Figure 4 shows the scratch morphologies of Ti/TiN/Zr/ZrN multilayer coatings with different surface roughnesses. The adhesion forces of the coatings, corresponding to the substrate roughness (R_a) of 1.348, 0.435, 0.326 and 0.037 μm, are 31, 46, 53 and 58 N, respectively. The results indicate that the adhesion force increases as the substrate surface roughness decreases. Generally, thick multilayer coatings always lead to weak adhesion strength. Here, the adhesion force of Ti/TiN/Zr/ZrN multilayer coatings with the thickness of 11.37 μm can reach up to 58 N when the roughness is less than 0.40 μm. For comparison, the same adhesion force is obtained for TiN/ZrN multilayer coatings with a small thickness of 3 μm [14]. It may be due to the low stress in the Ti/TiN/Zr/ZrN multilayers produced by metal layers.

3.3 Impact of surface roughness of substrate on erosion resistance

Erosion pits can be observed when $Cr_{17}Ni_2$ stainless steel was tested by sand erosion. Figure 5 shows the erosion pits depth for Ti/TiN/Zr/ZrN coated and bare $Cr_{17}Ni_2$ stainless steels (R_a=0.4 μm). The depth of erosion pits for Ti/TiN/Zr/ZrN coated $Cr_{17}N_2$ steel is about 4 times lower than that of bare $Cr_{17}Ni_2$ stainless steel, indicating the significant improvement of erosion resistance after surface coating. This is mainly because of the alternated soft and hard mutilayers, from which the relative soft metal layers are inserted into hard metal nitride ceramic layer. The soft metal layer acts as a buffer and resists the propagation of cracks when suffered external force, thus effectively improving the sand erosion resistance of $Cr_{17}Ni_2$ stainless steel.

During the process of sand erosion, abrasive particles were continuously ejected and impinged on the coating surfaces till that erosion pits emerged. The sand erosion resistance was evaluated by the mass of abrasive particles. Surface macrographs of eroded coatings with different surface roughnesses of substrate are presented in Fig. 6. For the coatings deposited on substrates with roughness of 1.348 μm, the erosion pits appear when the abrasive particle mass reaches up to 300 g. The damaged region is relatively large and occurs at the location of machining processing stripe. Furthermore, the alternant Ti/TiN and Zr/ZrN layers are hard to be distinguished. Figure 6(b) shows the erosive appearance of coatings with the substrate surface roughness of 0.435 μm, from which the damage is observed with the abrasive particle mass of 500 g. Similar sand erosion resistance can be obtained when the substrate surface roughness decreases down to 0.326 μm as shown in Fig. 6(c). The alternant Ti/TiN and Zr/ZrN layers in Fig. 6(d) can be clearly observed when the substrate roughness decreases down to 0.1 μm. The abrasive particle mass increases greatly up to 800 g. These results indicate that good erosion resistance can be obtained on $Cr_{17}Ni_2$ stainless steel with low surface roughness. The alternant Ti/TiN and Zr/ZrN layers with seven periods are clearly distinguished in the eroded region.

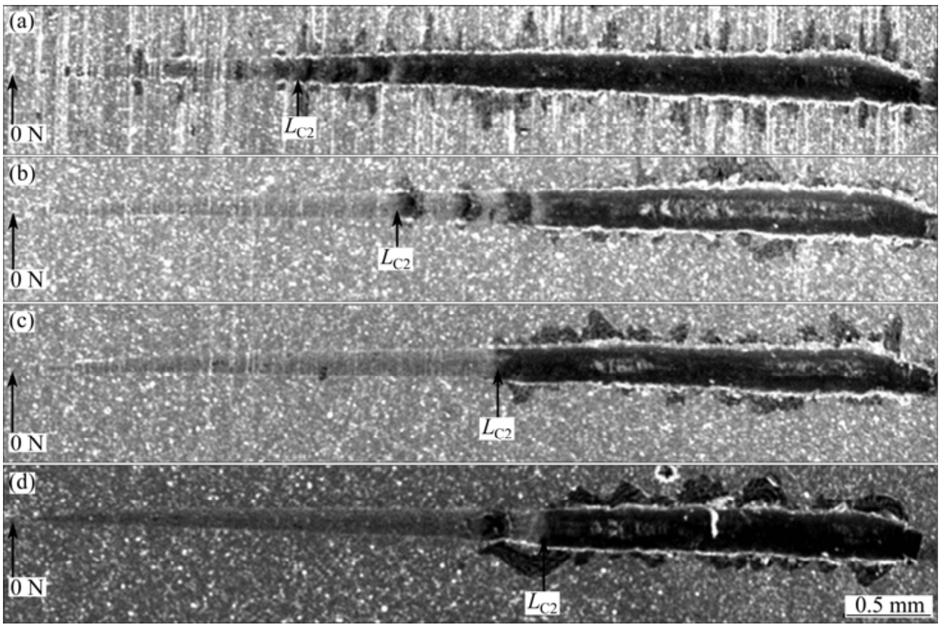

Fig. 4 Scratch morphologies of Ti/TiN/Zr/ZrN multilayered coatings on different surface roughness substrates: (a) R_a=1.348 μm; (b) R_a=0.435 μm; (c) R_a=0.326 μm; d) R_a=0.037 μm

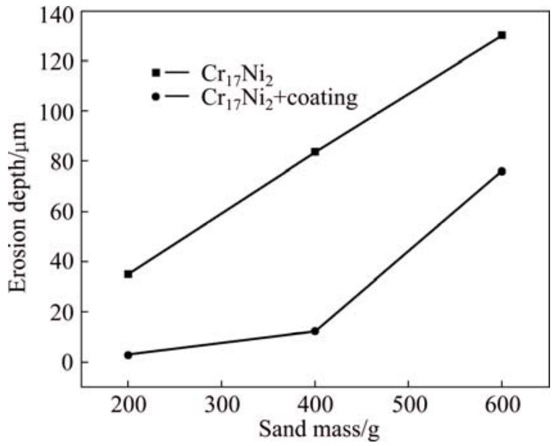

Fig. 5 Comparison of anti-erosion performance between Ti/TiN/Zr/ZrN coating and $Cr_{17}Ni_2$ substrate

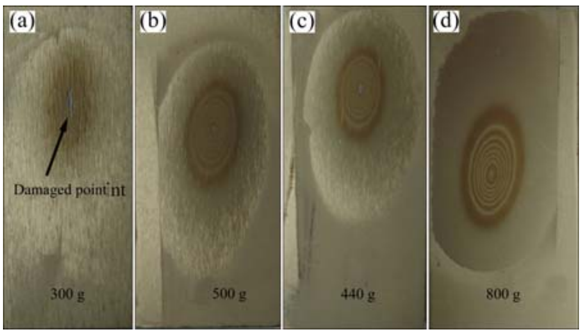

Fig. 6 Macrographs of sand eroded Ti/TiN/Zr/ZrN multilayered coatings on different surface roughness substrates: (a) R_a=1.348 μm; (b) R_a=0.435 μm; (c) R_a=0.326 μm; (d) R_a=0.037 μm

The results illustrate that the sand erosion resistance of the coatings can be greatly affected by the surface roughness of the substrate even under the same conditions. The sand erosion resistance can be improved by decreasing the surface roughness of the substrate. When the substrate surface roughness is less than 0.1 μm, the Ti/TiN/Zr/ZrN coatings show better erosion resistance. Previous work showed that a certain anti-high temperature erosive wear coating with the thickness of 8−40 μm was developed [15]. However, the coating was broken under the small abrasive particle mass of 140 g under the same testing conditions. In contrast, the Ti/TiN/Zr/ZrN multilayer coatings show better erosion resistance when the substrate roughness is less than 0.4 μm.

3.4 Impact of surface roughness of substrate on corrosion resistance

The corrosive appearance of multilayer coatings after 96 h salt spray test is presented in Fig. 7. Rusty spots can be observed on the Ti/TiN/Zr/ZrN coatings with the substrate roughness of 1.348 μm after 24 h. The same phenomena appear on the coatings with the substrate roughness of 0.435, 0.326 and 0.037 μm after 72, 96 and 96 h, respectively. Relatively, rusty corrosion products are identified on $Cr_{17}Ni_2$ steel substrate (0.435 μm) after 48 h, a half shorter than that of the coated samples. The corrosion resistance properties of the Ti/TiN/Zr/ZrN coatings can be weakened as the surface roughness of the substrate increases. The results here indicate that the long salt spray corrosion can be obtained only when the surface roughness is controlled in the range of 0−0.40 μm.

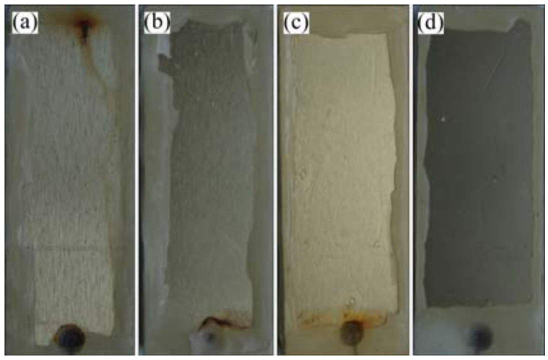

Fig. 7 Macrographs of Ti/TiN/Zr/ZrN multilayered coatings after 96 h neutral salt spray test on different surface roughness substrates: (a) R_a=1.348 μm; (b) R_a=0.435 μm; (c) R_a=0.326 μm; (d) R_a=0.037 μm

As mentioned above, these Ti/TiN/Zr/ZrN multilayer coatings were deposited under the same deposition parameters except for the surface roughness of substrates. The surface roughness of the substrate contributes to the improvement of erosion and corrosion resistance properties of Ti/TiN/Zr/ZrN multilayer coatings. Generally, multilayer structure is employed to inhibit the growth of cracks and thereby increases the coatings corrosion and erosion resistance [16]. This effect is attributed to the variation of the adhesive strength and the cross-sectional morphologic properties between adjacent layers, which originates from different surface roughness of substrate in the present work.

The basic mechanism can be understood as follows. Firstly, small substrate roughness facilitates the adhesion strength, and Ti/TiN/Zr/ZrN multilayer coatings can tolerate large impact stress if the surface roughness of substrate is low. The large adhesion strength and strong interfaces between the adjacent layers can reduce the nucleation of cracks and their propagation, prohibiting the failure of coatings. Secondly, the integrality of the adjacent metal/nitride layers in the coatings can be significantly improved by reducing the surface roughness of substrate. The wrinkles and waves formed on rough substrate would become the original failure points when suffering sand erosion [17]. Furthermore, the smooth interfaces between metal and nitride are also in favour of preventing the introduction of external corrosive species. To sum up, multilayer coatings on smooth substrate can constrain the growth of wrinkles together with the droplets. Thus, the penetrated cracks are greatly reduced.

4 Conclusions

1) Ti/TiN/Zr/ZrN multilayer coatings are successfully prepared by vacuum cathodic arc deposition technique. The film thickness is ~11.37 μm and the Vickers hardness is 29.36 GPa. XRD result indicates that the multilayer film mainly contains ZrN and TiN phases, including a small amount of Zr and Ti phases.

2) The sand erosion resistance and salt spray corrosion resistance of $Cr_{17}Ni_2$ substrates can be effectively improved by Ti/TiN/Zr/ZrN multilayer coatings.

3) The performance of multilayer coatings is affected by the surface roughness of substrate. The decrease of the surface roughness of substrate results in better mechanical and adhesion properties of Ti/TiN/Zr/ZrN multilayer coatings. The optimized performance of Ti/TiN/Zr/ZrN multilayer coatings can be achieved provided that the surface roughness of substrates is lower than 0.4 μm.

References

[1] SUBRAMANIAN B, ASHOK K, SELVAN G, KUMAR V S, JAYACHANDRAN M. Effects of deposition temperature on materials properties of magnetron sputtered titanium nitride coatings on mild steel substrates with Ni interlayer [J]. Surface Engneering, 2010, 26: 555−561.

[2] CHIPATECUA Y L, OLAYA J J, DIEGO F A. Corrosion behaviour of CrN/Cr multilayers on stainless steel deposited by unbalanced magnetron sputtering [J]. Vacuum, 2012, 86: 1393−1401.

[3] PIETERS R, LIU S. Shortlisted-particle erosion resistance of laser nitrided Ti−6Al−4V [J]. Surface Engneering, 2001, 17: 159−162.

[4] BAYON R, IGARTUA A, FERNANDEZ X, MARTINEZ R, RODRIIGUEZ R J, GARCIA J A, FRUTOS A, ARENAS M A, DAMBORENEA J. Corrosion-wear behaviour of PVD Cr/CrN multilayer coatings for gear applications [J]. Tribology International, 2009, 42: 591−599.

[5] ZHANG Xiao-hua, LIU Dao-xin. Effect of TiN/Ti multilayer on fretting fatigue resistance of Ti-811 alloy at elevated temperature [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(3): 557−562.

[6] KIM G S, LEE S Y, HAHN J H. Effects of the thickness of Ti buffer layer on the mechanical properties of TiN coatings [J]. Surface and Coating Technology, 2003, 171(1): 83−90.

[7] ULRICH S, ZIEBERT C, STUBER M. Correlation between constitution, properties and machining performance of TiN/ZrN multilayers [J]. Surface and Coatings Technology, 2004, 188−189(3): 331−337.

[8] SONG Gui-hong, LOU Zhuo, LI Feng, CHENG Li-jia. Structure and corrosion properties of Ti/TiN multilayers prepared by arc ion plating [J]. The Chinese Journal of Nonferrous Metals, 2012, 22(2): 509−514. (in Chinese)

[9] LIN Song-sheng, DAI Ming-jiang, ZHU Xia-gao, LI Hong-wu, HOU Hui-jun, LIN Kai-sheng, KUANG Min, DAI Da-huang. Growth and microstructure of CrTiAlCN multi-composite thin films[J]. The Chinese Journal of Nonferrous Metals, 2009, 19(2): 259−264. (in Chinese)

[10] SHUM P W, LI K Y, SHEN Y G. Improvement of high speed turning performance of TiA1N coatings by using a pretreatment of high-energy ion implantation [J]. Surface and Coating Technology, 2005, 198(3): 414−419.

[11] ARIAS D, DEVIA A, VELEZ J. Study of TiN/ZrN/TiN/ZrN multilayers coatings grown by cathodic arc technique [J]. Surface and Coatings Technology, 2010, 204: 2999−3003.

[12] HUANG J H,MA C H, CHEN H. Effect of Ti interlayer on the residual stress and texture development of TiN thin coatings deposited by unbalanced magnetron sputtering [J]. Surface and Coatings Technology, 2006, 201: 3199−3204.

[13] PAULITSCH J, MAYRHOFER P H, MUNZ W D, SCHENKEL M. Structure and mechanical properties of CrN/TiN multilayer coatings prepared by a combined HIPIMS/UBMS deposition technique [J]. Thin Solid Coatings, 2008, 517: 1239−1244.

[14] CAICEDO J C, AMAYA C, YATEC L. Hard coating performance enhancement by using [Ti/TiN], [Zr/ZrN], and [TiN/ZrN] multilayer system [J]. Materials Science and Engineering B, 2010, 171: 56−61.

[15] GTF Aerospace Inc. Turbine blade coating. [EB/OL]. 2012. http://www.gtfaerospace.com/attachments/053_Turbine%20Blade%20Coating EN.pdf

[16] BORAWSKI B, TODD J A, SINGH J, WOLFE D E. The influence of ductile interlayer material on the particle erosion resistance of multilayered TiN based coatings [J]. Wear, 2011, 271: 2890−2898.

[17] MATTOX D M. Surface effects on the growth, adhesion and properties of reactively deposited hard coatings [J]. Surface and Coatings Technology, 1996, 81: 8−16.

基体材料表面粗糙度对 Ti/TiN/Zr/ZrN 多层膜性能的影响

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摘 要：采用真空阴极电弧沉积技术，在 4 组表面粗糙度不同的 $Cr_{17}Ni_2$ 钢基体上制备 Ti/TiN/Zr/ZrN 多层膜。采用扫描电镜、X 射线衍射仪、显微硬度计、结合力划痕仪、砂粒冲刷试验仪和盐雾试验机分析测试多层膜的截面形貌、膜层厚度、相组成、硬度、膜/基结合力、抗砂粒冲刷性能和耐腐蚀性能等。结果表明：所制备的多层膜厚度为 11.37 μm，维氏硬度为 29.36 GPa；多层膜能显著地提高 $Cr_{17}Ni_2$ 钢基体的抗砂粒冲刷和耐盐雾腐蚀能力；基体材料表面粗糙度对膜层性能的影响很大，基体表面粗糙度越小，其膜/基结合力、抗砂粒冲刷性能和耐盐雾腐蚀性能越佳；为了获得具有良好综合性能的膜层，待表面处理的基体表面粗糙度必须控制在 R_a<0.40 μm。

关键词：Ti/TiN/Zr/ZrN 多层膜；表面粗糙度；抗砂粒冲刷性能；耐腐蚀性能；真空阴极电弧沉积；TiN；ZrN

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