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TiB_2/Ni coatings on surface of copper alloy electrode prepared by electrospark deposition

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Abstract: In order to improve the lifespan of spot-welding electrodes used for welding zinc coated steel sheets, titanium diboride was deposited onto their surface after precoating nickel as an intermediate layer. The microstructures and phase compositions of TiB_2 and Ni coatings were characterized by SEM and XRD. The coating hardness was measured using a microhardness tester. The results indicate that a satisfactory TiB_2 coating is obtained as a result of the intermediate nickel layer acting as a good binder between the TiB_2 coating and the copper alloy substrate. Owing to its capacity of deforming, the precoated nickel layer is dense and crack free, while cracks and pores are observed in the TiB_2 coating. The hardness of the TiB_2/Ni coating decreases with the increase of voltage and capacitance because of the diffusion of copper and nickel and the oxidation of the coating materials. Because of the good thermal and electrical conductivities and high hardness properties of TiB_2, the deformation of the electrode with TiB_2/Ni coating is reduced and its spot-welding life is by far prolonged than that of the uncoated one.

Key words: titanium diboride; electrospark deposition; copper; electrode; nickel; coating

1 Introduction

There has been a growing interest in improving the lifespan of spot-welding electrodes for zinc coated steel sheets. Two major methods are applied: one of which is related to matrix reinforcement by hard particles such as Al_2O_3, TiC, TiB_2 and Zr_2O_3; and the other is related to surface modification by ion injection of tungsten, surface titanizing and Co brushing. Among these methods, TiC coating prepared by electrospark deposition (ESD) is the most promising and research has proven that it is capable of prolonging the lifespan of electrodes[1]. While it seems to be unavoidable that cracks and delamination occur within the superhard TiC coating[2−4]. This can be reduced by using a patent rod[5] and an intermediate nickel layer[6]. Meanwhile, it provides an opportunity for the exploitation and development of TiB_2 coatings since TiB_2 is superior to TiC in terms of hardness, and electrical and thermal conductivities[7], which meet the requirements of the electrode. The present work was conducted on this basis and nickel was prepared as a transitional layer between the copper substrate and the TiB_2 coating to improve the poor wettability owing to its good intermiscibility with both of them.

2 Experimental

The substrate (cathode) of the ESD was a standard B nose domed flat electrode, which was precipitation strengthened and cold worked Cu-0.7Cr-0.2Zr alloy. The top surface of the substrate was cleaned with acetone before deposition. A specially sintered TiB_2-based (TiB_2-20Ni-7Co) ceramic rod with 7 mm in diameter and 20 mm in length, and a commercially pure nickel rod were used as the anodes. Deposition was carried out under the condition of a capacitance of 2 000 C, a voltage output of 16 V and a time of 120 s.

Phase compositions of the coatings were determined by X-ray diffraction (XRD) analysis with monochromatic Cu K_α radiation. The microstructure and compositions were determined by a scanning electron microscope (SEM) LEO1450VP equipped with an energy-dispersive spectrometer. Metallographic analysis was carried out with a Neophot32 optical microscope. The microhardness of the coating was measured with an

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MH−5 unit with a load of 1 N for 15 s.

3 Results and discussion

3.1 Precoated nickel

Fig.1 shows the top surface microphotographs of the precoated nickel coating with a coarse surface (Fig.1(a)). A slice in the centre of the enlarged image of Fig.1(a) is shown in Fig.1(b), which suggests the coating having a lamellar structure[8]. The slice is probably a result of the last single-pulse deposit.

The nickel coating is dense and crack free, and the cross-sectional image of the nickel coating reveals that there is no delaminating. It is a characteristic of cracks which are always observed when hard objects such as TiC, TiB_2, WC and Cr_7C_3 are coated by ESD. It is assumed that the hard materials are more difficult to deform than soft ones such as nickel. The pulse energy affects the as-deposited coating during electrosparking, and high frequent thermal shock attacks the coating, which results in thermal stress. This phenomenon occurs because of the different thermal conductivities of the coating and substrate. For a soft coating, the stress can be released easily by deformation; however, it is difficult for a brittle material to distort. Therefore, the residual stress in a ceramic material, such as the TiB_2 coating, will be accumulated to a certain degree until it is released by forming cracks. A continuous and dense nickel coating gained is helpful for being used as a beneficial transitional layer.

Optical microscopy shows that the precoated nickel layer is an uneven multi-layer structure[9], as shown in Figs.1(c) and (d). When cathode and anode materials are melted under the conditions of high temperature generated by electrosparking and mixed in the melting pool, an intermediate layer forms between the top surface of the coating and the substrate, which is a solid solution of copper (from the substrate) and nickel (from the coating). This layer is darker than the surface coating and the substrate when the specimen has been etched with 5% $FeCl_3$ solution (Fig.1(d)). It is because that the anticorrosion properties of a solid solution are poorer than those of the pure metals of which it consists.

Fig.2 shows the XRD pattern of the top surface of precoated nickel. The major phase of the top surface is Ni, while Cu is detected too. This is an evidence of the mixing of copper with nickel in a melting pool generated by electrosparking and the diffusion of copper to the surface afterwards. It is also a character of ESD.

3.2 TiB_2 coating structure

Fig.3(a)−(d) present the microphotographs of the TiB_2 coating deposited on the surface of the intermediate nickel layer. It is neither even nor dense, which is different from that of the nickel coating (Fig.1(b)). Cracks are clearly seen in the enlarged image (Fig.3(b)), and a crack is even cross-sectional, as shown in Fig.3(c). Pores and delamination appear at the interface (Fig.3(c)); however, it is much less than the coating without an intermediate nickel layer. This results from the intermediate nickel layer existing as a whole between the copper substrate and the surface coating

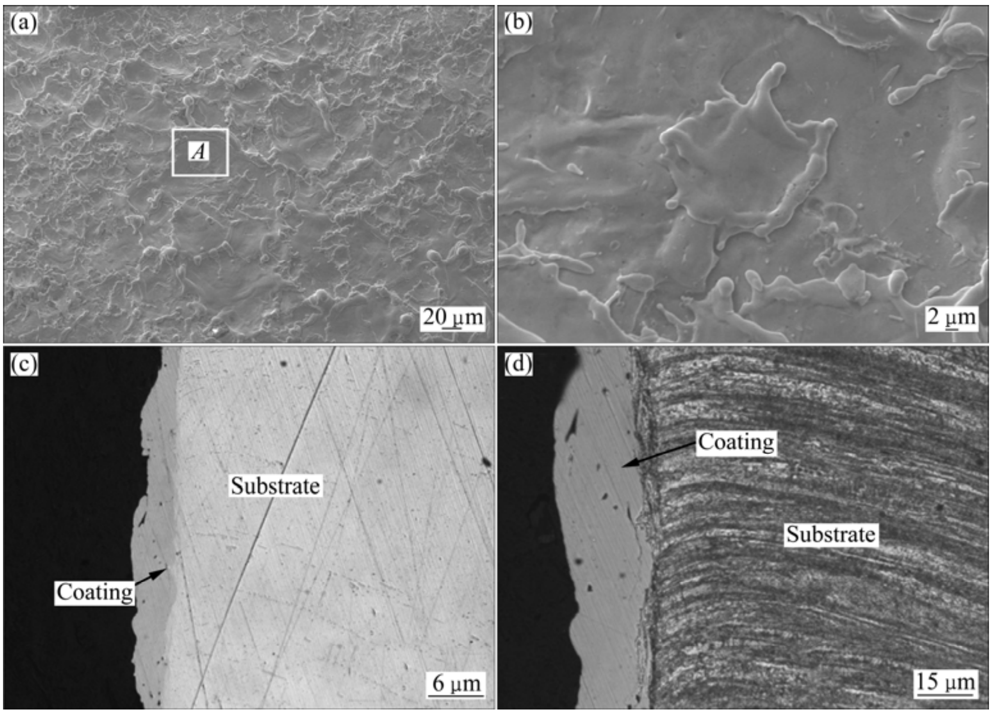

Fig.1 SEM images of surface of pre-coated nickel (a), enlarged area of *A* (b), cross section (c) and cross section etched with 5% $FeCl_3$ solution (d)

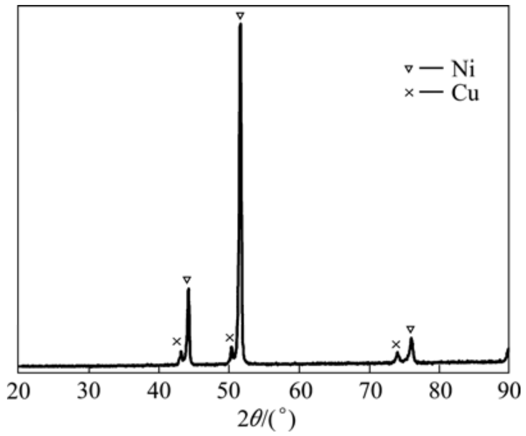

Fig.2 XRD pattern of top surface of precoated nickel

(Fig.3(d)), avoiding their direct contact.

The linear scanning results for the cross-section of TiB_2/Ni coating are presented in Fig.4. Copper and nickel have diffused into the top surface of the TiB_2/Ni coating. EDS shows that copper on the top surface is 8.0% and nickel is 2.3% (molar fraction). A solid atomic bonding between the coating and the matrix is formed consequently[10]. This suggests that nickel has acted as a good binder between the TiB_2 coating and the copper substrate. On one hand, the atomic radii of nickel and copper are 0.124 6 nm and 0.127 8 nm, respectively, and their electronegativities are 1.91 and 1.90. Since the atomic radii and electronegativities of Ni and Cu are very close to each other, they can resolve into each other completely. On the other hand, the wetting angle of nickel on TiB_2 is 64°, indicating that nickel can wet TiB_2, while TiB_2 cannot wet copper due to the wetting angle of copper on TiB_2 being 136°. Therefore, nickel is a good binder to connect TiB_2 with copper.

Since nickel has a good wettability with TiB_2, it should be rich within the coating. On the contrary, its concentration is very low, and it is not even observed in the XRD patterns of the coating, as seen in Fig.5. This happens in other researching works[3, 11]. A possible reason is that nickel may have evaporated at high temperatures generated by electrosparking and rest forms a non-crystal structure in cooling at a super high speed ($10^{-5}-10^{-6}$ K/s).

3.3 Spot-welding life

The spot-welding life of TiB_2/Ni coated electrode was tested using a spot-welding machine. Lives of uncoated and TiC coated electrodes were tested as comparisons. The decreases of their lives and average height (for each weld) are illustrated in Fig.6. The hardness of the uncoated, TiC and TiB_2/Ni coated electrodes are HV160, HV610 and HV520, respectively. The height decreases (wear) of the coating electrodes are reduced due to the existence of the high-hardness TiC and TiB_2. Due to the low thermal conductivity, TiC and TiB_2 coatings can also prevent the welding heat from transferring to the substrate of the electrodes. Therefore,

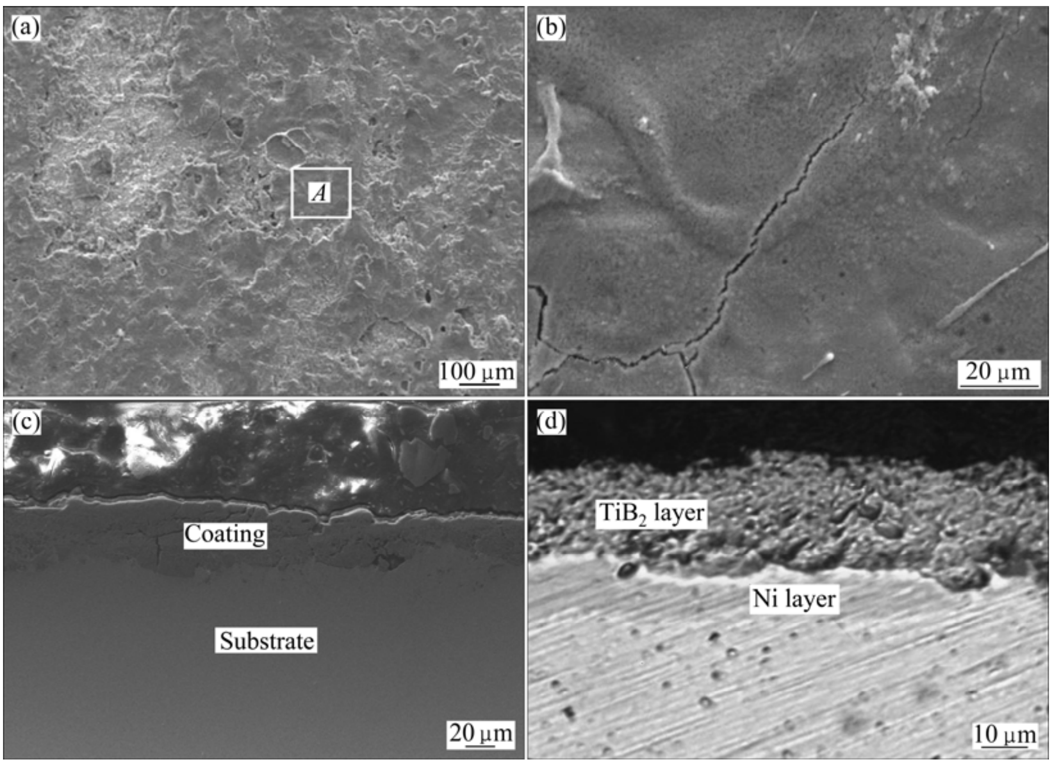

Fig.3 SEM images of TiB_2/Ni coating surface (a), enlarged area of *A* (b), cross section (c) and optical microscopy of cross section (d)

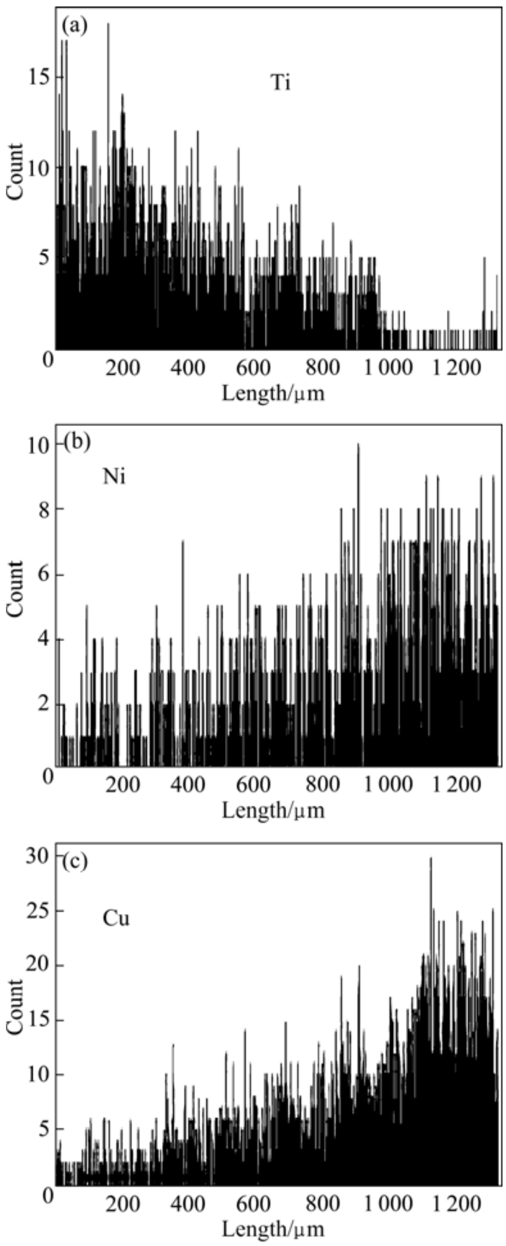

Fig.4 Linear scanning results for cross-section of TiB_2/Ni coating, for Ti (a), Ni (b), Cu (d)

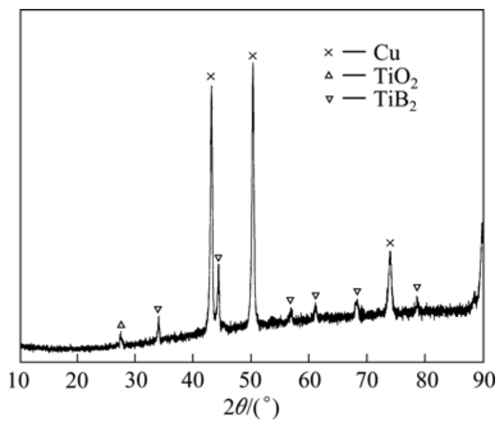

Fig.5 XRD pattern of TiB_2 coating

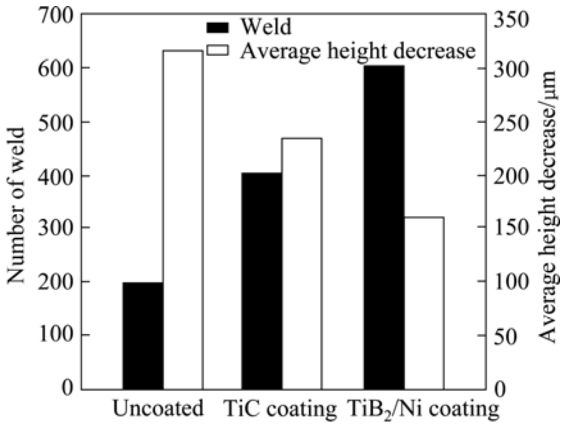

Fig.6 Spot-welding lives for electrodes with different coatings and their average height decreases

the temperature increment during the welding is lower for the TiC and TiB_2/Ni coated electrodes than that for the uncoated ones. Hence, the deformation of the tip of the coated electrodes is lessened. As a result, the spot-welding lives are prelonged for the TiC and TiB_2/Ni coated electrodes since the tip deformation and wear are two major factors responsible for the failure of the spot-welding electrodes[12−13]. TiB_2 has better thermal and electrical conductivities than TiC (Table 1), which contributes to a lower electrical resistance (a higher welding current and stronger weld adhesion) and lower temperature rise (lower tip deformation)[14−15]. Consequently, the life of TiB_2/Ni coated electrode is longer than that of TiC coated one; although the hardness of the former is a little lower than that of the latter.

Table 1 Physical properties of TiC, TiB_2 and Cu

Material	Melting point/K	Hardness, HV	Thermal conductivity/ $(W\cdot m^{-1}\cdot K^{-1})$	Electrical conductivity/ $(\mu\Omega\cdot cm^{-1})$
TiC	3 340	2 800	24.3	52.5
TiB_2	3 498	3 225	65.0	30.0
Cu	1 356	55	390.0	2.0

4 Conclusions

1) Nickel acts as a good binder for the coating and substrate materials. It resolves fully with the copper substrate and wets well with the TiB_2 coating. The intermediate coating with phase compositions of nickel and copper is dense and crack free.

2) The TiB_2/Ni coating is not dense. Cracks penetrate the whole coating and pores at the interface are observed. Copper and nickel diffuse to the coating surface and reach concentrations of 8.0% (molar fraction) and 2.3%, respectively.

3) There is no crack in the intermediate nickel

coating because the residual stress can be released by deformation easily. TiB_2 and TiC are difficult to deform, so the residual stress will accumulate until cracks form in the coating.

4) The spot-welding life of TiB_2/Ni coated electrode is much longer than that of the uncoated and TiC coated ones.

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电火花沉积法在铜电极表面制备 TiB_2/Ni 涂层

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摘 要：为了提高镀锌钢板用点焊电极的使用寿命，在铜电极表面涂覆过渡层 Ni 后沉积了 TiB_2 涂层。通过 SEM 和 XRD 分析了 Ni 和 TiB_2 涂层的物相和微观结构，并测试了其显微硬度。结果表明：由于材料具有良好的塑性，预涂覆的 Ni 涂层结构致密无裂纹，与基体 Cu 无分层；而 TiB_2 涂层内存在裂纹和孔洞。通过过渡层 Ni 将 TiB_2 涂层和基体 Cu 粘结起来，获得了较理想的涂层。随着电火花放电电容和电压的增加，TiB_2 的氧化程度增强，Cu 和 Ni 大量扩散进入涂层表面，使 TiB_2/Ni 涂层的硬度降低。由于 TiB_2 良好的导电和导热性能及高的硬度，TiB_2/Ni 涂层电极在点焊时的塑性变形降低，寿命比无涂层电极和 TiC 涂层电极得到了明显提高。

关键词：二硼化钛; 电火花沉积; 铜; 电极; 镍; 涂层

(Edited by LI Xiang-qun)