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The effect of boron on the wear behavior of iron-based hardfacing alloys for nuclear power plants valves

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Abstract

The effect of boron of Fe–Cr–C–Si alloys, replacing Stellite 6 traditionally used in nuclear power industry, on the high temperature wear resistance was characterized. Sliding wear tests of Fe–Cr–C–Si–xB ($x = 0.3$, 0.6, 1.0 and 2.0 wt%) alloys were performed in air at temperatures ranging from 300 to 725 K under a contact stress of 103 MPa. Low-boron alloys containing less than 0.6 wt% boron showed the excellent wear resistance than any other tested alloys in an elevated temperature. The improvement was associated with the matrix hardening by promotion of the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation occurred during wear. In addition, protective oxide layers formed on the contacting surface reduced the wear loss by minimizing the direct metal-to-metal contact. However, high-boron alloys containing more than 1 wt% boron showed somewhat larger amount of wear loss than low-boron alloys due to the absence of the strain-induced martensitic transformation and the presence of the brittle FeB particles connected with easy crack initiation.

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1. Introduction

Co-based Stellite alloys have been traditionally used as hardfacing materials for nuclear power plant valves owing to their superior corrosion resistance as well as sliding wear resistance [1]. However, Co is known to be one of a main contributor to the occupational radiation exposure. Thus, for safety concerns, it is desirable to replace the Stellite 6 with Co-free hardfacing alloys having the equivalent properties [2].

Strain-induced martensitic transformation has been reported to be an important high temperature wear resistance mechanism in an iron-based hardfacing alloy below the M_d temperature, which is the maximum strain-induced martensitic transformation occurrence temperature [3]. As an alternative option for improving the wear resistance, generation of boride can be attractive for a wide ranging application. Borides that form with the transition metals have long been known to possess high potential for extreme applications because of their high hardness and excellent wear, friction and corrosion resistance [4]. Therefore, it is likely that worn surfaces could be hardened and suppressed from further plastic deformation.

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In this study, the effect of boron on the high temperature sliding wear behavior of Fe–20Cr–1.7C–1Si–xB ($x = 0.0$–2.0 wt%) hardfacing alloys was determined and the role of $\gamma \rightarrow \alpha'$ strain-induced martensitic transformations in the high temperature wear resistance of iron-based hardfacing alloys was investigated.

2. Experimental procedure

Fe–20Cr–1.7C–1Si–xB alloy blocks with x varying from 0.0 to 2.0 wt% were prepared by arc-melting under an argon atmosphere. The chemical compositions of the alloys were measured using an ARD 3460 optical emission spectrometer and their nominal chemical compositions are summarized in Table 1. Specimens for sliding wear tests are shown in Fig. 1. To ensure a constant surface finish, the surface of each specimen was polished to a final average roughness R_a of 0.2 μm using 2000 grit emery paper.

The block-on-block type sliding friction machine supplied by Plint & Partners Ltd. was used for the highly loaded sliding tests. The self-mated tests were performed in air at temperatures ranging from room temperature to 725 K, which was higher than maximum operating temperature of nuclear power plant valves. The contact stress was 103 MPa, which was the maximum allowed value for highly loaded valves [5]. The sliding speed of the wear test was 3 mm s^{-1} and the stroke was 9 mm. The total weight losses of the moving disc and the fixed plate were measured after 1000 cycle of sliding.

The worn surfaces of moving specimens after 1000 cycle of sliding were examined by XRD in order to investigate the strain-induced martensite formed during wear. The wear mechanism and the presence of oxide layers were identified from scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) analyses.

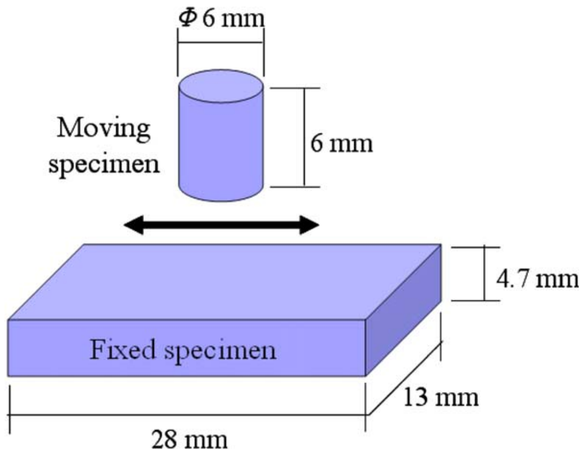

Fig. 1. Schematic and geometry of sliding wear test specimens.

3. Results and discussion

For boron contents lower than 1.0 wt%, the alloys were hypoeutectic with primary austenite dendrites interspersed by eutectic carbides and borides. As the boron content increased, grain size was refined as can be seen from the optical images in Fig. 3(a)–(d). The amount of eutectic phase rose from 34 to 59 vol.% (for 1.0 wt% boron added alloy) lineally from an image analyzer. As the boron contents increased higher than 2.0 wt%, the phase changed into a hypereutectic structure and consisted of primary coarse borides in an interdendritic eutectic phase as shown in Fig. 3(e) indicated by arrows.

The wear losses of boron added alloys compared to boron-free and Stellite 6 alloys as a function of temperature are presented in Fig. 4. As the temperature increased from 300 K, the wear loss of boron added alloys increased until 575 K. After a slight drop at 675 K, the wear loss began to increase again for all boron added alloys. However, the wear loss of both boron-free and Stellite 6 alloys increased lineally throughout the tested temperature range.

Table 1
Microhardness and nominal chemical composition of specimens (wt%)

Alloy	Hardness ($Hv_{0.05}$)	Fe	Cr	C	Si	B	Ni	Co
Fe–20Cr–1.7C–1Si–0.0B	507	Bal.	20.34	1.64	0.98	0.005	0.005	–
Fe–20Cr–1.7C–1Si–0.3B	605	Bal.	19.32	1.743	0.897	0.341	0.001	–
Fe–20Cr–1.7C–1Si–0.6B	652	Bal.	19.94	1.733	1.021	0.707	0.001	–
Fe–20Cr–1.7C–1Si–1.0B	895	Bal.	19.65	1.718	0.938	1.050	0.001	–
Fe–20Cr–1.7C–1Si–2.0B	945	Bal.	19.54	1.723	0.918	1.987	0.001	–
Stellite 6	508	2.09	29	1.25	0.81	–	2.21	Bal.

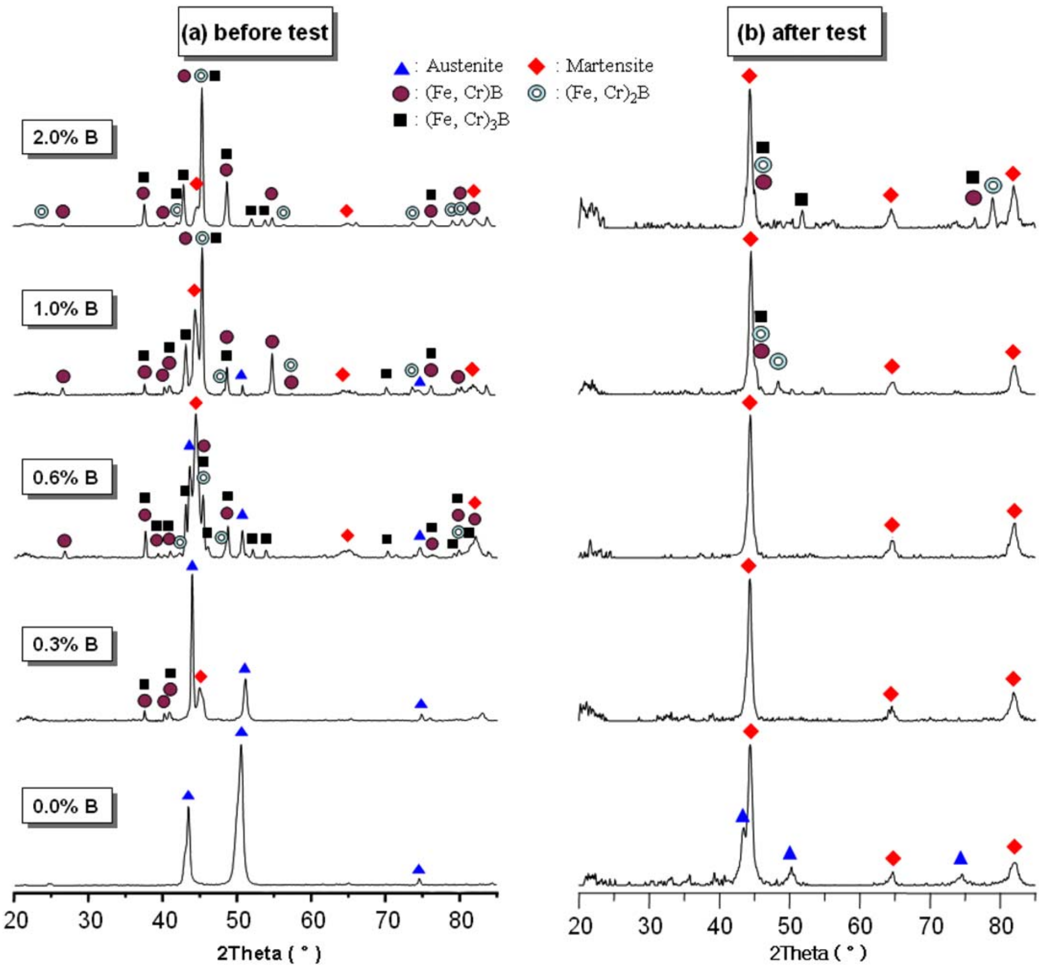

Fig. 2. XRD pattern analysis of Fe–20Cr–1.7C–1Si–xB specimen: (a) from the electro-polished surface; (b) after 1000 cycle of sliding at 725 K.

The worn surfaces at various temperatures under a contact stress of 103 MPa are presented in Fig. 5. As shown in Fig. 5(b) and (c), large portion of worn surfaces was found to be smooth and severe plastic deformation was not observed. The major wear mechanism is considered to be the mild adhesive wear. Some adhered layers were found on the worn surfaces tested above 575 K as indicated by arrows in Fig. 5(b2) and (c2). Results of EDS analysis of the worn surface from the 0.6 wt% boron added alloy tested at 725 K are presented in Fig. 6. It can be seen from Fig. 6(b) that a significant amount of oxygen was detected in the adhered layer. Thus, the adhered layers were considered to be the oxides formed on the contacting surfaces from compaction of wear debris particles. The oxide layers reduce the amount of wear loss by prohibiting the direct metal-to-metal contact [6]. Although the temperature at which the oxide layers began to form was not measured, the oxide layers formed on the wear surface was likely to contribute to the low wear loss of the boron added alloys between 575 and 675 K. Therefore, it was concluded that the improved wear resistance at elevated temperature was due to the wear transition from an adhesive to oxidative wear by formation of wear protective oxide layers. In the case of all boron added alloys as shown in Fig. 5, the mild oxidative wear was maintained up to 725 K. It is a well known phenomenon in some Fe- and Ni-base alloys that oxidative wear can take place at temperatures of about 475 K or higher due to the formation of wear protective oxide layers [7].

In order to evaluate the effect of work hardening by strain-induced phase transformation, the microh-

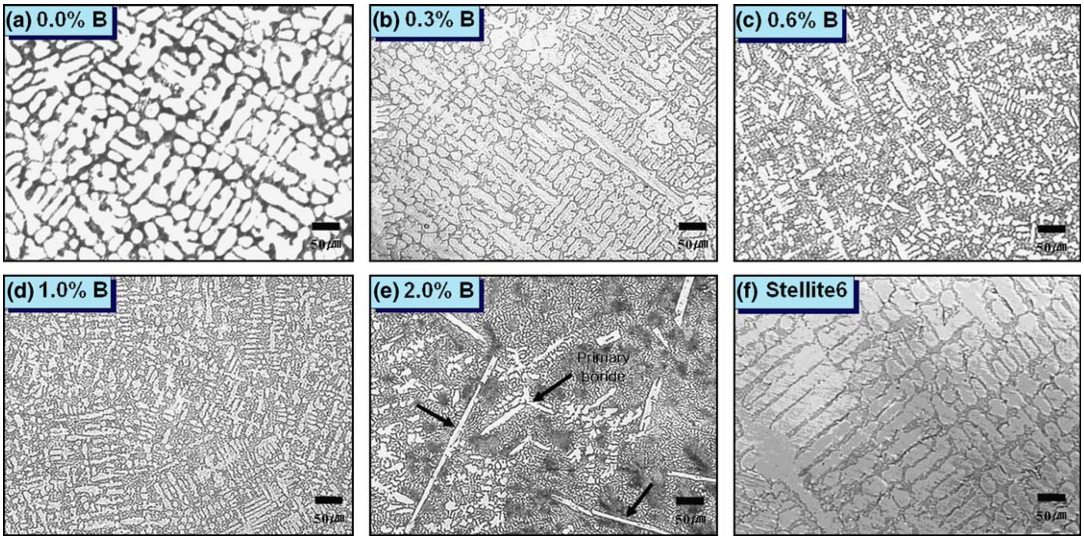

Fig. 3. Optical microstructure of Fe–20Cr–1.7C–1Si–xB and Stellite 6 alloys.

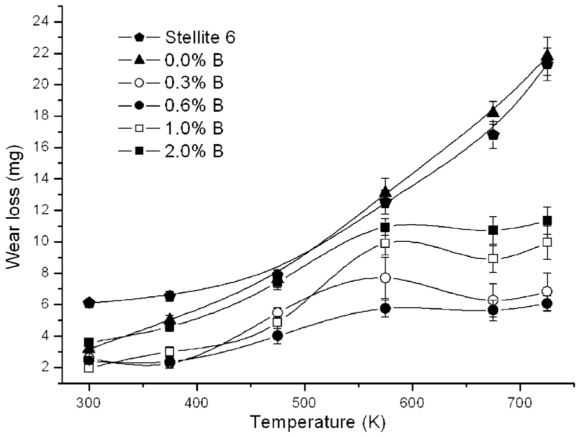

Fig. 4. The wear losses of Stellite 6 and boron added alloys as a function of temperature after 1000 cycle of sliding.

ardness variation beneath the worn surfaces of Fe–20Cr–1.7C–1Si–xB ranging from 0.0 to 2.0 wt% boron and Stellite 6 specimens were measured after 1000 cycle tested at 725 K and shown in Fig. 7. From the result, the worn surfaces of low-boron alloys were hardened up to more than 950 $Hv_{0.05}$ and the increment were about 400 $Hv_{0.05}$. The magnitude of the increase in microhardness for low-boron alloys was much larger than those for other tested alloys. In the case of the high-boron added alloys showing the increment of about only 20 $Hv_{0.05}$, the worn surfaces were hardly work-hardened.

This work hardening behavior of the boron added alloys was consistent with their wear loss result at 725 K as shown in Fig. 8. From this figure, it can be seen that the decrease of wear resistance with increasing boron content in high-boron alloys is mainly associated with the absence of work hardening, in spite of their initial high hardness compared to the low-boron alloys.

In order to confirm that the strain-induced phase transformation during wear led to the observed work hardening, the worn surfaces of the moving specimens after 1000 cycle of sliding were examined by XRD analysis in Fig. 2(b). In the case of low-boron alloys, the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation was observed at 725 K. Therefore, it was considered that the reason why the low-boron alloy showed the excellent wear resistance in an elevated temperature was the occurrence of the strain-induced martensitic phase transformation. And no evidence of matrix hardening by $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation was observed in boron enriched alloys, because these alloys did not have the austenite phase to be transformed into martensite during wear as shown in Fig. 2(a).

Although 2.0 wt% boron added alloy has the initial highest hardness containing primary coarse hard phases such as FeB type boride from Table 1, it had poor wear resistance than other boron added alloys due to the low toughness, which causes spalling during the wear test. The presence of the brittle FeB particles in the microstructure may easily induce crack nucleation. In fact, FeB boride is well known for its detrimental effect on wear resistance characteristic, because it is usually connected with high internal tensile stress and thus is likely

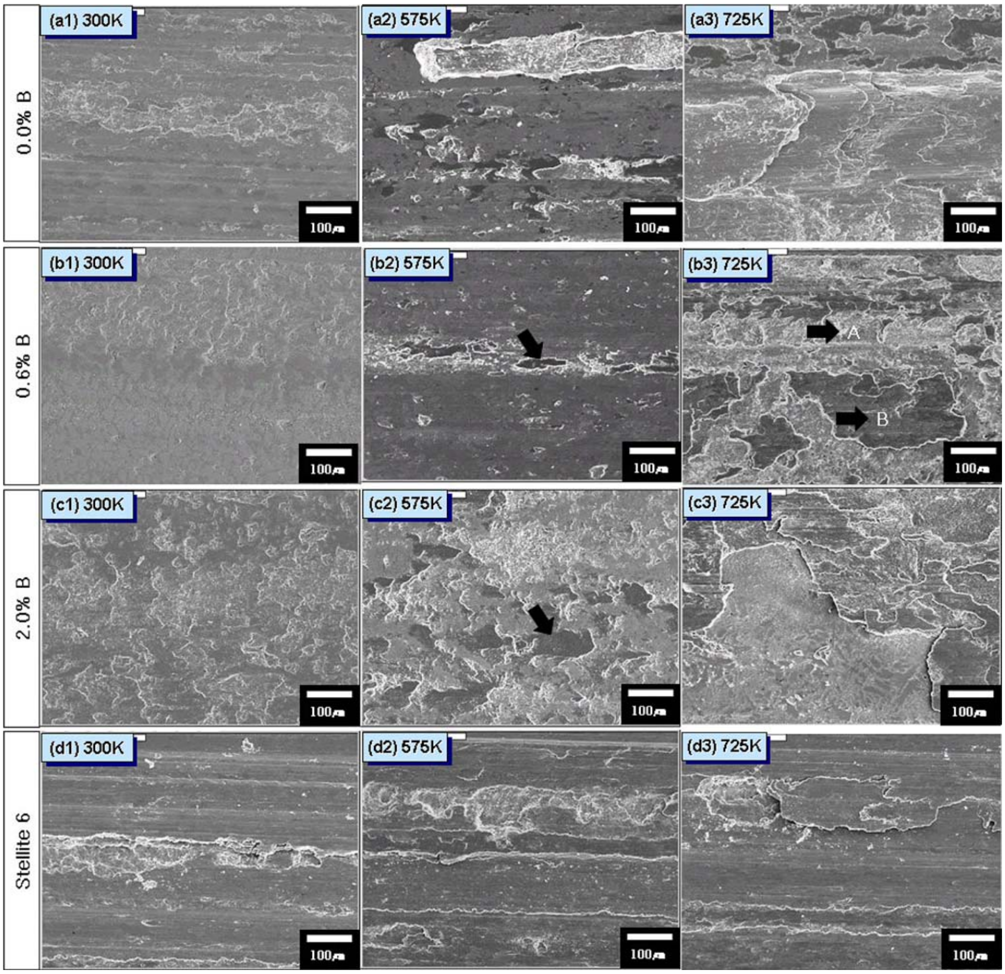

Fig. 5. SEM micrographs of worn surfaces after 1000 cycle of sliding tested at various temperatures.

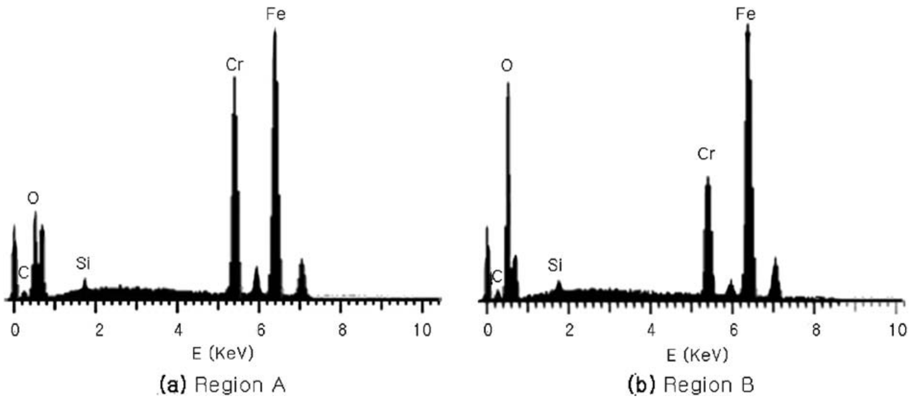

Fig. 6. EDS spectrums of worn surfaces of 0.6 wt% boron added alloy tested at 725 K.

to flake away during wear [8]. It is observed from the optical images in Fig. 9 that the eutectic matrix surrounding the borides has been collapsed, leaving the borides unsupported. Some borides have been fractured and detached from the surface leaving deep holes in places.

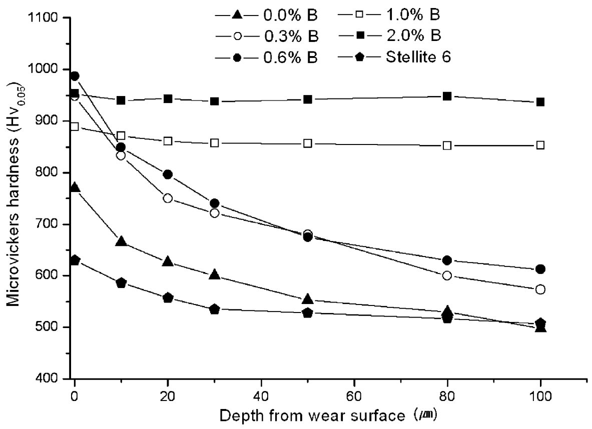

Fig. 7. Microhardness variations beneath the worn surfaces after sliding of 1000 cycle tested at the temperature of 725 K.

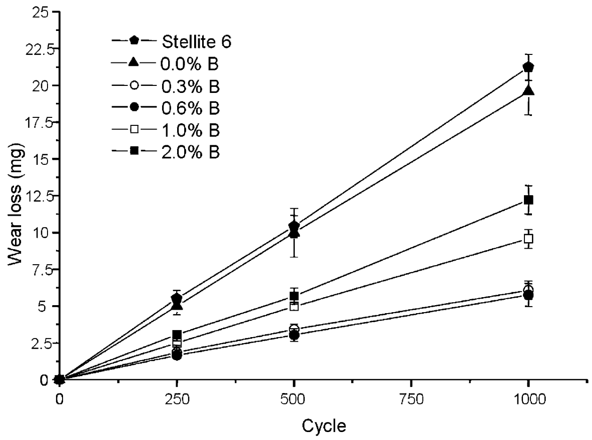

Fig. 8. The wear losses of boron added alloys and Stellite 6 as a function of sliding wear cycles tested at the temperature of 725 K.

Consequently, the optimized composition for sliding wear resistance is near Fe–20Cr–1.7C–1Si–0.6B alloy due to the matrix hardening by strain-induced martensitic transformation and the mild oxidative wear in high temperature as well as the improved initial hardness by grain size refinement and high volume fraction of eutectic phase.

Although the sliding wear test needs to be conducted in a pressurized water to realistically simulate the operating conditions of a nuclear power plant, the water environment has not been considered. However, it is well known that the water molecules prohibit the direct metal-to-metal contact and consequently reduce the adhesive wear [9]. Therefore, we could reach a conclusion that the new alloy can be used as hardfacing material for nuclear power plant valves even under the high contact stress of 103 MPa.

4. Conclusions

From sliding wear tests of Fe–20Cr–1.7C–1Si–xB ($x = 0.0$–2.0 wt%) alloys in air at temperatures of 300–725 K under a contact of stress of 103 MPa, the following conclusions could be drawn:

1. The excellent wear resistance composition was found to be Fe–20Cr–1.7C–1Si–0.6B.
2. The high wear resistance of Fe–20Cr–1.7C–1Si–0.6B is mainly due to the matrix hardening by strain-induced martensitic transformation as well as increased hardness by grain size refinement and high volume fraction of eutectic phase.
3. In the case of all boron added alloys tested in this present study, the mild oxidative wear was maintained up to 725 K, which was higher than maximum operating temperature of nuclear power plant valves.

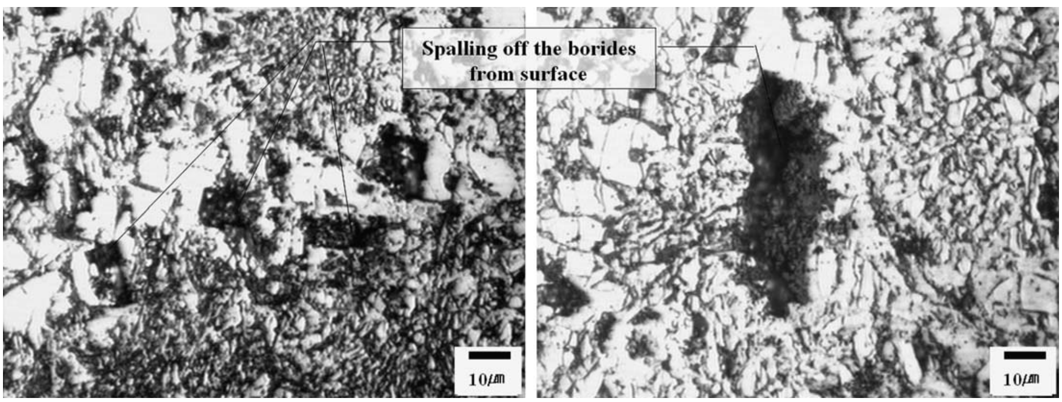

Fig. 9. Optical micrographs of the wear track of 2.0 wt% boron added alloy after 1000 cycle of test at 725 K.

4. However, the reason why highly added boron alloy showed somewhat larger amount of wear loss than other boron added alloys is that the presence of the brittle FeB particles in the microstructure may be associated with easy crack initiation. Therefore, the particles also have a low toughness, which causes spalling during wear test.

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