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Effect of metal borides on the hardness and wear of STD11 steel

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Abstract

This study aimed to manufacture a steel with high hardness and wear resistance by utilizing the precipitation of metal borides, which have much higher hardness than the high-hardness Cr carbide of the existing STD11 rolled steel. For this purpose, an alloy composition consisting of Mo 13–20%, Co 18–30%, V 3–6%, Cr 3–5%, C 1.5–3.5%, Si 0.5–1.2%, Mn 0.1–0.5%, B 2.5–4.5%, Nb 1–2%, W 1–3%, Al 0.1–0.2%, Ti 0.1–0.3%, and rare earth metals (RE) 0.1–0.2% as additives was designed. The mold for die casting was manufactured by installing a vent hole at the end of the product for gas escape, not installing a riser, installing a large sprue for quick molten metal injection, and making the sprue also serve as a riser. In particular, since the mold designed and manufactured in this study was based on a vertical split casting method, a well instead of a separate runner was installed to prevent eddies. After mold casting, quenching and tempering treatments were performed on the prototype, resulting in a high-hardness product with a hardness value of HRC66~68.

Keywords: Hardness, heat treatment, metal boride, mold casting, STD11 steel.

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1. Introduction

Metal borides are unique materials that possess properties of both ceramics and metals. Borides generally exhibit high hardness and strength, resulting in excellent wear resistance. Metal borides also have high melting points and excellent chemical corrosion resistance, enabling their widespread use as coating films. Unlike ceramic materials, metal borides also have very high electrical conductivity. It is believed that the covalent bonds between boron (B) atoms are the main cause of the high hardness and high melting points of metal borides. Although borides may seem difficult to process due to their high hardness and strength, their high electrical conductivity allows them to be processed similarly to mold steel when using a discharge machine for metals. Metal borides, which are compounds formed between transition metals of groups IIIa~VIII and boron, have properties such as high melting points, high wear resistance, and high corrosion resistance, making them widely used in industrial fields. More specifically, they are used as base materials for super-hard tools, metal surface hardening materials, crucible materials for molten metal (MB2 boride), and additives for grain refinement of metal materials. Additionally, since borides are very expensive as raw materials themselves, not as applied products, they have very high development potential. However, like other non-oxides, borides have a weakness in that they are easily oxidized in high-temperature oxidizing environments. When the temperature in the air exceeds 1200 K, a visible surface oxide film forms. For example, ZrB_2 oxidizes and converts to ZrO_2 when the temperature exceeds 900 K [1-5]. Although the mechanical properties of borides have not been reported in detail, they generally possess a very high elastic modulus but are brittle at low temperatures. In terms of technology, the manufacturing processes for borides are primarily divided into boride synthesis, powder manufacturing technology, and application technology. Borides are sometimes used alone, but more often they are mixed with other metals or compounds to produce sintered bodies. Among these, a composite material of ceramics and metals is called Cermet, which has been prominent for a long time because it exhibits excellent properties such as high hardness, wear resistance, and high-temperature strength of ceramics, as well as ductility and toughness of metals. As described above, since borides have high added value and industrial applications, relevant technological development is very important [3, 5-8].

Recently, a method for forming a cobalt boride coating layer on a ferrous metal surface using a pack cementation process has been developed. In recent years, a composite coating layer consisting of an outermost layer of cobalt boride (Co_2B) and an inner layer of iron-cobalt boride ($(Fe, Co)_2B$) was formed on the steel surface, creating a dense coating with almost no defects such as pores. Additionally, a method for forming a cobalt (Co) boride coating layer that improves the corrosion resistance, wear resistance, and oxidation resistance of steel has also been proposed [4]. As described above, the material that can withstand continuous friction and wear by high-hardness steel balls is high-Cr white cast iron (Cr15-18%-Mo3%), which has been the best wear-resistant material commercially available. Some manufacturers produce $27Cr_2Mo$ white cast iron for use, but its wear resistance is inferior to that of 15Cr3Mo white cast iron. Additionally, some products with a carbon (C) content of 2.5% or more in tungsten (W)-based high-speed steel are commercially available at high prices, but their wear resistance is only about 50% better than that of high-Cr white cast iron. Recently, a new product (TD1) has been developed in Korea to replace imported products, but the developed product TD1 is similar to the cold die tool steel material STD11, and is not a cast product. Instead, it is produced by machining a plate made through rolling or forging, followed by vacuum heat treatment. To address these issues, this study designed an alloy composition utilizing precipitation of metal borides, which have much higher hardness than the Cr carbide in the existing STD11 rolled material. The study developed a steel with high hardness and high wear resistance using mold casting.

2. Materials and Methods

2.1. Mold Design

In this study, a special casting method designed as presented in Figure 1, was used to improve castability, prevent pores and shrinkage pores, and to homogenize and refine the structure when casting a steel with high hardness and wear resistance using the precipitation of metal boride. Sand casting was also performed to compare the mechanical properties. Considering mold life, STD61 (JIS; SKD61), a hot tool steel, is suitable for mold material, but S15C (or S20C) carbon steel was used in this development because it is economical. The reason for designing the sprue in the mold in Figure 1 as large as it is, is to increase the injection speed and to replace the sprue with a riser. Additionally, the well was designed to serve as a buffer to reduce flow rate and allow the molten metal to flow smoothly toward the inlet (gate), thus preventing impurities such as slag from entering the product. The inlet was installed on the wider side of the mold space because this side connects to the inlet, allowing high-temperature molten metal to pass through and enter the mold space, resulting in slow cooling and coarsening of the structure. A vent hole (gas release) was installed at the end of the product to allow air in the mold space to escape when the molten metal fills the mold, preventing compressed air from blocking the entry of molten metal. Figure 1 shows a cross-sectional view of both the front and side casting methods. The actual mold was manufactured based on a vertical division method. The roles of each component in the injection process are explained as follows: the funnel-shaped center is the sprue (1), the plate shapes on both sides are the product space (2) to be cast, and the wing-shaped connection between the sprue (1) and the product space (2) is the injection port (3). The injection port (3) is designed with an upper injection port (3-1) and a lower injection port (3-2), with vent holes (4) at both ends of the prototype to discharge air and gases generated during injection. The well (5) is concavely formed to prevent eddy formation in the molten metal. When the molten metal is injected through the sprue (1), it first fills the well (5), then the molten metal with a slow flow rate is injected into the product space through the lower injection port (3-2), and finally, the molten metal fills the mold space (2) through the upper injection port (3-1). During this process, as the flow rate slows, impurities such as slag or sand particles remain in the sprue, allowing only clean molten metal to flow into the product space, thus preventing the mixing of non-metallic inclusions or slag. From a side view in Figure 1, the injection port (3) has a cross shape with one side missing, designed to prevent solidification shrinkage. The injection port was installed on the wide side of the product, with the upper and lower injection ports positioned at the top and bottom, respectively. The vent hole was installed at the end of the product and was not designed to accommodate a riser. Since rapid injection is necessary, the sprue was made large and functions as a riser. Notably, because this development adopted a vertical split casting method, a well was installed instead of a separate runner to prevent eddies.

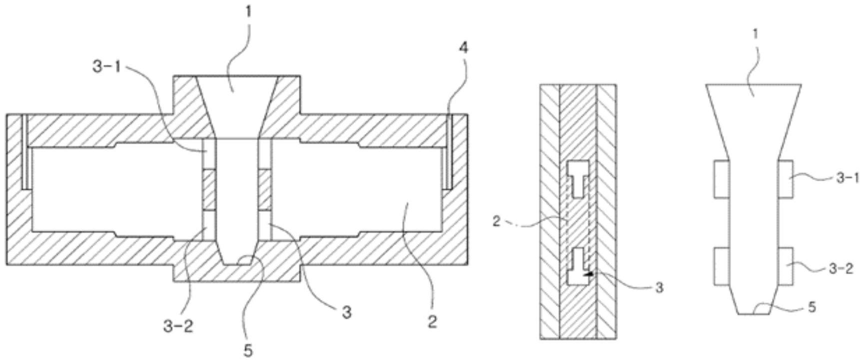

Figure 1.
Mold casting method.

2.2. Mold Material and Casting Process

Figure 2 presents the manufacturing process of cast steel products with added boron (B). For comparison, the casting methods are divided into sand casting and metal mold casting. For the sand casting mold, a CO_2 molding method using sodium silicate as a binder was used, and for the metal mold casting, a carbon steel (S15C or S20C) mold was employed. The contents of carbon (C), chromium (Cr), vanadium (V), and tungsten (W) were adjusted for alloy design with added boron, and the mold was melted in a high-frequency induction furnace according to the sample composition. The maximum melting temperature was set to 1650 ℃, and the pouring temperature was about 60 ℃ higher, at 1500 ℃ for sand casting and 1560 ℃ for metal mold casting. This increase in temperature helps prevent the shape of the blade product from becoming deformed or wrinkles from forming on the surface due to rapid cooling.

Figure 2.
Casting process for cast steel products with added boron (B).

3. Results and Discussion

3.1. Chemical Composition Analysis and Microstructure

The chemical substances and composition of the finished product samples 1 ~ 6 were analyzed using a spectrometer, and Table 1 presents the comparison results of the chemical compositions of the blade product samples. Figure 3 presents the results of optical microscopic structure and SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray Analysis) analysis for sample 2, as a representative example. The microstructure predicts high hardness due to the precipitation of fine MC-type carbides and the formation of large amounts of square, coarse intermetallic compounds such as boron carbides and tungsten carbides, resulting from the large addition of Mo, W, and B. However, it was thought to be a brittle structure with low toughness. Many cases where these high-hardness carbides were unevenly distributed were also observed in other samples.

Table 1.
Chemical compositions of cast steel with added boron (B) (wt.%).

Sample No.	C	Si	Cr	V	Mo	Co	Nb	W	B
Sample 1	2.1	0.8	3.2	3.8	18	25	1.0	2.5	3.0
Sample 2	2.0	0.7	3.3	3.7	18	24	1.1	2.8	3.5
Sample 3	2.4	0.8	3.5	3.2	17	25	1.0	3.0	3.0
Sample 4	2.5	0.9	3.3	3.6	18	23	1.2	2.4	3.0
Sample 5	3.0	0.7	4.0	4.0	17	23	1.0	2.6	3.0
Sample 6	3.1	0.8	3.8	4.1	18	25	1.1	2.7	2.9

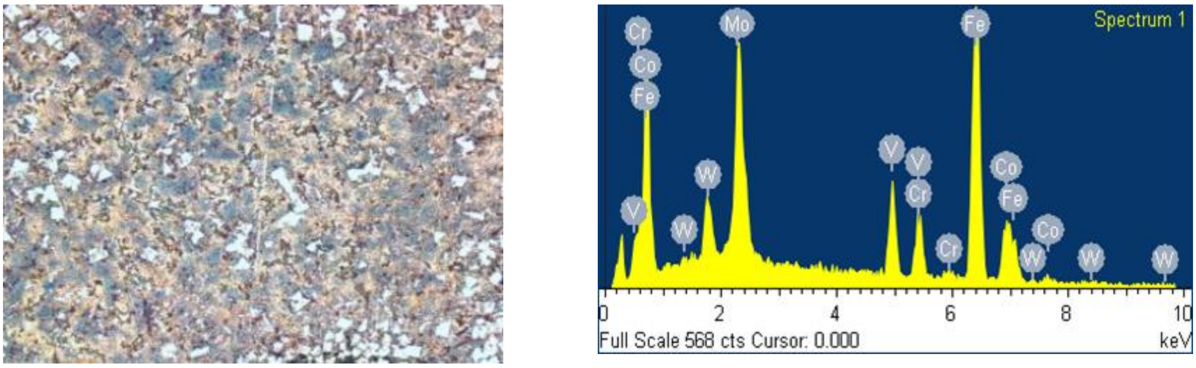

Figure 3.
Optical microscopy (×200, Nital etching) and EDX analysis for sample 2

3.2. Heat Treatment and Hardness Measurement

The manufactured samples were normalized at 750~850°C to remove casting stress, then austenitized at 1050°C and quenched with oil. Tempering was performed immediately after quenching, maintaining the temperature at 530~580°C for 120~140 minutes, followed by air cooling. As presented in Table 2, all samples exhibited higher hardness (HRC) in mold casting than in sand casting. This is thought to be due to the faster cooling rate in mold casting, which refines the crystal grains and increases the amount of martensite in the matrix structure. The hardness after heat treatment was measured at HRC 68~69 for mold casting, higher than the HRC 66~68 observed in sand casting, suggesting higher wear resistance. However, despite the high hardness, the impact value was relatively low, indicating high brittleness, as shown in Table 2. Table 2 also presents the chemical compositions of six samples cast with this development technology, including the as-cast conditions during sand and mold casting, and the hardness values after heat treatment, along with six other comparative samples. Comparative sample 1 is a high V-high Nb alloy without added boron (B); comparative sample 2 has slightly reduced B, Co, and Mo contents; comparative sample 3 is a high-chromium white cast iron (15Cr3Mo), known for its excellent hardness and wear resistance; comparative sample 4 is an alloy that has undergone forging and rolling, representing the best wear resistance among high-speed steels (HSS) according to ASTM standards; comparative sample 5 has the highest wear resistance among existing Stellite alloys; and comparative sample 6 is the STD11 steel rolled material. As shown in Table 2, increasing the carbon (C) content in samples 1 through 6 of the actual blade increased the hardness, and increasing boron (B) content also raised the hardness. Additionally, the difference in hardness between sand casting and mold casting was approximately HRC 2.5~3.0, slightly higher in mold casting cases.

Table 2.
Comparison of chemical compositions and hardness values of developed product samples and comparative product samples.

Sample No.	Chemical compositions (wt.%)									As-cast condition Hardness (HRC)		Hardness (HRC) after heat treatment (Q.T)	
	C	Si	Cr	V	Mo	Co	Nb	W	B	Sand casting	Mold casting	Sand casting	Mold casting
Sample 1	2.1	0.8	3.2	3.8	18	25	1.0	2.5	3.0	63.1	66.5	66.2	68.5
Sample 2	2.0	0.7	3.3	3.7	18	24	1.1	2.8	3.5	63.7	66.8	67.1	69.4
Sample 3	2.4	0.8	3.5	3.2	17	25	1.0	3.0	3.0	63.5	66.8	66.5	69.0
Sample 4	2.5	0.9	3.3	3.6	18	23	1.2	2.4	3.0	63.4	66.7	66.4	68.9
Sample 5	3.0	0.7	4.0	4.0	17	23	1.0	2.6	3.0	65.0	67.5	67.7	69.5
Sample 6	3.1	0.8	3.8	4.1	18	25	1.1	2.7	2.9	65.4	67.8	67.9	69.7
Comparative sample 1	3.0	1.0	4.0	10	8.0	3	6.0	2.0	-	60.9	62.1	64.7	65.8
Comparative sample 2	3.0	0.8	4.0	8.0	13	8	2.0	3.5	2.0	62.7	63.9	64.6	65.4
Comparative sample 3	3.5	0.6	16	-	3.0	-	-	-	-	60.0	62.1	63.5	65.1
Comparative sample 4	1.5	0.4	4.0	5	1	5	-	12	-	-	-	Forging	65.9
Comparative sample 5	3.2	1.0	27	-	-	50	-	13.5	-	48.8	52.3	52.4	58.7
Comparative sample 6	1.5	0.4	13	0.5	1	-	-	-	-	-	-	Forging	64.3

Table 3 presents the results of impact and wear tests on each sample, indicating that the six samples prepared with this development technology (Samples 1 to 6) have high hardness values, thus exhibiting better wear resistance than the six comparative samples, which have relatively low hardness values. However, the Charpy impact value of these developed product samples (Samples 1 to 6) is significantly lower, averaging 6.0 to 7.2 ft-lb, compared to 14.6 ft-lb of the STD11 rolled steel (comparative sample 6), indicating high brittleness of the product. Based on these results, it is believed that hardness and impact values are inversely proportional to each other.

Table 3.
Impact and wear test results of developed product samples and comparison product samples.

Cat.	Hardness after heat treatment (HRC)	Wear test (Loss amount)	Impact value (Charpy)
Sample 1	68.5(Mold casting)	22.7 mg	7.2 ft-lbs
Sample 2	69.4(Mold casting)	19.7 mg	6.8 ft-lbs
Sample 3	69.0(Mold casting)	20.1 mg	7.0 ft-lbs
Sample 4	68.9(Mold casting)	21.6 mg	7.1 ft-lbs
Sample 5	69.5(Mold casting)	19.1 mg	6.2 ft-lbs
Sample 6	69.7(Mold casting)	18.8 mg	6.0 ft-lbs
Comparative sample 1	65.8(Mold casting)	32.9 mg	7.2 ft-lbs
Comparative sample 2	65.4(Mold casting)	29.8 mg	7.4 ft-lbs
Comparative sample 3	65.1(Mold casting)	58.6 mg	6.8 ft-lbs
Comparative sample 4	65.9(Forging)	45.4 mg	12.1 ft-lbs
Comparative sample 5	58.7(Mold casting)	66.1 mg	28.7 ft-lbs
Comparative sample 6	64.3(Forging)	74.3 mg	14.6 ft-lbs

4. Conclusions

This study aimed to manufacture steel with high hardness and wear resistance through the precipitation of metal borides, which have much higher hardness than Cr carbide in the existing STD11 rolled steel. For this purpose, an alloy composition consisting of Mo 13~20%, Co 18~30%, V 3~6%, Cr 3~5%, C 1.5~3.5%, Si 0.5~1.2%, Mn 0.1~0.5%, B 2.5~4.5%, Nb 1~2%, W 1~3%, Al 0.1~0.2%, Ti 0.1~0.3%, and rare earth metals (RE) 0.1~0.2% as additives was designed. In addition, a mold for mold casting was designed and manufactured. After mold casting with the above alloy composition, quenching and tempering heat treatments were performed. The hardness of the product manufactured by mold casting using the alloy design that can precipitate a large amount of metal boride and the special casting method greatly increased to HRC68~69, which in turn greatly increased the hardness and wear resistance compared to the existing commercial STD11 steel (e.g., chemical composition is C 1.4~1.6 wt.%, Si 0.4 wt.% or less, Mn 0.6 wt.% or less, Cr 11~13 wt.%, Mo 0.8~1.2 wt.%, V 0.2~0.5 wt.%, and the maximum hardness is HRC65). However, the impact toughness is considerably lower than that of the existing STD11 steel, indicating that further studies are needed prior to field applications that require impact wear resistance.

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