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The Influence of Carbon Content on the Oxidation and Wear Resistance of Fe-20%Cr Alloy at Elevated Temperatures

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Oxidation tests on Fe-20%Cr alloys with carbon contents ranging from 0,82 to 2,94 per cent were carried out at 900°C for 100 hours. The kinetic oxidation curves were determined at the same temperature for 8 hours by use of a thermal balance. Abrasion-wear tests were conducted at 800°C in a self-made high-temperature wear tester. The oxidation-worn surfaces were analysed by SEM. The subsurfaces were observed under SEM, and the chromium distribution was determined by microprobe.

The main findings were as follows. (1) With increasing carbon content, a change from normal external oxidation to catastrophic internal oxidation took place, resulting in a decrease in oxidation resistance. (2) Although the oxidation resistance of the high-carbon alloy was low, the coarse carbide, $(Cr.Fe)_7C_3$, was hard and stable, and could be utilized to increase the high-temperature wear resistance of the alloy. At 800°C, an increase in carbon content increased the high-temperature wear resistance. (3) Carbide fibres fractured at high temperatures owing to plastic deformation of the matrix. Hence, the resistance to plastic deformation of the matrix played an important role in supporting the carbide fibre and increasing the high-temperature wear resistance. (4) When oxidation was predominant in the process, a low-carbon alloy was preferable. When wear was predominant, a high-carbon alloy was more desirable.

Introduction

Reportedly, much work has been done on the abrasive wear of materials at room temperature. Some of the researchers have indicated that the bulk hardness of the materials and the hard eutectic carbide played very important roles in increasing the wear resistance[1-3]. This is the reason that high-chromium cast iron is widely used, being an excellent resistant material to abrasive wear at room temperature. However, materials that are used at high temperatures are subjected to both abrasive wear and corrosion due to oxidation[4]. Levy and his co-workers have published a number of papers on high-temperature erosion[5-7]. However, as the erosion process is different from abrasive wear, their work did not provide direct information on high-temperature abrasive wear. In the literature, there are only a limited number of papers on abrasive wear at elevated temperatures. Soemantri[8] and Fischer[9] have done some work on the high-temperature abrasive wear of pure metals and steels, but they did not address the wear of alloys containing high carbon and a considerable amount of eutectic carbide.

According to the conditions experienced by materials at high temperatures, research should be conducted on two aspects, i.e. oxidation corrosion and abrasive wear at elevated temperatures. Although some papers have been published on the oxidation and corrosion of materials[10-12], the materials investigated were pure metals and steel of very low carbon content. Obviously, the results do not apply to alloys containing high carbon and eutectic carbide. The present paper describes tests conducted on the Fe–20%Cr alloy with carbon ranging from 0,82 to 2,94 per cent.

Test Materials and Procedure

The chemical composition and structures of the test materials at room temperature are listed in Table I. All the specimens were annealed at 980°C for 2 hours and then machined to ∅10 x 20 mm for oxidation test specimens and ∅10 x 43 mm for wear test specimens.

Two kinds of oxidation test were carried out:

(1) kinetic oxidation curves, which were used in a study of the oxidation behaviour of the alloy during the process

(2) isothermal oxidation tests, which are useful in the evaluation of the oxidation tendency of an alloy.

The kinetic oxidation curves were based on determinations made on a heating furnace and a balance with a sensitivity of 0,1 mg. Each test lasted 8 hours. The isothermal oxidation test was conducted in a chamber furnace. Each test lasted 100 hours. The temperature during these two series of tests was 900°C. To reduce the error resulting from the non-uniform distribution of temperature in the furnace, three specimens of one group were put at different positions in the furnace. Two holes of 20 mm

TABLE I
CHEMICAL COMPOSITION (IN WEIGHT PER CENT) AND STRUCTURES OF TEST SPECIMENS AT ROOM TEMPERATURE

Specimen no.	C	Si	Mn	Cr	S	Structures at room temperature*
1	0,82	1,06	0,72	20,3	0,048	F+$(Cr, Fe)_{23}C_6$
2	1,63	1.01	0,82	19,6	0,030	F+$(Cr, Fe)_{23}C_6$+$(Cr, Fe)_7C_3$
3	2,24	0,93	0,72	20,8	0,030	F+$(Cr, Fe)_7C_3$
4	2,94	0,97	0,87	20,0	0,023	F+$(Cr, Fe)_7C_3$

diameter were located at the front and back walls of the furnace so that the interior of the furnace was connected to the atmosphere. After each test, the specimens were allowed to cool with the furnace, and were weighed together with the small spalled pieces. The oxidation weight gain was converted according to the unit area of the specimen.

Figure 1 is a sketch of the high-temperature wear tester. An abrasive wheel was placed horizontally in the test chamber, which was located in a heating furnace. A small amount of loose abrasive material was put onto the abrasive wheel. A group of specimens of the same composition was clamped onto the specimen holder and pressed onto the abrasive wheel, which was covered with loose abrasive material. When the shaft started to rotate (40 r/min), a relative movement took place between the tips of the specimens and the abrasive material on the wheel (Figure 2). This represented the process of abrasive wear. The test temperature was controlled by a thermocouple in the test chamber. Before each test, blank runs were made to ensure a uniform contact between the specimens and the wheel. Each test was run for 400 revolutions, the total travel being 138,16 m. The weight loss was measured by a balance with a sensitivity of 0,1 mg. The test temperature was 800°C. The abrasive wheel was made of 46-mesh white alumina (Al_2O_3), and the loose abrasive material was white alumina of 40 to 50 mesh. The total load on the three specimens was 55,4 N, and thus the load per unit area on the specimens was 0,24 MPa.

The reproducibility of the tester was checked by the use of specimens made of steel containing 0,4 per cent C, 10 per cent Cr, and 2 per cent Si. The test temperature was 710°C. The results of running these three groups (nine specimens) showed that the standard deviation of the measurements was 5,2 per cent, which was regarded as acceptable for research purposes.

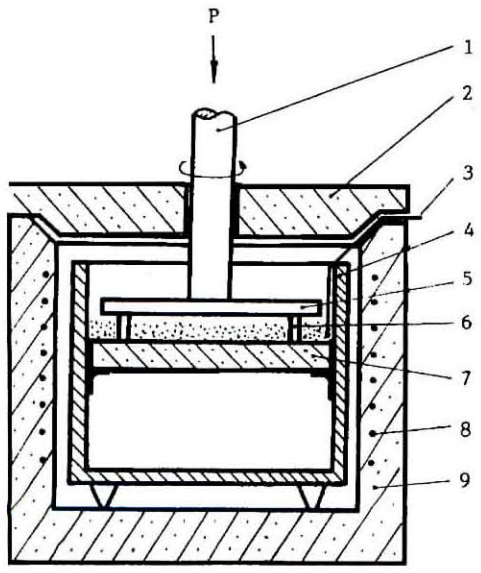


FIGURE 1. Sketch of the high-temperature wear tester

1 Shaft 2 Cover 3 Thermocouple 4 Test chamber 5 Specimen holder 6 Specimens 7 Abrasive wheel 8 Heating coils 9 Resistance furnace

Results and Discussion

Figure 3 shows typical metallographic structures of the test alloys. It can be seen that the low-carbon alloy (No. 1) has a small amount of carbide, $M_{23}C_6$. With increasing carbon content (alloy No. 4 containing 2,94 per cent C), a large amount of carbide, M_7C_3, is present.

Oxidation Resistance

Figure 4 gives the kinetic oxidation curves at 900°C for the four test alloys. Kazuyoshi[12] has reported that the kinetic oxidation curve for an Fe–Cr alloy of very low carbon content was parabolic. The parabolic shape means that the oxidation is diffusion-controlled. There is a preference for chromium to combine with oxygen, forming a dense Cr_2O_3 film. This film protects the matrix from further oxidation. The further oxidation rate is thus controlled by diffusion. If this film is damaged by stresses, cracks will occur, resulting in a significant weight gain. Whether the parabolic shape can be maintained depends on the crack-repairing ability of the alloy. The higher the chromium content, the stronger the repairing ability. As a result, the rate of weight gain would be greatly reduced.

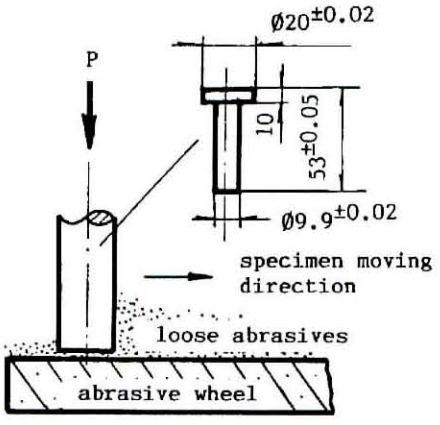
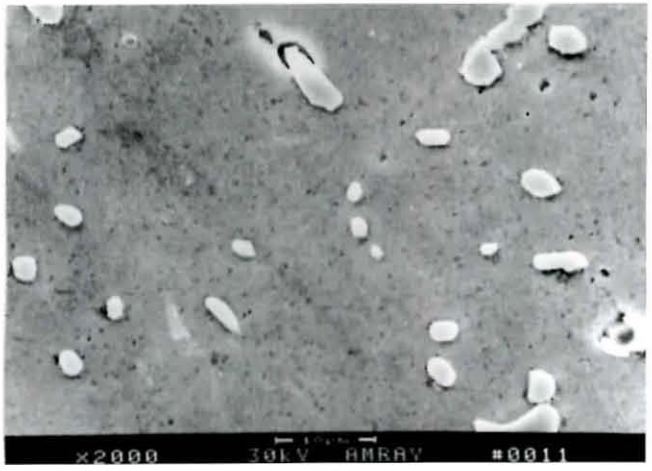


FIGURE 2. Sketch of the wear test

This behaviour was clearly seen on the curve of alloy No. 2. About 4,5 hours after the start of the test, an abrupt change in oxidation rate can be seen on the curve, implying the presence of cracks at that instant. The further oxidation was still parabolic. This phenomenon indicates a good repairing ability of the alloy. For alloy No. 1, it seems at first glance that the oxidation rate is linear, but careful observation of the curve shows that it is composed of a number of parabolic segments.

The oxidation behaviour of alloy No. 4 was quite different. At the beginning, the curve was almost linear. About 5,5 hours later, there were many jumps, indicating severe spalling of the oxidation film. This phenomenon is closely related to the chromium content in the matrix of the alloy. Table II shows the distribution of chromium in the matrix and eutectic carbide. With increasing carbon content from 0,82 to 2,94 per cent, the chromium content in the matrix decreased from 14,99 to 12,60 per cent. The decreased chromium content in the matrix of alloy No. 4 would reduce its crack-repairing ability. The instability of the curve shape means that cracking and spalling of the oxide film occur continuously.

(a)



(b)

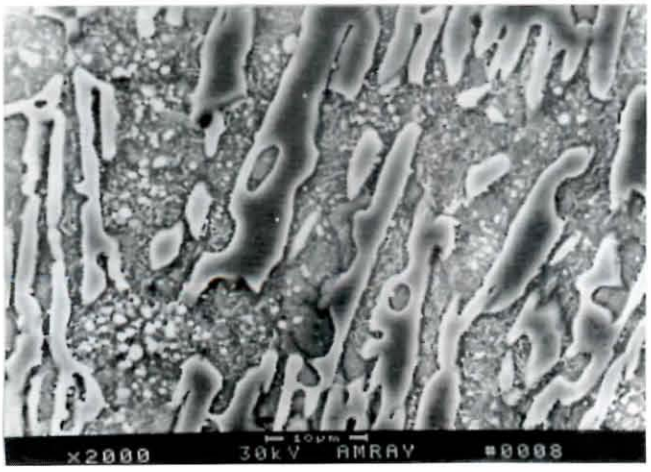


FIGURE 3. Typical metallographic structures of the test alloys
(a) Specimen No. 1 (F+$(Cr, Fe)_{23}C_6$)
(b) Specimen No. 4 (F+$(Cr, Fe)_7C_3$)

TABLE II
DISTRIBUTION OF CHROMIUM IN SPECIMENS (IN WEIGHT PER CENT)

Specimen no.	Matrix		Carbide	
	Cr	Fe	Cr	Fe
1	14,99	85,01	50,48	49,52
2	13,81	86,19	54,18	45,82
3	13,23	86,77	54,32	45,68
4	12,60	87,40	56,01	43,99

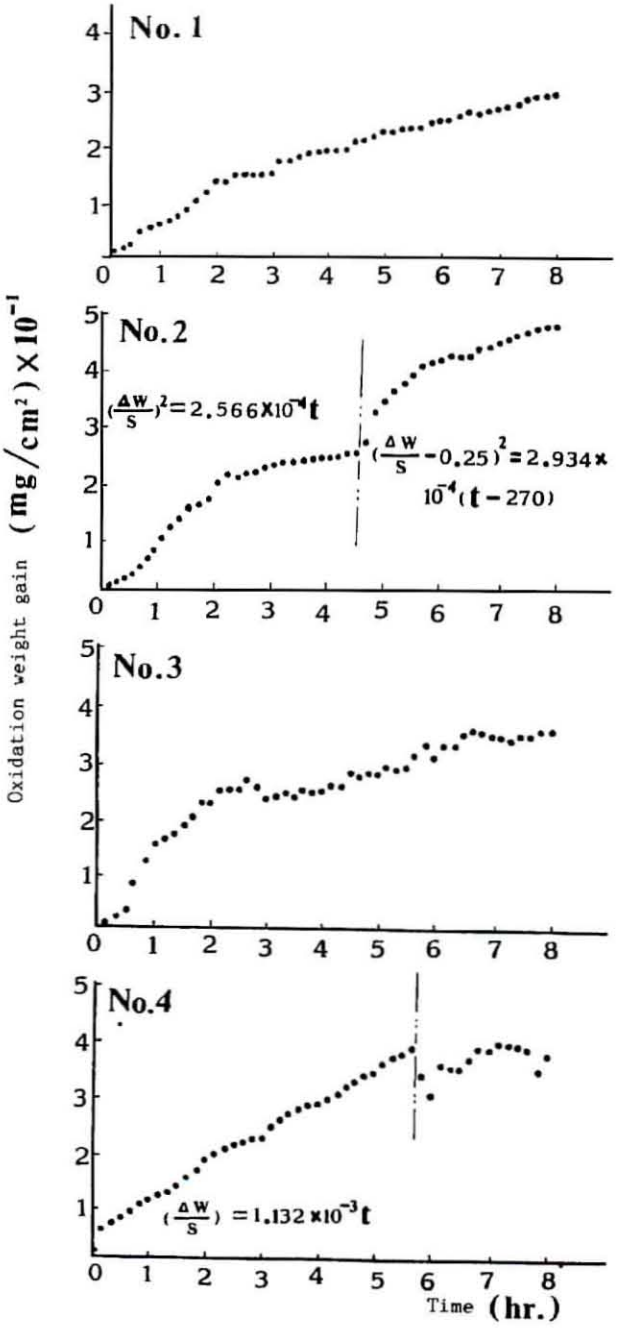


FIGURE 4. Kinetic oxidation curves at 900°C
Δw Oxidation weight gain (mg)
s Surface area of specimen (cm^2)
t Time (min)

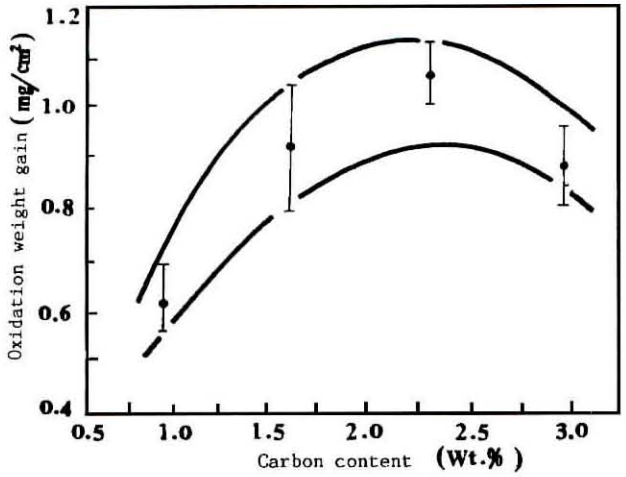
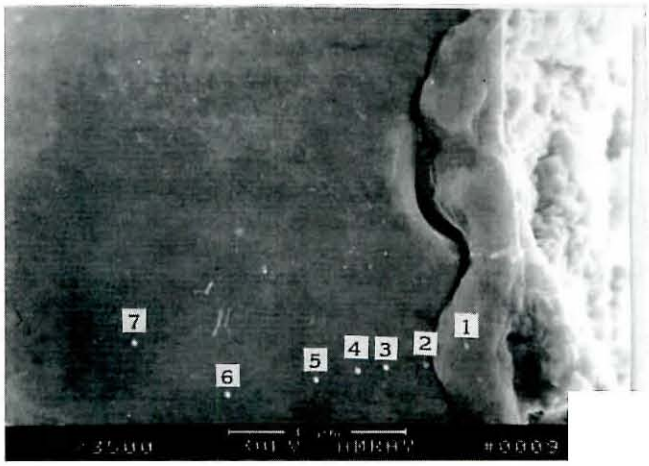


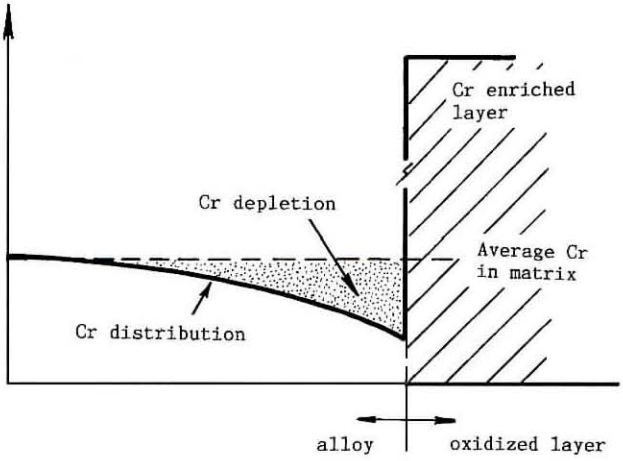
FIGURE 5. Relation between oxidation weight gain and carbon content at 900°C for 100 hours

Figure 5 illustrates the test results of the oxidation test at 900°C for 100 hours. It is seen that, with increasing carbon content (hence, increasing eutectic carbide), the weight gain increased to a maximum, and then decreased slightly.

Figure 6 is a photomicrograph of a normal section of specimen No. 1 after 100 hours of oxidation. The location of the microprobe-analysis points is indicated by the numbers. It can be seen that, in the subsurface beneath the oxide film, the original carbide, $M_{23}C_6$, has completely decomposed, and that the oxide film has covered the matrix fairly well. The microprobe analyses indicated a high enrichment of chromium in the oxide film. It can be expected that the oxide would be Cr_2O_3. (The 93,96 per cent chromium is the relative content in the sum of Cr_2O_3 and iron oxide in the oxide film, since oxygen was not detected.) Beneath the oxide film, there was a depletion of chromium in the subsurface layer. This layer shows that the oxidation was an external process[12]. It has also been shown that the normal external oxidation process has a good protecting effect. The formation of such a protective film in specimen No. 1 is due to its higher chromium content (14,99 per cent) in the matrix. The decomposition of $M_{23}C_6$ in the subsurface could provide much chromium in the matrix and is beneficial for oxidation resistance.

A quite different oxidation phenomenon was observed in specimen No. 4. As can be seen in Figure 7, there was no evidence of carbide decomposition beneath the oxide film, and some cracks were found in the oxide film and in the subsurface beneath the film. There was no clear interface between the film and the matrix. There was some enrichment of chromium in the oxide film, but the degree of enrichment was lower than that for specimen No. 1. Another difference was that there was no depletion of chromium underneath the oxide film. The chromium content was higher than the average content in the matrix. This means that there was some oxide at the point of determination.Therefore, the oxidation had a catastrophic effect internally[12]. This was mainly because of the presence of a large number of cracks in the oxide film and the matrix beneath it. The presence of these cracks was probably due to the existence of many eutectic carbides, which provided a great number of interfaces. These cracks themselves were channels for invading oxygen, resulting in severe internal





Results of microprobe analysis of Cr (wt.%)

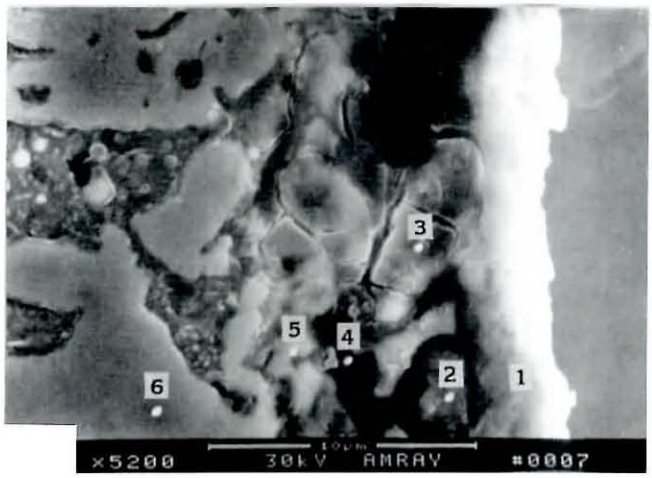
average	Cr	in	matrix	14.99
point	1	2	3	4
Cr	93.96	73.48	11.57	11.82
point	5	6	7	
Cr	12.00	12.36	13.36	

FIGURE 6. Normal section and chromium distribution in specimen No. 1 after oxidation at 900°C for 100 hours

oxidation. This process was controlled by the chemical-reaction rate. The kinetic oxidation curve was reasonably linear. It was noted that the large pieces of eutectic carbides, $(Cr,Fe)_7C_3$, were fairly stable. There was no obvious decomposition of the carbides. A comparison of the chromium content of the carbide of specimen No. 4 as given in Table II with that at point 6 in Figure 7 showed that there was no obvious difference. This was due to the stability of the carbides and their resistance to oxidation. This may be the reason why the weight gain decreased at high carbon levels (Figure 5). Also, these carbides could resist abrasion wear at elevated temperatures because of their stability and higher hardness.

Resistance at 800°C

Figure 8 shows the results of the wear test at 800°C. The



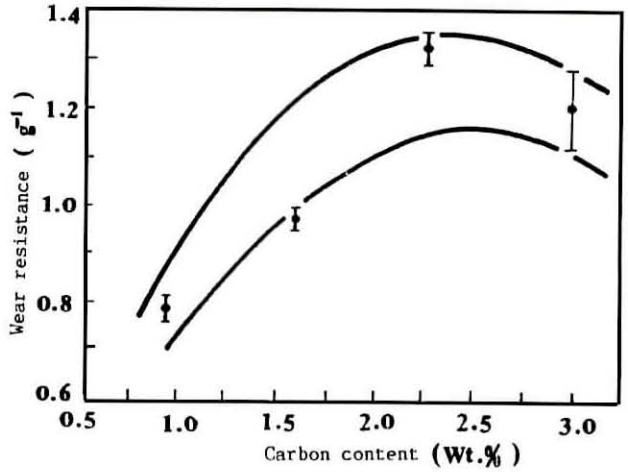
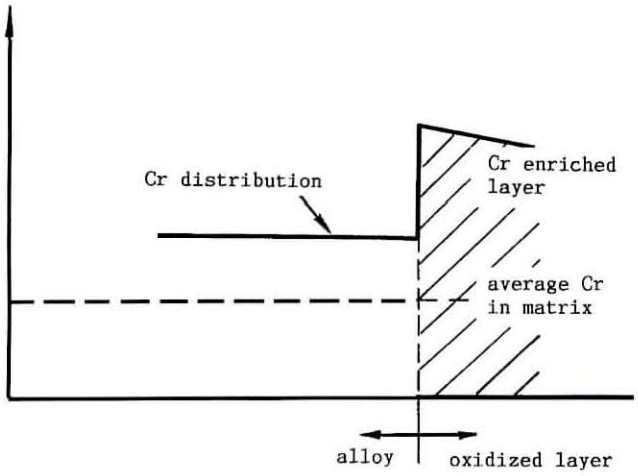


FIGURE 8. High-temperature (800°C) wear resistance as a function of carbon content



Results of microprobe analysis of Cr (wt.%)

average Cr in matrix			12.60
point	1	2	3
Cr	67.07	74.91	19.06
point	4	5	6(eutectic carbide)
Cr	20.04	20.04	53.36

FIGURE 7. Normal section and chromium distribution in specimen No. 4 after oxidation at 900°C for 100 hours

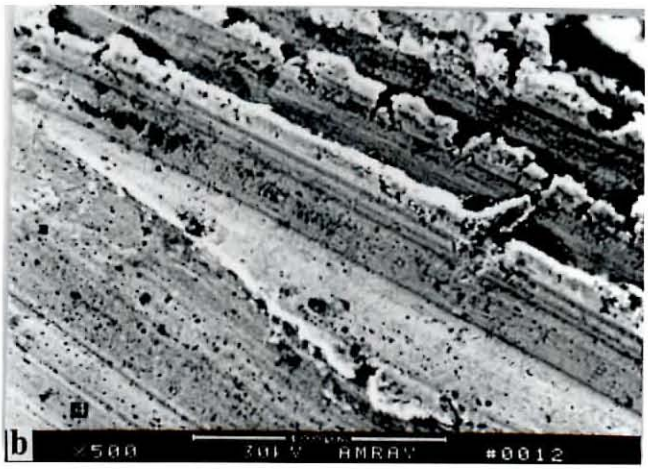


FIGURE 9. Morphology of the worn surface (SEM)
(a) Specimen No. 1
(b) Specimen No. 4

wear resistance is expressed as a reciprocal of the weight loss (g^{-1}). At first, the wear resistance increased as the carbon content increased, and then decreased. This phenomenon was closely related to the behaviour of the eutectic carbide in the wear process.

Figure 9 shows the wear morphology of the worn surface. The similarity in these two photomicrographs is that they both exhibit long-travel cutting wear. However, they differ in that many rolling traces accompany the cutting wear in the specimen of low carbon content. This is due to the improved plastic deformability of the material, especially at 800°C. With increasing carbon content, the cutting grooves became sharper until the carbon content reached 2,94 per cent of specimen No. 4. The wear was still cutting but, at the sides of the cutting grooves, much saw-shaped tearing occurred.

In addition, observation of the normal section of specimen No. 4 (Figure 10) under the subsurface at a depth of 10 μm revealed severely cracked carbides along the direction of wear. Obviously, this was due to increased plastic deformation of the matrix. The hard, brittle carbides could not follow the deformation of the matrix and hence fractured. The fracture of the carbide was harmful to the wear resistance. The fractured carbides became finer and were probably wholly pulled up by the roots under the action of abrasive particles. The fine particles of carbide were also likely to spall off from the matrix. Figure 11 shows a tapered section of specimen No. 4. There were a number of pits of a size corresponding to that of the carbides at the bottom of the cutting grooves, as indicated by the arrows in Figure 11. As a result, the wear resistance was lowered.

On the other hand, the fact that the carbides could resist wear is shown in Figure 12. On the worn surface it can be seen that an abrasive particle was stopped and fractured, and then embedded in the surface. In front of such stopped carbide, eutectic carbides usually occurred, as indicated by the arrows in Figures 10 and 13. This phenomenon shows the beneficial effect of carbides in resisting wear.

Therefore, in the wear process, the carbides exhibited contradictory twofold effects on wear resistance: on the one hand, the carbide might fracture and spall and, on the other hand, it could resist wear. The combined result would be a peak on the curve of wear resistance as a function of carbon content.

From the above discussion, it can be concluded that the wear resistance of a material can be improved if the fracturing and spalling of the carbides are not very severe. This depends strongly on the support that can be offered by the matrix. If the matrix is strong enough at elevated temperatures and is capable of resisting the plastic deformation resulting from abrasive wear, the carbide fibres are less likely to fracture. It can be supposed that the matrix plays an important role in improving the wear resistance at high temperatures of alloys containing eutectic carbides.

Conclusions

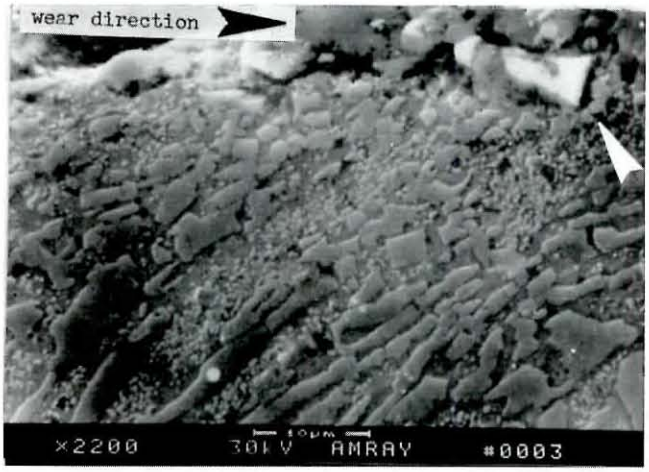


FIGURE 10. Normal section of specimen No. 4 (SEM)

FIGURE 12. Worn surface of specimen No. 4 (SEM) – fractured and embedded abrasive particle stopped by carbide

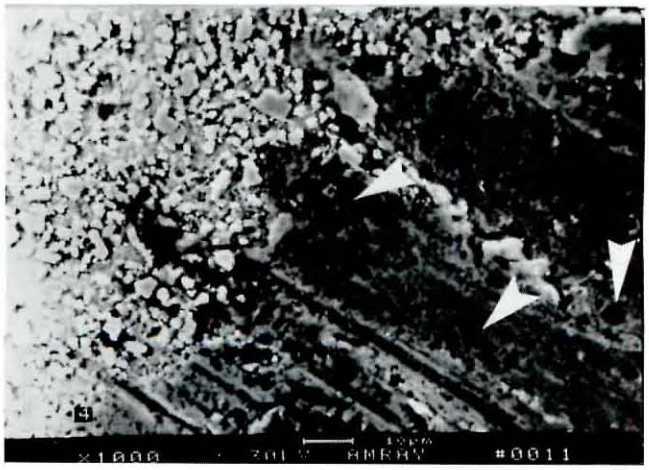


FIGURE 11. Tapered section of specimen No. 4 (SEM) – pits formed by spalled particles of carbide

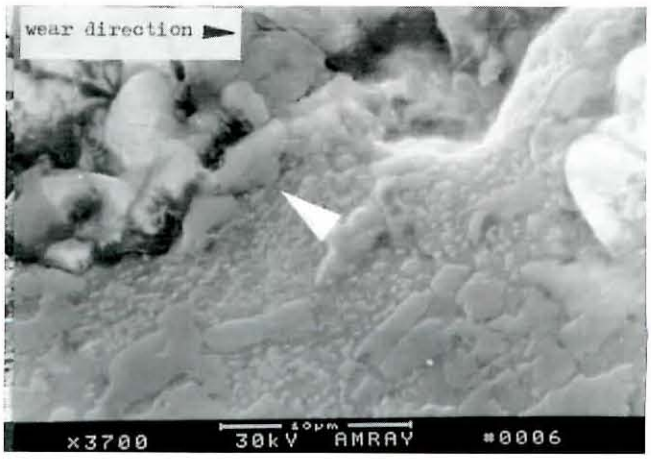


FIGURE 13. Normal section of specimen No. 4 (SEM) – moving abrasive particle stopped by carbide

(1) In Fe–20%Cr alloys with carbon contents increasing from 0,82 to 2,94 per cent, the oxidation changed from normal external to catastrophic internal, resulting in a decrease in the oxidation resistance of the alloy.

(2) High-carbon alloys are less oxidation resistant, but the coarse carbide M_7C_3 is stable and does not decompose at high temperatures. This provides an opportunity to utilize the carbide for resisting wear at elevated temperatures.

(3) Under the conditions in the present tests, an increase in carbon content (and, hence, in the amount of eutectic carbides) increased the wear resistance at 800°C.

(4) The fibres of eutectic carbides fractured severely in the subsurface layer owing to plastic deformation of the matrix. Although the fractured carbides lost wear resistance, if not spalled, they are still capable of resisting wear.

(5) The resistance of the matrix to plastic deformation is very important in supporting the carbides and, as a result, in increasing the wear resistance at high temperatures. Therefore, those elements which could increase the high-temperature strength of the alloy could also increase the high-temperature wear resistance.

(6) If the process is dominated by oxidation, an alloy of low carbon content is preferable. If the process is dominated by wear, a high-carbon alloy will be more desirable.

References

1. Xing, J.D., Lu, W.H., and Xang, X.T. (1983). An investigation on the wear resistance of high chromium cast iron. Ludema, K.C. (ed.) *Proceedings International Conference on the Wear of Materials, Reston.* New York, American Society of Mechanical Engineers. pp. 45–61.
2. Yan, P., and Zhou, Q.D. (1987). The influence of boron on the abrasive wear resistance of 17%Cr white cast iron. Ludema, K.C. (ed.). *Proceedings International Conference on the Wear of Materials, Houston.* New York, American Society of Mechanical Engineers. pp. 743–752.
3. Su, J.Y., and Jia, Y.D. (1987). The effect of orientation and thickness of carbides on abrasive wear resistance of high chromium cast iron. *Ibid.*, pp. 661–671.
4. Xing, J.D., Hu, B., and Zhou, Q.D. (1989). Failure analysis of clinker cooler grate plate. *Friction and Wear* (Tribology Institute of Chinese Mechanical Engineering Society), no. 1. pp. 28–33. (In Chinese).
5. Levy, A., Yan, J., and Patterson, J. (1986). Elevated temperature erosion of steels. *Wear,* vol. 108, no. 1. pp. 43–60.
6. Levy, A., and Hickey, G. (1986). Erosion of corrosion-resistant surface treatments on alloys and steels. *Ibid.*, pp. 61–80.
7. Levy, A., and Man, Y.F. (1986). Elevated temperature erosion–corrosion of 9Cr–1Mo steel. *Wear*, vol. 111, no. 2. pp. 135–159.
8. Soemantri, S., McGee, A.C., and Finnie, I. (1985). Some aspects of abrasive wear at elevated temperatures. *Wear*, vol. 104, no. 1. pp. 77–92.
9. Fischer, A. (1989). Construction of a new wear tester for elevated temperatures and first results of sliding abrasion tests. Ludema, K.C. (ed.). *Proceedings International Conference on the Wear of Materials, Denver.* New York, American Society of Mechanical Engineers. pp. 729–734.
10. Amano, T., Yajima, S., and Saito, Y. High temperature oxidation behaviour of Fe–20Cr–4Al alloys with small additions of cerium. *J. Jap. Inst. Metals*, vol. 41. pp. 1074–1082. (In Japanese).
11. Shoji, Y., Akiyama, S., Kisaichi, M., Nagatoshi, K., and Hoshi, H. (1976). Effect of carbon and titanium contents on the oxidation resistance of Fe–Cr–Al alloys at high temperatures. *Tetsu-to-Hagane*, vol. 62, no. 1. pp. 108–125. (In Japanese).
12. Nii, K. (1977). High temperature oxidation of alloys. *J. Boshoku Gijutsu*, vol. 26, no. 7. pp. 389–400. (In Japanese).