A STUDY OF THE MICROSTRUCTURES AND PERFORMANCE OF CHROMIUM BORIDE COATINGS ON AISI 52100 STEEL

ŠTUDIJ MIKROSTRUKTUR IN LASTNOSTI KROM-BORIDNIH PREVLEK NA JEKLU AISI 52100

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In the present work thermal reactive diffusion (TRD) coatings of Cr+B were prepared on AISI 52100 steel using a chromizing treatment and a boriding treatment. The microstructures, phase compositions and elemental distributions of the coatings were systematically investigated. In addition, the influence of treatment temperature on the thickness and phase composition of the coating layer was also further determined. The results demonstrated that the phases formed on the steel surface were CrB, Cr_7C_3 and Fe_2B. The higher treatment temperature resulted in a thicker chromium boride coating. The thickness of the chromium boride coatings increased from 48 μm to 272 μm with an increase of the treatment temperature. The boron reacted with the chromium carbide layer formed in the chrominizing stage and then penetrated into the layer to form Fe_2B.

Keywords: chromium boride coating, AISI 52100 steel, microstructures, Fe_2B

V pričujočem prispevku avtorji opisujejo Cr+B prevleko na jeklu AISI 52100, pripravljeno z reaktivno termično difuzijo (TRD). Za to so uporabili tehniki kromiranja in boriranja. Sistematično so preiskovali mikrostrukture, fazno sestavo in porazdelitev elementov prevlek. Nadalje so določili vpliv temperature obdelave na debelino in fazno sestavo prevleke. Rezultati preiskav so pokazali, da so se na površini jekla tvorile faze CrB, Cr_7C_3 in Fe_2B. Posledica višje temperature obdelave je bila debelejša plast krom-boridne prevleke. S povišanjem temperature obdelave je debelina krom-boridne prevleke narasla z 48 μm na 272 μm. Element bor je reagiral s krom-karbidno plastjo, tvorjeno v fazi kromiranja in je nato penetriral v plast, da bi se tvoril še Fe_2B.

Keywords: krom-boridna prevleka, jeklo AISI 52100, mikrostrukture, Fe_2B

1 INTRODUCTION

In recent years, various surface-hardening processes have been implemented to modify the performance of metals. Generally, two methods, namely, interstital solid solutions and compounds, are used to improve the surface performance. The former involves the diffusion of small atoms into the metal surface, and the latter utilises the chemical reaction between the diffused atoms and the original metal. Boronizing is a hardening process in which boron atoms are diffused into the surface of the metal creating borides on the original matrix. Therefore, in this process, the diffused atoms have a chemical reaction with the original metal. Boronizing is available for many materials involving ferrous metals, non-ferrous metals and ceramic metals.[1]

Basically, the thermal diffusion process of boride compounds requires a temperature range from 850 °C to 1050 °C,[2–4] and the process can be achieved by three methods that involve solid boriding, liquid boriding and gaseous boriding.[5] The most common method is pack boronizing, similar to pack carburizing. In particular, powder-pack boronizing is simple and cost-saving compared to the other boronizing processes.[6–8] Boron atoms can be easily diffused into ferrous metals due to their relatively small size and high mobility. According to the Fe-B binary phase diagram, a single layer of Fe_2B or a double layer both consisting of Fe_2B and FeB can be formed at the interface. The single layer (Fe_2B) is considered to be a desired phase compared to the double layer because the FeB is more fragile than the Fe_2B. Cracks may occur between two layers due to the occurrence of residual stresses induced by different thermal expansion coefficients from different compounds at high temperatures.[9–11]

Chromium is easy to form stable borides, such as CrB. This compound has a high melting temperature, hardness, and wear resistance, like the borides of Zr, Ti, V and other transition metals.[12] At present, no literature has reported on metal treatment with Cr followed by boronizing, especially for the AISI 52100 steel. Chromium is also a strong CFE (carbide forming element), and chrome carbides can be formed during the treatment of the steel with Cr, which are supposed to impede the diffusion of B when boronizing. Our interest in steel treatment with Cr has been guided by the influence of the properties of the Cr-metallized layer on the next boronizing process.

The purpose of this research is to study chromium boride coatings produced by the TRD technique on the AISI 52100 steel samples. The microstructure and

Table 1: The chemical composition of the substrate, in mass fractions (*w*/%)

Steel	C	Cr	Ni	Si	Mn	Mo	S	P	Fe
AISI52100	0.95	1.45	0.107	0.194	0.318	0.014	0.076	0.0143	balance

phases in the chrome boride layer were investigated using an optical microscope, scanning electron microscope and X-ray diffraction. In addition, the microhardness was also measured to evaluate the performance of the boride layer.

2 MATERIALS AND METHODS

The used material in the experiments was AISI 52100 steel, and its chemical composition is shown in **Table 1**. This material is usually known as ball-bearing steel and has a high degree of carbon. At the preparation stage, the samples were cut into a shape with a diameter of 16 mm and a length of 20 mm, and then were ground up to 1000 grit using the emery paper and washed by ultrasonic for 15 min in ethyl alcohol.

The chromium carbide coating was prepared on the samples via packing in the box, consisting of ferro-chromium, ammonium chloride and NaF at a temperature of 850 °C for 8 h as the first stage of the chromium boronizing treatment. Secondly, the pre-chromiumed steel was boronized by packing in the powder including B_4C (5 %), KBF_4 (5 %) and SiC (90 %) at temperatures of (850, 900, 950 and 1050) °C for 8 h. The samples were directly immersed in the mixing powder in the alumina crucible sealed by an alumina lid. After the treatment, the box was removed at a high temperature and cooled down to room temperature slowly. After the boriding process, all the specimens were pre-heated (650 °C for 20 min), austenitized (840 °C for 20 min, oil quenched), cryogenic treatment (–78 °C for 1h), and low-tempered heat treatment (160 °C for 2h) to produce the desired tempered martensite structure.

The metallographic samples were ground with silicon carbide papers up to 2000 grit and then polished, and finally etched with Nital (4 % nitric acid in ethanol). Afterwards, the observation was conducted using an optical microscope (OM, ME F-3) and an SEM (Quanta 400) to investigate the cross-section morphology and the microstructure of the coating. The components of the ceramic layer were studied by employing an EDAX microprobe within the SEM. In addition, a phase analysis was implemented by XRD (Rigaku, D-Max diffractometer) with 2θ varying from 20° to 90°.

In order to further evaluate the performance of the samples, the microhardness depth profile was measured with a Vickers indenter. The test instrument was a DHV-1000, and the parameters were respectively 1.961 N load and 15 s loading time. For each specimen, the average hardness value was acquired and the depth of the indentation print was checked from three measurements to avoid the substrate effect. The surface roughness was also measured using a contact profilometer (XM200).

3 RESULTS AND DISCUSSION

3.1 Chromium carbide coating on AISI52100 steel

The SEM micrograph of chromium-carbide-coated AISI52100 steel at 850 °C for 8 h is shown in **Figure 1a**. As seen from **Figure 1a**, it is obvious that the chromium carbide coating is formed on the surface of the AISI52100 steel, which has a smooth and flat morphology. A sharp interface zone is detected between the chromium carbide coating and the substrate, which includes the chromium carbide layer and the steel matrix. It also reveals that a chromium carbide coating with a uniform thickness is formed on the surface of the AISI52100 steel all over the treated samples.

The element distribution at the interface is shown in **Figure 1b**. As can be seen from the EDAX profiles, it is clear that the Cr content decreases gradually while the Fe content increases continually from the surface to the matrix, which suggests that the interdiffusion between the Cr and the Fe occurs near the interface of the matrix. Actually, the iron content increases slowly, moving from
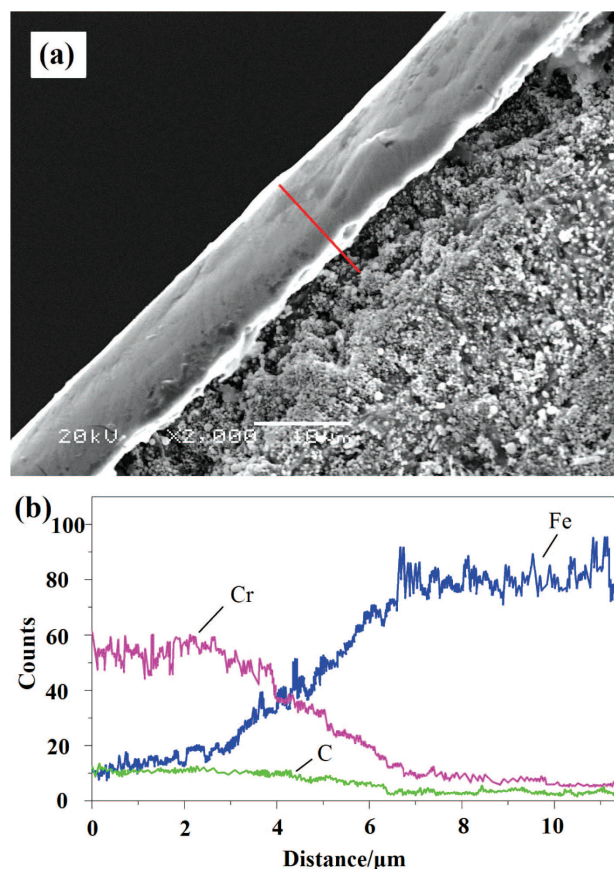

Figure 1: Fracture cross-section SEM image of the experimental specimen: a) micrograph of a cross-section, b) EDAX line scan analysis across the chromium carbide layer
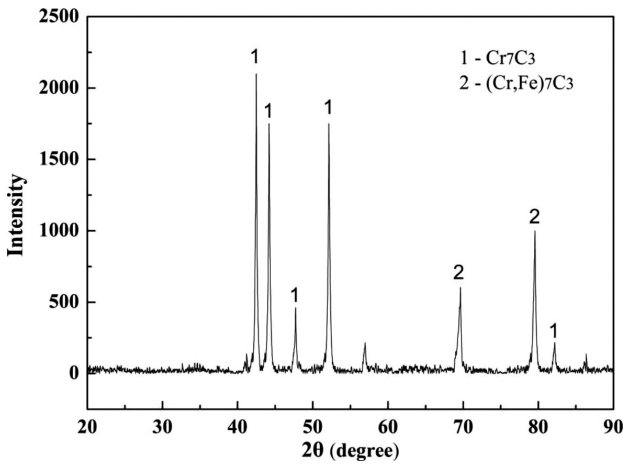
Figure 2: XRD patterns of the chromium carbide layer produced at 850 °C on AISI 52100 steel
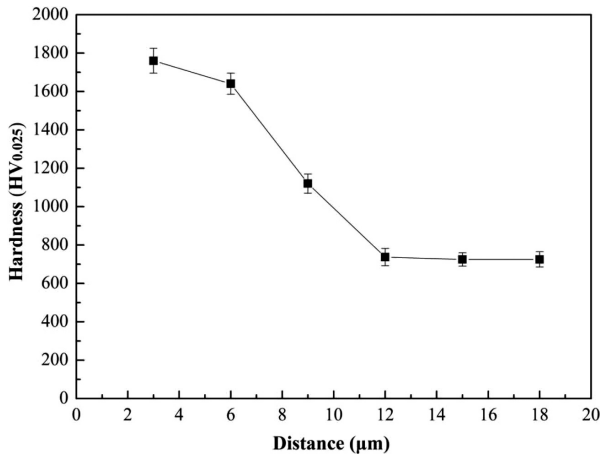

Figure 3: The microhardness curve of the specimen from the surface to the core

the surface to the core of the sample, and the iron and the chromium have a wide coexistence zone. These observations are in agreement with the result of X. S. Fan et al.,[13] and the effect may be attributed to the relatively
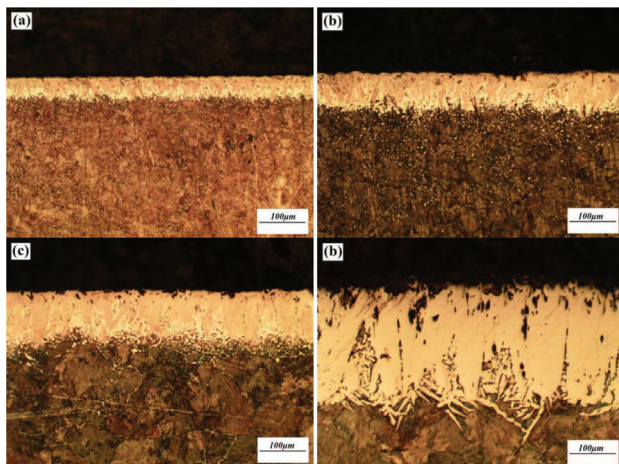

Figure 4: Optical micrographs of the cross-section of chromium boride layers at different exposure temperatures: a) 850 °C, b) 900 °C, c) 950 °C, d) 1050 °C
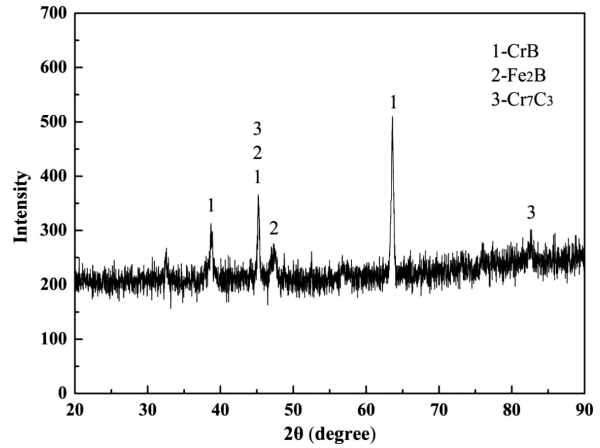

Figure 5: XRD patterns of chromium boride layer produced at 950 °C for 8 h

high (compared with other carbide forming elements, such as V) solubility product of chromium and carbon in austenite at the TRD temperature. This phenomenon especially occurred during the first period of the TRD process (prior to the ceramic coating formation). Subsequently, during the cooling process, chromium precipitated as a carbide because of the decreased solubility product.

In this study, chromium carbides were further identified using XRD analysis in **Figure 2**. In general, chromium carbide compounds, which form on the surface, may include Cr_7C_3 and Cr_3C_2 compounds. However, only
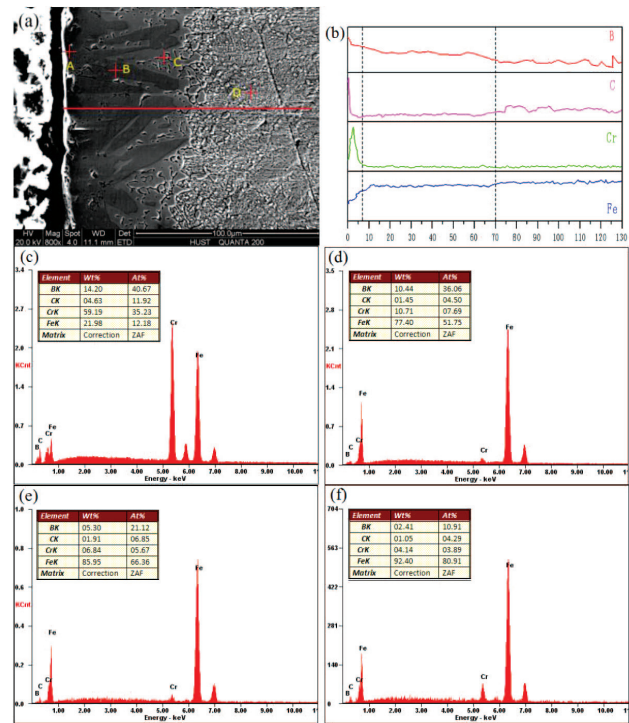

Figure 6: The SEM results of chromium boride layers: a) SEM image of chromium boride layers, b) EDAX line scan analysis across the chromium carbide layer, c) A composition, d) B composition, e) C composition, f) D composition
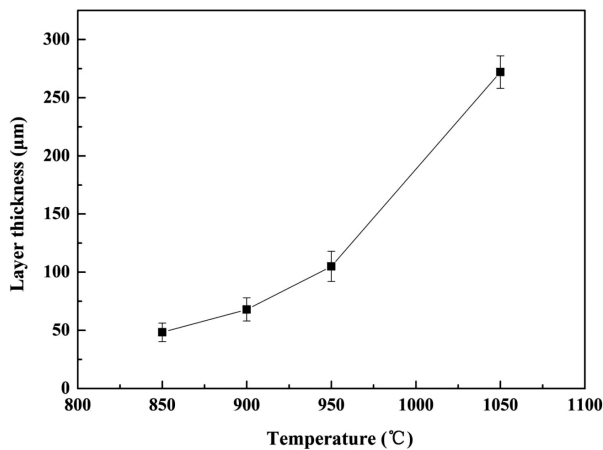
Figure 7: The thickness value of chromium boride layers with respect to the test temperature
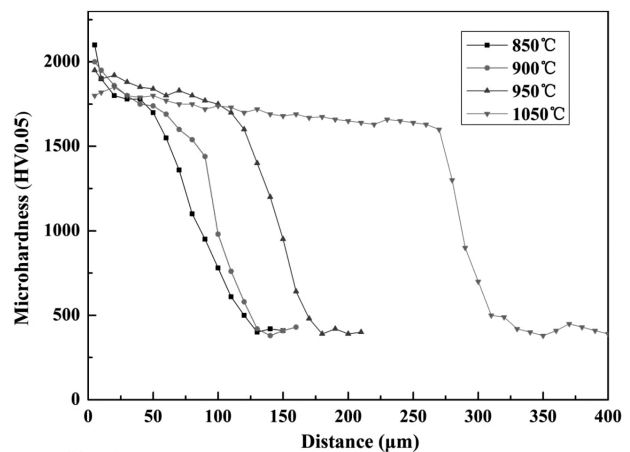

Figure 8: The hardness curves of specimens against depth at (850, 900, 950 and 1050) °C

the Cr_7C_3 compound is detected in the present experiment. The reason is that it is short of carbon phases, comparing with a lot of reactive chromiums during the process of chromizing. Therefore, it can be concluded that the reaction is mainly controlled by the diffusion of the carbon element.

The thickness value of the chromium carbide layer formed on the substrate is about 7.3 μm. **Figure 3** shows the microhardness curve of the specimen from the surface chromium coating to the substrate. As can be seen, the hardness distribution from the surface to the substrate gradually varies. The average microhardness of the outer layer is 1775±45 HV after the chromium treatment, which is much higher than that of the substrates (723HV). The presence of hard Cr_7C_3 and $(Cr, Fe)_7C_3$ phases in the coating layer can provide an extremely hard surface. During thermo-reactive diffusion chromium carbide treatments, a high hardness is easily achieved by means of the formation of transition metal carbides during the treatment.

3.2 Chromium boride coating on AISI52100 steel

Figure 4 shows the cross-section of optical micrographs of chromium boride layer of AISI 52100 steel at (850, 900, 950 and 1050) °C. It can be seen that the diffusion layer becomes thick and the microstructure differs from that of Cr-treated steel after the boronizing. The coating-substrate interface reveals the saw-tooth morphology in all test series, indicating that boron can diffuse through the chromium carbon layer to form boron-iron compounds. The coating layer consists of four different parts: (a) a chromium boride layer on the surface of the coated steel, (b) an iron boride layer under

the chromium boride layer, (c) the zone where borides occurred at the grain boundaries and (d) a matrix without being affected by boron. As shown in **Figure 5**, the XRD analysis indicates that the layer on the coated steel samples involves CrB, Cr_7C_3 and Fe_2B.

Figure 6 demonstrates the SEM micrograph and EDAX patterns of the chromium boride layer produced at 900 °C for 8 h on AISI 52100 steel. As can be seen, the contents of chromium and carbide elements are quite high, and the boron element also concentrates on the surface ranging from 0 μm to 8 μm. However, it can also be seen that the contents of chromium and carbide elements are low, and the iron element has an evident increase on the surface, varying from 8 μm to 70 μm. Energy-dispersive X-ray spectroscopy point analysis (**Figure 6c** to **6f**) shows that the layer on the surface of the coated steel is rich in chromium, and the component of CrB compounds is identified by the XRD analysis. This is because the chromium has a lower diffusivity in the matrix. Compared with Cr, the B element has a small atomic radius so that the B element reacts with other elements and diffuses through the chromium carbide layer to form the compound of Fe_2B with iron. The chromium and carbide have a low solubility in Fe_2B, so they mainly concentrate in the surface layer. Cr is an intensive carbide-forming element, thus it can easily form chrome carbides rather than conducting the diffusion of B when treating the steel with Cr. Due to depressing the boron potential at the surface, the generated iron borides are mainly Fe_2B composites which have a better combination property than FeB.

The thickness of the chromium boride layers, ranging from 48 μm to 272 μm, depends on the treatment temperature (**Figure 7**). The higher the treatment tempera-

Table 2: The surface roughness of untreated, chromium-treated and chromium-boride-treated 52100 steel

Surface roughness	Untreated	Cr-treated	Chromium boride treated			
			850 °C	900 °C	950 °C	1050 °C
R_a (μm)	0.193	0.231	0.256	0.263	0.278	0.322

ture is, the thicker the chromium boride layer is. During the TRD boriding process, some factors influence the coating-layer thickness, including the bath composition, substrate, treatment time and temperature.[14]

Figure 8 shows the micro-hardness distribution from the surface to the substrate. It can be seen from **Figure 8** that the hardness of the layer decreases from the surface to the interior at all treatment temperatures. The hardness of the surface layer decreases with increasing treatment temperature. It is mainly because the diffusion ability of B increases with increasing the treatment temperature. In addition, the pores in the surface increase, which leads to a decrease of the layer density so as to affect the hardness of the layer. The hardness of the chromium boride layers, ranging from 1850 HV to 2130 HV, depends on the treatment temperature

Table 2 gives the surface roughness of the AISI 52100 at different heat-treatment conditions. It can be seen from **Table 2**, the surface roughness increases from 0.193 μm to 0.231 μm after chromium treatment, which indicates that the surface roughness increases ranging from 0.256 μm to 0.322 μm with increasing the temperature, due to the presence of the pores on the surface. In most cases, an increase in the pores often results in a decrease of the density, which affects the surface roughness of the layer.

4 CONCLUSIONS

A qualitative research was conducted to understand the chromium boride coatings on AISI 52100 steel. Major findings are shown as follows:

1) Chromium boride coatings were successfully produced by the TRD technique on the AISI 52100 steel sample. The coating layer presented the saw-tooth morphology.

2) The boron element reacted with the chromium carbide layer formed in chrominzing stage and then penetrated into the layer to form Fe_2B. XRD analyses verified that the chrome boride layer consisted of Cr_7C_3, CrB and Fe_2B phases.

3) The formation of chromium borides increased the surface hardness of Cr-treated AISI52100 steel. The hardness of boride layer on the Cr-treated AISI52100 steel varied from 1850 to 2130HV.

Acknowledgment

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