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Eutectic Modification in a Low-Chromium White Cast Iron by a Mixture of Titanium, Rare Earths, and Bismuth: Part II. Effect on the Wear Behavior

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In this work, we studied the wear behavior of a low-Cr white cast iron (WCI) modified with ferrotitanium-rare earths-bismuth (Fe-Ti-RE-Bi) up to 2%. These additions modified the eutectic carbide structure of the alloy from continuous ledeburite into a blocky, less interconnected carbide network. The modified structure was wear tested under pure sliding conditions against a hardened M2 steel counter-face using a load of 250 N. It was observed that wear resistance increased as the modifier admixture increased. The modified structure had smaller more isolated carbides than the WCI with no Fe-Ti-RE-Bi additions. It was observed that large carbides fracture during sliding, which destabilizes the structure and causes degradation in the wear behavior. A transition from abrasive to oxidative wear after 20 km sliding occurred for all alloys. In addition, the modified alloys exhibited higher values of hardness and fracture toughness. These results are discussed in terms of the modified eutectic carbide microstructure.

Keywords eutectic, fracture toughness, modifier mixture, wear behavior, white iron

1. Introduction

In previous research small additions of a modifier mixture composed of ferro-titanium (Fe-Ti), rare earths (RE), and bismuth (Bi) were made to a low-Cr white cast iron (WCI) whose chemical composition is shown in Table 1 (Ref 1). The ledeburite structure of cementite in the alloy was modified into isolated carbide blocks. It was concluded that the modified structure was the result of the combined effect from each component of the modifier admixture (Ref 1). Titanium, found in the proaustenitic matrix as a carbide (TiC) or carbo-nitride [Ti(C,N)], is likely to act as nuclei for this phase refining the dendritic structure prior to the eutectic reaction. Rare earths and Bi, found at the matrix/carbide interface, have been classified as insoluble elements, which tend to segregate to the solidification front. Several theoretical explanations about the modifying effect of solute accumulation at the solidification front have been discussed with respect to the modified structure in WCI (Ref 1).

The volume fraction of eutectic carbide decreased for the higher fraction modifier admixtures, and smaller, more isolated carbides were obtained in the structure. Hanlon et al. have shown that an order of magnitude reduction in carbide size results in a substantially reduced depth of deformation, or carbide fracture, below the worn surface during sliding wear of a high-Cr WCI, resulting in a significant improvement in wear resistance (Ref 2). On this basis, it was expected that improved wear behavior for the modified alloys would result.

2. Experimental Procedure

Hardness and matrix microhardness were carried out on Vilella-etched samples. For microhardness tests, a 100 g load was applied to the diamond indenter for 15 s. Macro-hardness measurements used the Rockwell C scale.

Fracture toughness was determined using three-point bending of V-notched specimens 25 × 25 × 150 mm on edge. A 50 T universal testing machine was used following ASTM E 399 (Ref 3).

Wear tests were performed on a pin-on-ring apparatus. Pins 1 cm in diameter by 1.5 cm in height were worn for 50 km against a hardened 6 cm diameter ring counter-face of M2 steel at a speed of 300 rpm. A 250 N load was used to test all alloys. Both pin and counter-face were polished to 0.25 μm finish prior to testing. Mass losses on each sample were registered after each 10 km sliding distance using a high precision analytical balance. The worn surfaces were analyzed by scanning electron microscopy (SEM) to identify operative wear mechanisms.

3. Results and Discussion

3.1 Effect of the Modifier Additions on the Bulk Hardness and Microhardness

Figure 1 depicts hardness as a function of the admixture addition, where a small increase from 42-47 Rockwell C (HRC) is observed as the amount of the modifier mixture is

Table 1 Chemical composition for the experimental white iron (wt.%)

C	Cr	Fe	Mn	Mo	Ni	P	S	Si
2.91	2.9	85.1	2.14	0.95	5.11	0.021	0.016	0.83

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increased. Since the eutectic carbide volume fraction decreased for higher amounts of the admixture, a decrease in hardness values would be expected for the alloys. As a rule of thumb, an increase in the volume of the hard phase leads to an increase in hardness of the alloys and the results from the present work could be thought contradictory. However, another factor that may also influence hardness is the eutectic grain size or the level of structure refinement, and the degree of dispersion of the hard phase. A finer dendrite structure and better dispersed cementite in the matrix may be responsible for the increase in hardness, despite the diminished volume fraction of cementite. On the other hand, microhardness of both cementite and austenite did not change with the admixture additions (Fig. 2). Although the results show some variation, the mean values fall within the range where no real change can be observed. Cementite microhardness was 770 (HV_{100}) while austenite hardness was ~340 (HV_{100}) for the different admixture additions. No change in microhardness for these phases was expected since RE elements and Bi segregate to the carbide/matrix interface and do not influence matrix solid solution strengthening. The only element that could cause an increase in hardness of the matrix is Ti since it is found as small TiC precipitates in the proeutectic matrix. The presence of such small precipitates may cause strengthening of the matrix, but for the amounts added in this study, the volume fraction of particles should be too small to lead to significant strengthening.

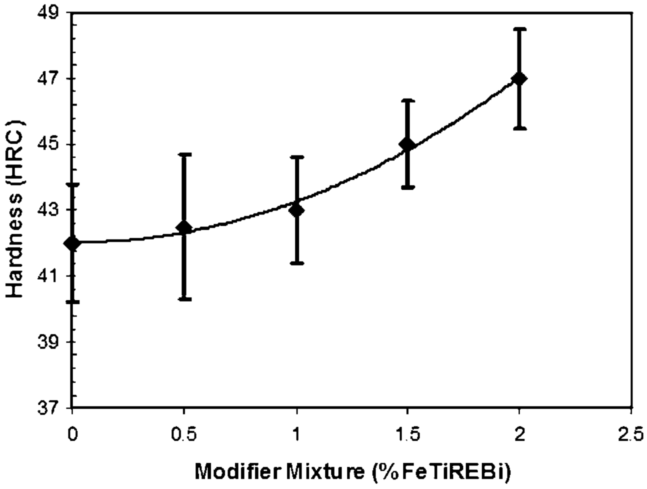

Fig. 1 Hardness of WCI as a function of Fe-Ti-RE-Bi admixture additions

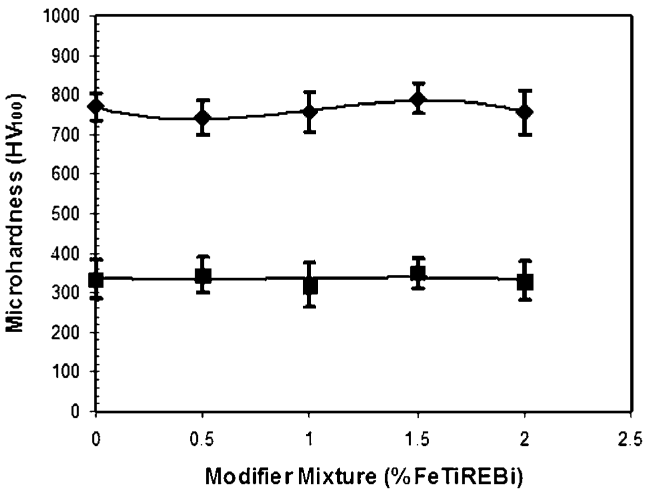

Fig. 2 Microhardness of WCI as a function of Fe-Ti-RE-Bi admixture additions

3.2 Fracture Toughness

Fracture toughness results are the most visible evidence of the effect of admixture additions. The observed discontinuity of eutectic cementite is further supported by these results. If the carbide phase is really discontinuous, implying a higher continuity of austenite, fracture toughness should increase. This was observed in the current study. Figure 3 shows the fracture toughness results (testing method described in Ref 3). For additions up to 1% of Fe-Ti-RE-Bi, no visible discernible change in fracture toughness occurred, and the mean value was equal to 5 MPa $m^{1/2}$. However, for additions of 1.5 and 2% of Fe-Ti-RE-Bi admixture, a clear increase in fracture toughness

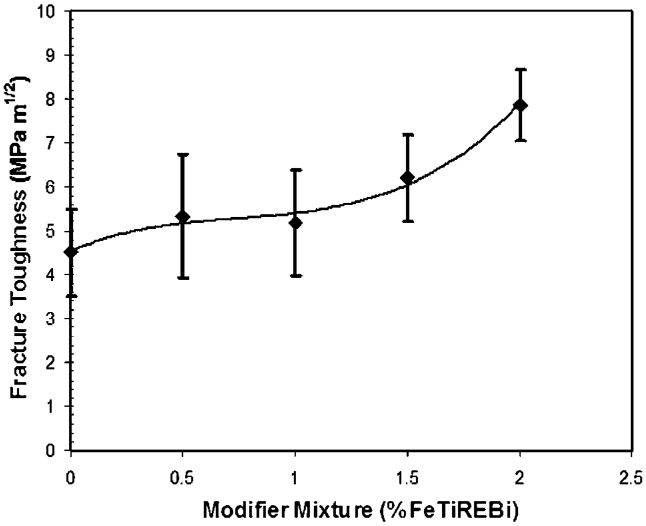

Fig. 3 Fracture toughness WCI as a function of Fe-Ti-RE-Bi admixture additions

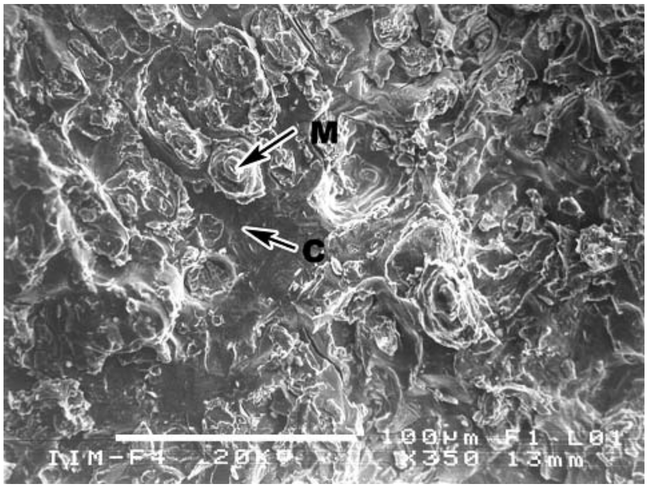

Fig. 4 SEM micrograph showing the fracture surface of the WCI with 1.5% of the modifier admixture. Arrows indicate areas where eutectic carbide (C) or matrix (M) is exposed

was observed, with values of 7 and 8 MPa m$^{1/2}$, respectively. Consequently, a decrease is suspected in the eutectic carbide continuity during solidification due to the modifier additions.

SEM fractography studies on freshly fractured samples shows evidence of the previous results. Figure 4 shows the typical fracture topography of a WCI where rough areas (M) and flat areas (C) are observed. The rough areas indicate ductile fracture, while the flat areas indicate brittle fracture, corresponding to the cleavage planes of cementite.

Fracture toughness gives an indication of the resistance of a crack propagating through the alloy. A crack will tend to propagate preferentially through and around a brittle phase. For WCI, the preferential path for crack propagation is the carbide phase. It has been well documented that in low- and high-Cr WCI, cracks propagate either along the carbide/matrix interface or through the cleavage planes in the carbide (Ref 4-6). Therefore, the presence of a high number of eutectic carbides on the fracture surface indicates a preferred path for crack propagation. Figure 5 shows the fracture surfaces of two WCI alloys, without modifier (Fig. 5a) and with the addition of 2% of the admixture modifier (Fig. 5b). A flatter surface for WCI without Fe-Ti-RE-Bi additions is observed in (Fig. 5a). It is then likely that the crack path has progressed through the continuous carbide phase by fracturing carbides along the cleavage planes with little resistance. Fracture toughness was 4.5 MPa m$^{1/2}$ for this sample. On the other hand, more tortuousness to the fracture surface was observed for the WCI with 2% Fe-Ti-RE-Bi modifier. In this case, it is likely the crack propagating through the sample propagated through large matrix areas to continue its propagation through and around the carbides. Under these conditions, crack propagation through the matrix shows signs of localized plastic deformation just ahead of the tip of the crack. According to Pearce, such localized deformation generates a high dislocation density, thereby strengthening the material locally (work-hardening), and it is this strengthening mechanism that leads to a higher applied stress for the crack to propagate (Ref 6). Therefore, fracture toughness values are higher and in this case the toughness is approximately 7.8 MPa m$^{1/2}$. Figure 6 shows detail of the brittle cleavage fracture of cementite.

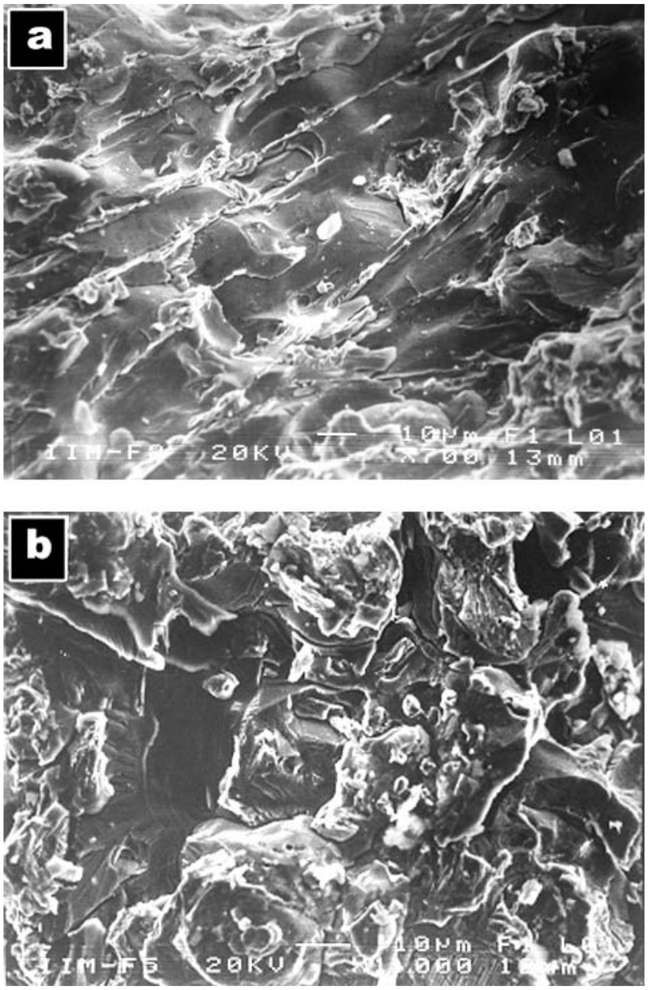

Fig. 5 SEM micrograph of fracture surface of two WCI samples: (a) no modifier additions and (b) 0.2% of Fe-Ti-RE-Bi admixture additions

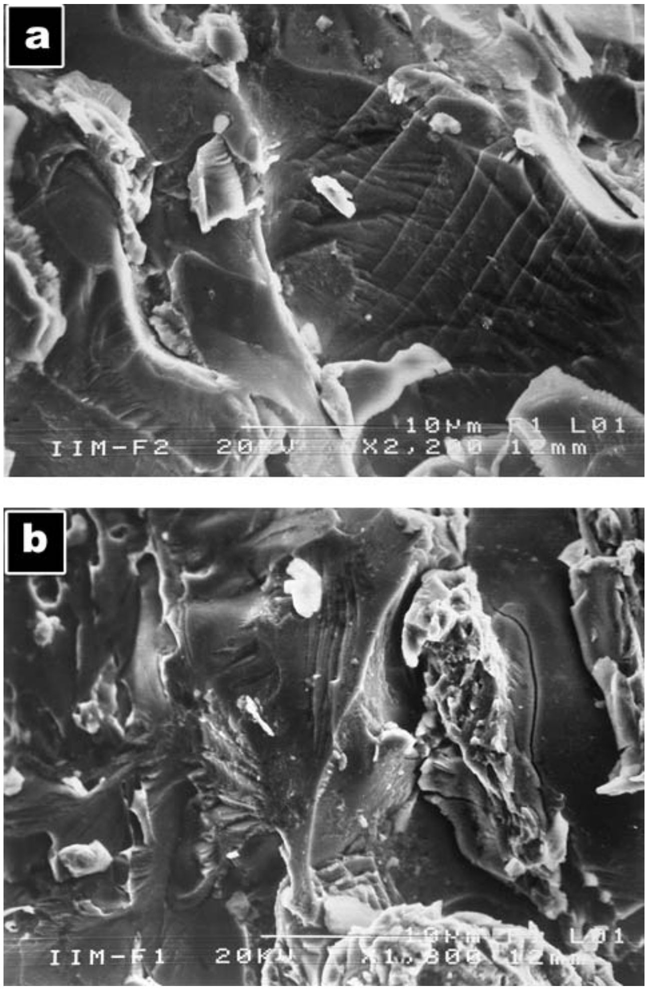

Fig. 6 SEM micrograph of fracture surface of two WCI samples showing the brittle fracture through the cleavage planes of eutectic carbide: (a) no modifier additions and (b) 2% of Fe-Ti-RE-Bi admixture additions

3.3 Wear Behavior

As mentioned above, one of the main uses of these alloys is in castings exposed to severe wear conditions. For this reason it is important to evaluate the mechanical response and microstructural behavior under these conditions. A pin-on-disk wear test was used. Figure 7 shows a plot of mass loss versus admixture fraction after 50 km. From this figure, mass loss decreased for the alloys with higher Fe-Ti-RE-Bi additions. Thus, there is an increase in wear resistance as the amount of the modifier admixture increases in the WCI.

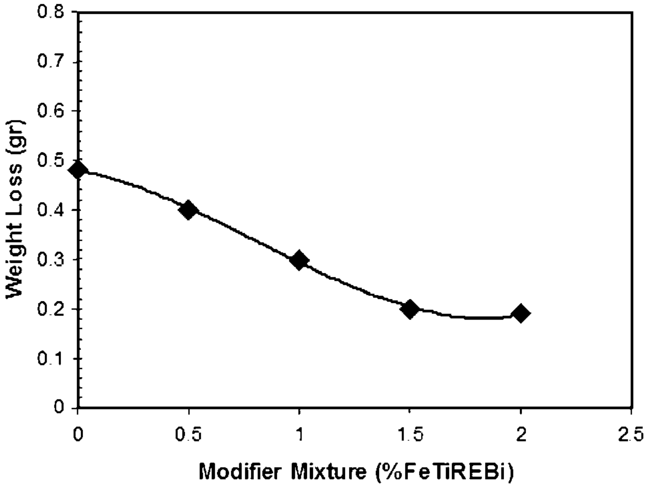

Fig. 7 Mass loss as a function of the modifier admixture for WCI after 50 km, 250 N applied load

Usually, wear resistance increases by increasing the carbide volume fraction. This does not occur for these alloys, as the results indicate that an increase in the modifier admixture decreased the carbide volume fraction. However, wear behavior is complex, and it is highly influenced by the particular tribological system and the wear mechanisms operating. For this particular case, carbide size and distribution increased wear resistance and carbide volume fraction had less influence on the wear behavior. The presence of smaller and less continuous carbides improves wear behavior under sliding conditions since a thin film on the surface of the sample undergoes high tangential stresses during sliding, generating elastic and plastic deformation in the film (Ref 7-9). If the carbides are small, they can dissipate stresses to the matrix without experiencing major damage. On the other hand, if the carbides are large, high-tensile stresses are developed at the rear of the carbide, bending and, perhaps, fracturing them (Ref 10). Figure 8 shows a sequence of SEM micrographs of the worn surface of the WCI after 10 km. Samples (a) and (b), corresponding to WCI with 0% and 0.5% Fe-Ti-RE-Bi additions, respectively, show fractured carbides due to sliding wear. Samples (c) and (d) correspond to WCI with 1 and 2% of the Fe-Ti-RE-Bi additions. Note the size of the carbides compared with samples (a) and (b), and the level of damage to the carbides, which has diminished.

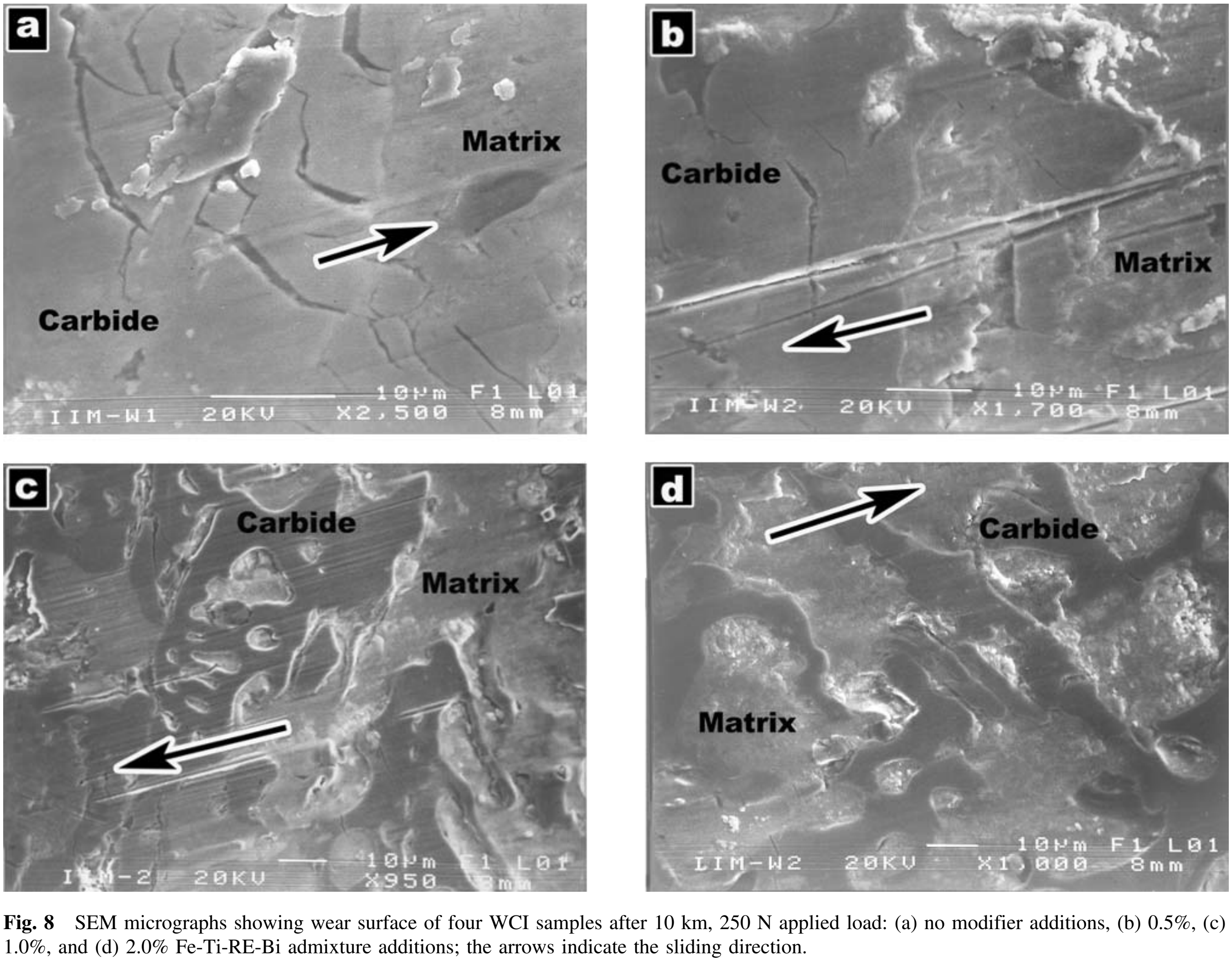

Fig. 8 SEM micrographs showing wear surface of four WCI samples after 10 km, 250 N applied load: (a) no modifier additions, (b) 0.5%, (c) 1.0%, and (d) 2.0% Fe-Ti-RE-Bi admixture additions; the arrows indicate the sliding direction.

Carbide fracture destabilizes the whole structure of the alloy. Carbide fragmentation allows easy detachment from the matrix. Therefore, the wear, or mass loss, during sliding is initially determined by the extent of fragmentation and detachment of the carbides. These results are in agreement with other research (Ref 9, 10). The presence of large carbides diminishes the wear resistance of these alloys under sliding conditions. Hanlon et al. have shown that an order of magnitude reduction in carbide size substantially reduces the depth of deformation and subsequent carbide fracture beneath the surface during sliding wear for high-Cr WCI (Ref 2). This resulted in significant improvement in wear resistance.

Bedolla-Jacuinde and Rainforth have also found an approximate linear relationship between depth of deformation and wear rate and established that deformation depth corresponds to the total depth where carbide fracture occurred (Ref 10). This provides evidence correlating wear rate with carbide fracture.

The operative wear mechanism changes as the wear test progresses. At the beginning of the test, a high metal-to-metal contact area exists. Due to the carbides, indications of abrasive wear are evident from the small grooves observed on some of the samples in Fig. 8. Metal-to-metal contact increases the friction coefficient during sliding, and therefore increases the tangential forces to a level that is deleterious to carbide integrity. The carbide subsequently fractures and detaches from matrix as small particles, causing the grooving. However, as sliding distance increases, the wear surface is covered by a thin oxide film. Such a film was first observed for sliding distances of >20 km. The film covers about 80% of the surface when the sliding distance has reached 50 km. This is observed from the SEM microphotographs in Fig. 9, which shows the worn surface of the WCI with 1% Fe-Ti-RE-Bi additions.

Oxide layer formation is due to the increase in temperature at the surface. It is estimated that the mean surface temperature may reach 280 °C (Ref 8), and under these conditions, it is likely the layer is composed of a mixture of Fe_2O_3 and Fe_3O_4. This oxide layer may be as thick as 10 μm and serves as a protective layer against further wear (Ref 10). The oxide layer adheres well to the substrate, particularly to the austenite matrix. This reduces the metal-to-metal contact that contributes to the severe abrasive wear. Under these conditions, the protective oxide layer acts as a lubricant since it has been shown to diminish the friction coefficient during sliding (Ref 7-10). This also reduces the tangential force. For long sliding distances, wear is dominated by the rate of oxide film formation and detachment. The oxide layer starts forming as the temperature increases, with continuous growth up to a critical thickness. Then the film detaches and starts to form once again from the metal on the surface. This repetitive process guarantees the

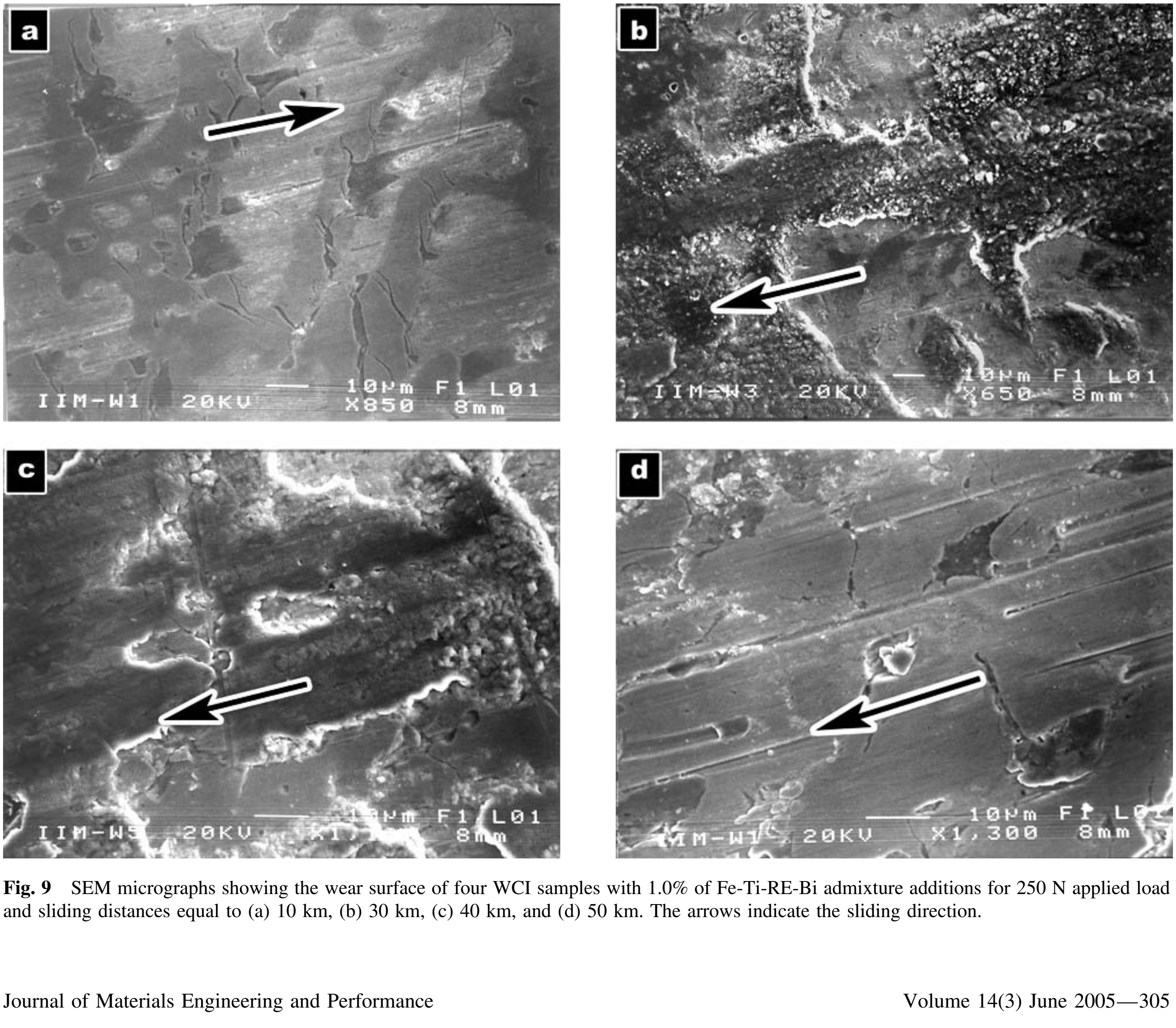

Fig. 9 SEM micrographs showing the wear surface of four WCI samples with 1.0% of Fe-Ti-RE-Bi admixture additions for 250 N applied load and sliding distances equal to (a) 10 km, (b) 30 km, (c) 40 km, and (d) 50 km. The arrows indicate the sliding direction.

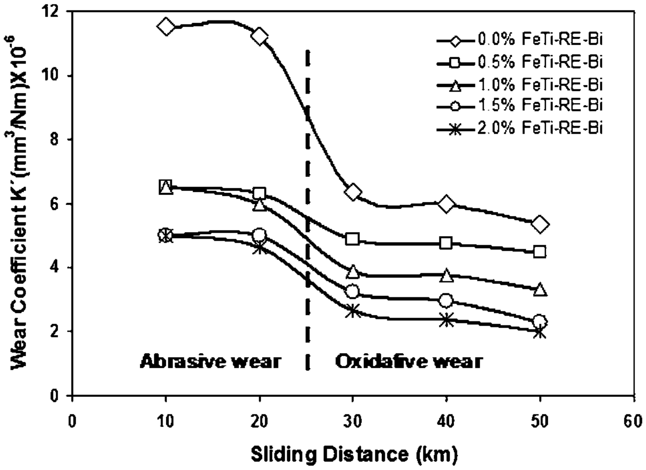

Fig. 10 Wear coefficients of WCI for different sliding distances. K' values decrease sharply after 20 km sliding, indicating a change in the wear mechanism from abrasive to oxidative

presence of a protective layer during sliding, making metal-to-metal contact less likely and, thereby, diminishing the friction coefficient and wear rate.

In summary, at sliding distances up to 20 km, the operative wear mechanism is abrasion. Abrasive wear is characterized by high mass loss with carbide fracture, comminution, and detachment that further abrades the surface during subsequent sliding. At this point, the wear rate is high compared with the wear rate the WCI experiences at longer sliding distances. At longer sliding distances, wear is dominated by metal oxidation, or oxidative wear (Ref 7-10). Since the friction coefficient decreases as a result of oxide layer formation, tangential forces that may destabilize the carbide and matrix also diminish, leading to a lower wear rate. This is clearly shown from Fig. 10 for plots of wear coefficient (K') versus sliding distance. The wear coefficient, or Lancaster coefficient, represents wear intensity as volume loss per unit load per unit sliding distance (mm^3/Nm). Volume loss was calculated from the mass loss using the density of the WCI (7.51 g/cm^3, measured by Archimedes method). If the same material removal mechanism was operating for the WCI, the curve would be linear and increasing with sliding distance (or the wear rate would be constant). As seen in Fig. 10, the wear rate changes between 20 and 30 km, indicating a change in the wear mechanism (abrasive to oxidative wear). From the same figure, the wear rate decreases as the amount of the modifier admixture increases in the WCI.

4. Conclusions

The effect of modifier admixture on the structure of high-Cr WCI is reflected in their mechanical properties. An increase in bulk hardness was observed as the amount of modifier increased. This is attributed to better carbide dispersal in the austenite for irons with >1% modifier. Microhardness of both eutectic carbide and matrix were not affected by the modifier additions.

Fracture toughness was slightly improved due to the diminution of the continuity of the eutectic carbides.

The wear rates, under sliding conditions, decreased as the amount of the modifier increased in the WCI. The presence of smaller and less continuous eutectic carbides contributed to microstructural stability under wear conditions, particularly for oxidative wear.

Acknowledgments

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