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Corrosion of Chromium Steel by Liquid Bismuth*

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Synopsis

The static corrosion of chromium steel by immersing in liquid bismuth at 600~950°C was studied, and the results obtained are as follows: (1) The corrosion loss increases with increasing chromium content. With the addition of zirconium as an inhibitor to liquid bismuth, the corrosion loss of high chromium steels becomes very slight, provided the carbon content is sufficiently high. (2) The growth of ZrC film at the steel surface is retarded by increasing the amount of chromium in steel. Thus, chromium steel is more favorable than carbon steel for a container of liquid bismuth.

I Introduction

In the previous paper, it was clarified that the corrosion of carbon steel by liquid bismuth was widely different with different carbon content in steel. When zirconium is added to liquid bismuth as an inhibitor, ZrC film is formed at the surface of steel.

In the present case, the corrosion was examined with chromium steels chiefly from the following two points of view: (1) the determination of the composition range of chromium steels which show a sufficient resistance to the corrosion as the container of liquid bismuth containing zirconium, and (2) the determination of conditions under which the sufficient protective film ZrC is formed when the steel is immersed in liquid bismuth containing zirconium.

Though low chromium steels containing 2.25 per cent Cr are generally used as a container for liquid bismuth⁽¹⁾⁽²⁾⁽³⁾, little attention was paid to the effect of alloying elements. Since chromium is easier to dissolve in liquid bismuth than iron⁽⁴⁾, chromium in steel may provide an infectious effect on the corrosion resistance, while it retards the diffusion of carbon. The principal purpose of the present investigation is to determine the inhibiting effect of zirconium on the corrosion of chromium steels containing various amounts of carbon and chromium. Steels used are listed in Table 1. Amounts of impurities are nearly the same as those of carbon steels in the previous paper.

* The 1094th report of the Research Institute for Iron, Steel and Other Metals.

(1) J.A. James and J. Trotman, *J. Iron and Steel Inst.*, **194** (1960), 319.

(2) J.R. Weeks and C.J. Klamut, *Nucl. Sci. Eng.*, **8** (1960), 133.

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(4) R.N. Ryon, *Liq. Metals Handbook*, June (1952), Atom. Energy Com.

Table 1. Chemical analysis

Alloy	Group	No.	C wt%	Cr wt%	Total N ₂ wt%	Soluble N ₂ wt%
Fe-Cr-0.1% C Alloy	D	1	0.11	1.11	0.012	0.002
		2	0.11	1.94	0.015	0.004
		3	0.11	2.84	0.019	0.007
		4	0.11	4.66	0.025	0.009
		5	0.14	9.92	0.023	0.014
		6	0.12	12.78	0.026	0.017
Fe-Cr-0.2% C Alloy	E	1	0.20	0.89	0.009	0.003
		2	0.21	1.83	0.004	0.002
		3	0.25	2.80	0.014	0.008
		4	0.25	4.87	0.014	0.010
		5	0.24	9.84	0.023	0.012
		6	0.23	12.78	0.032	0.016
Fe-C-2% Cr Alloy	F	1	0.055	1.81	0.009	0.001
		2	0.093	1.84	0.010	0.003
		3	0.17	1.90	0.009	0.002
		4	0.38	1.92	0.011	0.003
		5	0.43	1.92	0.009	0.003
		6	0.68	1.92	0.012	0.002
Fe-C-5% Cr Alloy	G	1	0.03	4.95	0.009	0.007
		2	0.10	4.68	0.011	0.009
		3	0.19	4.81	0.014	0.013
		4	0.32	4.97	0.014	0.011
		5	0.44	5.01	0.020	0.018
		6	0.70	4.72	0.016	0.015
Fe-C-10% Cr Alloy	H	1	0.71	9.12	0.012	0.011
		2	0.15	9.45	0.015	0.012
		3	0.34	9.31	0.014	0.013
		4	0.50	9.49	0.020	0.016
		5	0.64	9.35	0.023	0.020
		6	0.88	9.03	0.016	0.014

II. Experimental results

(1) Corrosion of chromium steels

Fig. 1 shows the relation between the corrosion loss at 700°C and the chromium content when zirconium is not added to liquid bismuth. Curves (a) and (b) refer to the steels containing 0.1 and 0.2 per cent of carbon, respectively. The corrosion loss in the case of 0.035 per cent C was already shown by curve (a) in Fig. 2 in the previous paper. In Fig. 1 it is seen that the corrosion loss increases with increasing chromium content, but that it decreased as the carbon content increases. As above mentioned, chromium easily dissolves into liquid bismuth compared with iron, and exists as carbide, dissolving partly in matrix; hence, the preferential dissolution of chromium will be retarded.

Above 5 per cent of chromium content, the corrosion loss is as high as 5~10 times than in pure iron. On the presumption that the corrosion of Fe-Cr alloys is controlled by the diffusion of chromium in matrix, the corrosion loss is to be considerably larger than would be expected from the solubility of chromium in bismuth. For instance, in Fe-14 per cent Cr alloy it may, at most, be two times higher than pure iron, but actually it was 5~10 times higher. To clarify this

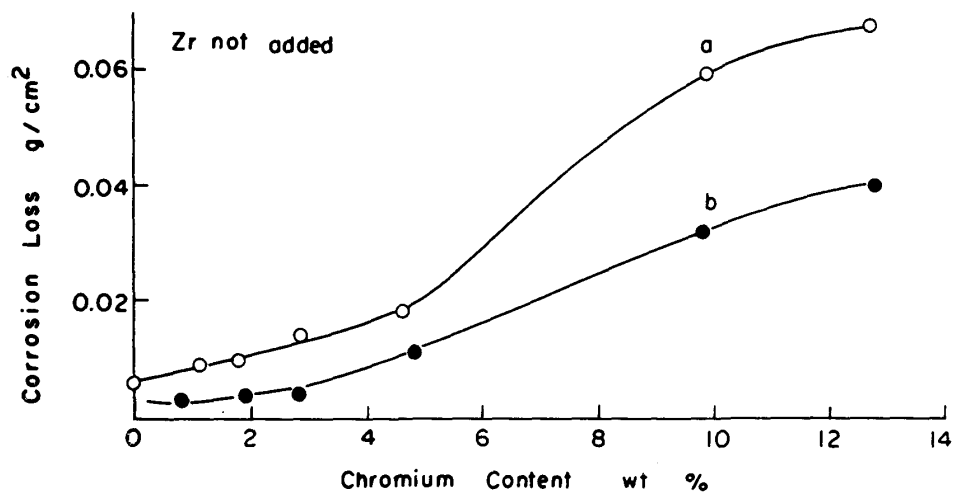


Fig. 1. Corrosion loss versus chromium content in Fe-C-Cr alloys ($700^{\circ}\text{C} \times 165$ hrs.)
 a: Fe-0.1%C-Cr, b: Fe-0.2%C-Cr

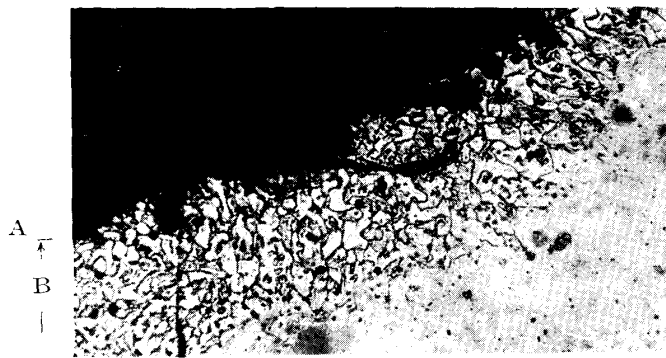


Fig. 2. Microstructure of a Fe-9.52% Cr alloy after immersion in Bi at 840°C for 165 hours ($\times 700$).

A: Surface B: Sub-grained layer

difference, the microstructures after corrosion were examined. Fig. 2 shows the structure of Fe-9.52 per cent Cr alloy after immersion at 840°C for 165 hours. The grains at the surface layer of specimen are considerably fine, showing many subgrains similar to that of pure iron. After the microscopic examination it was verified that as the chromium content is increased, the formation of subgrain becomes progressively marked and the grain boundaries are attacked severely. In accordance, it may be said that the corrosion in high chromium steels is accelerated by the preferential attack along grains or subgrain boundaries in addition to the preferential dissolution of chromium in bismuth, and that the formation of subgrain is promoted by the preferential dissolution of chromium.

(2) Inhibiting effect

Curve (a) in Fig. 3 shows the relation between the corrosion loss and the immersing temperature in Fe-14 per cent Cr alloy with extremely low carbon when zirconium is added as an inhibitor. The corrosion loss is one fourth that without

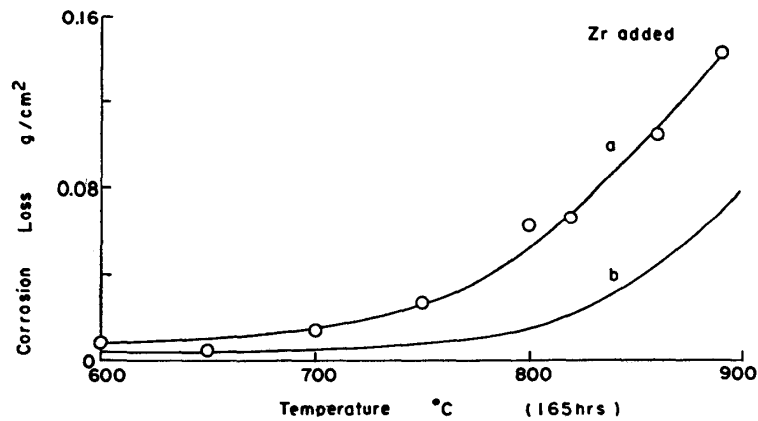


Fig. 3. Corrosion loss versus temperature in (a) Fe-14.02% Cr (0.025%C) alloy and (b) pure iron.

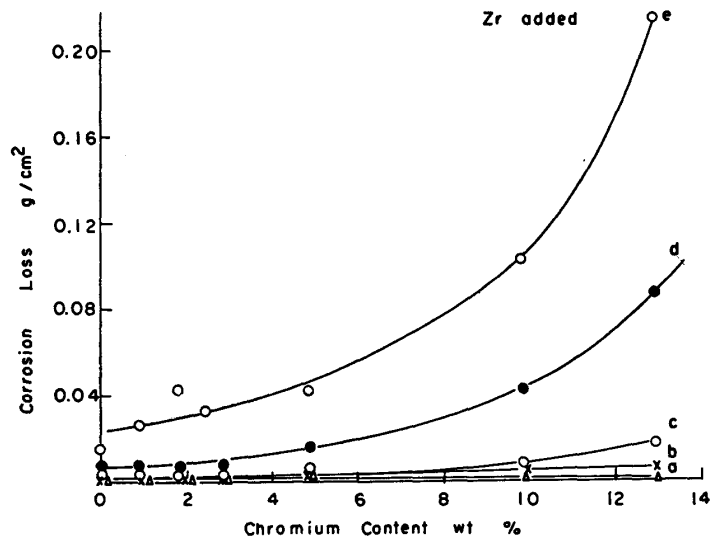


Fig. 4. Corrosion loss versus chromium content in Fe-0.2% C-Cr alloys. Time, 165 hrs. a: 730°C, b: 790°C, c: 820°C, d: 890°C, e: 950°C

zirconium, and two times higher than that of pure iron (curve b).

The relation between the corrosion loss and the chromium content in Fe-0.2 per cent C-Cr alloys is shown in Fig. 4. From Figs. 3 and 4, it is seen that the inhibiting effect of zirconium is less marked with increasing contents of chromium and carbon.

Further experiments were made to see the relation between the inhibiting effect and the chromium content. Figs. 5, 6 and 7 show the relation between the corrosion loss and the carbon content in Fe-Cr-C alloys containing 2, 5 and 10 per cent chromium, respectively. In each case, the inhibiting effect of zirconium becomes remarkable above 0.4 per cent of carbon, the corrosion loss being lowered down to nearly zero, while below 0.4 per cent of carbon the corrosion loss becomes high.

It is of importance that the chromium content affects the critical amount of carbon. According to the result at 800°C shown in Fig. 8, the critical amount of

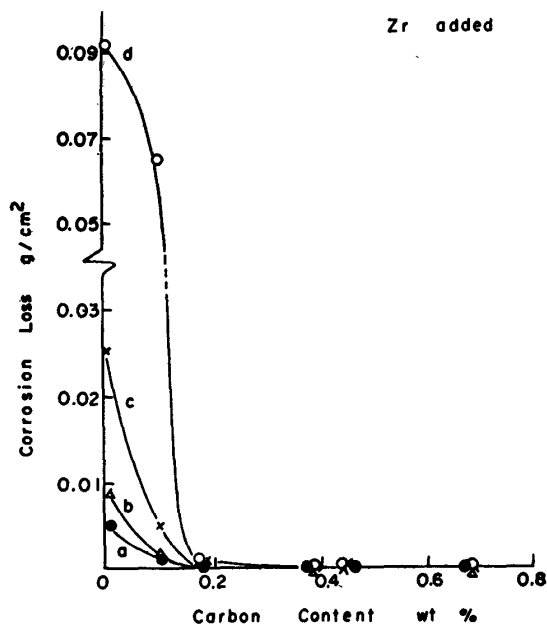


Fig. 5.

Fig. 5. Corrosion loss versus carbon content in Fe-2%Cr-C alloys. Time, 165 hrs.
a: 700°C, b: 750°C, c: 800°C, d: 870°C

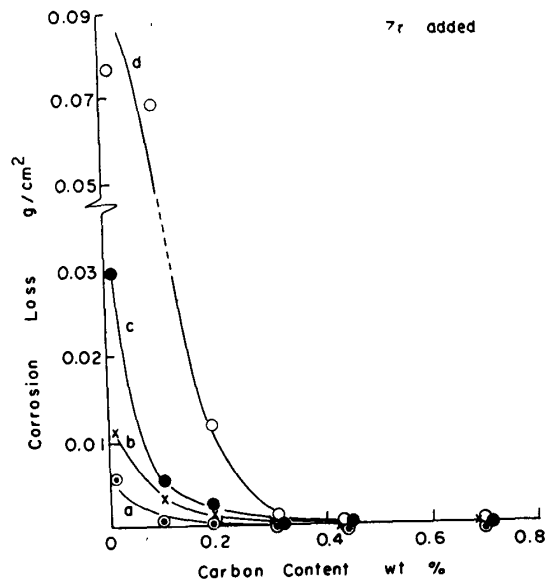


Fig. 6.

Fig. 6. Corrosion loss versus carbon content in Fe-5%Cr-C alloys. Time, 165 hrs.
a: 700°C, b: 750°C, c: 800°C, d: 870°C

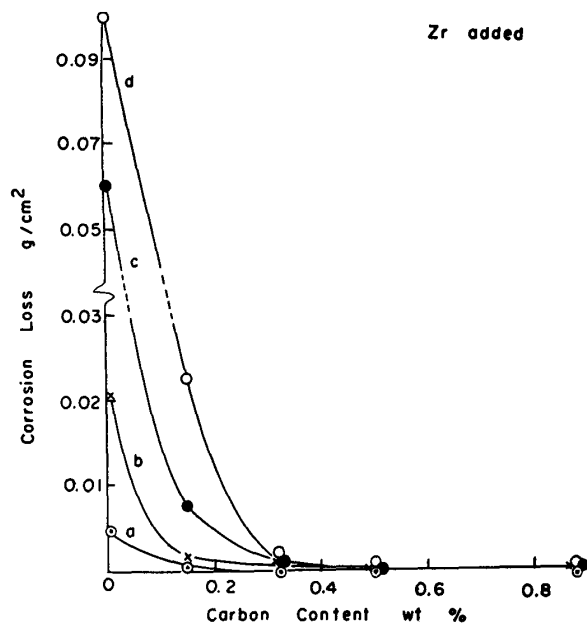


Fig. 7. Corrosion loss versus carbon content in Fe-10%Cr-C alloys. Time, 165 hrs.
a: 700°C, b: 750°C, c: 800°C, d: 870°C

carbon increases with increasing chromium content; in other words, a large amount of carbon is necessary for an effective inhibition by zirconium in high chromium steels.

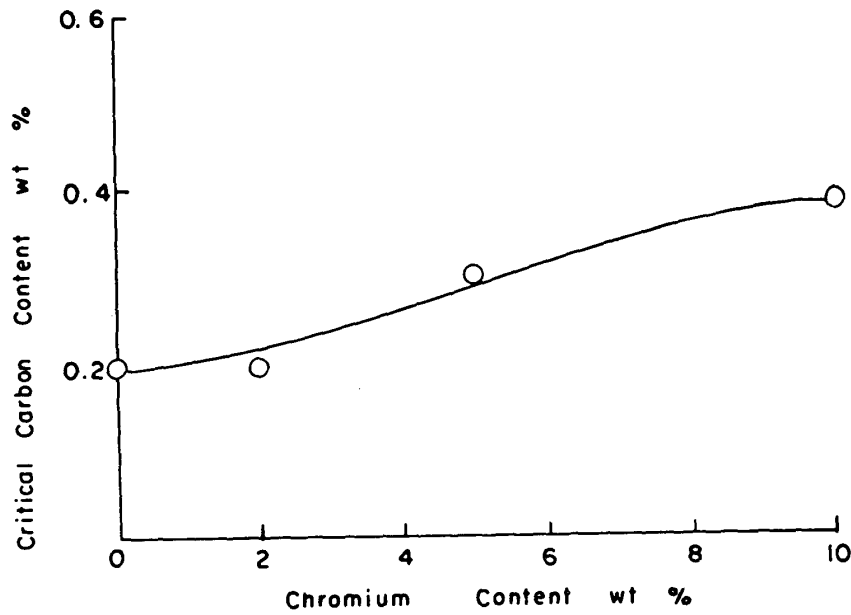


Fig. 8. Critical carbon content in Fe-C-Cr alloys for which the corrosion loss at 800°C (165 hours) is zero.

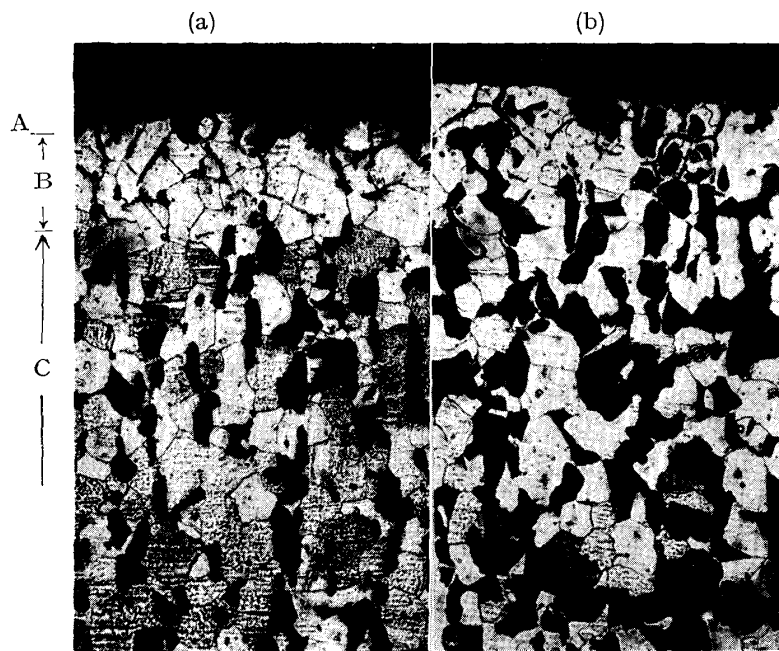


Fig. 9. Microstructures of Fe-Cr-C alloys after immersion in Bi containing Zr at 840°C for 165 hours ($\times 700$).

(a) Fe-0.20% C-0.89% Cr, (b) Fe-0.25% C-2.80% Cr

A: Surface, B: Decarburized layer, C: Unchanged part

To examine extensively the effect of chromium, the depth of decarburization at the surface layer of steel was measured. Fig. 9 shows the microstructures at the surface layer after immersion. As the chromium content increases, the depth of decarburization becomes small. The relation between the depth of decarburization and the chromium content in Fe-0.2 per cent C-Cr alloys is shown in Fig. 10, from

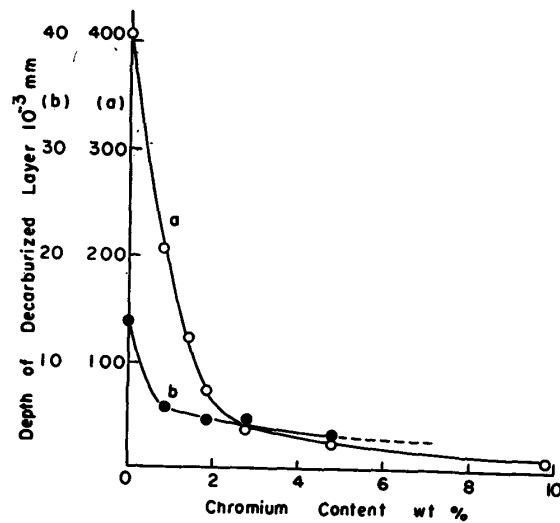


Fig. 10. Depth of decarburized layer versus chromium content in Fe-0.2% C-Cr alloys. Time, 165 hrs., a: 950°C b: 700°C

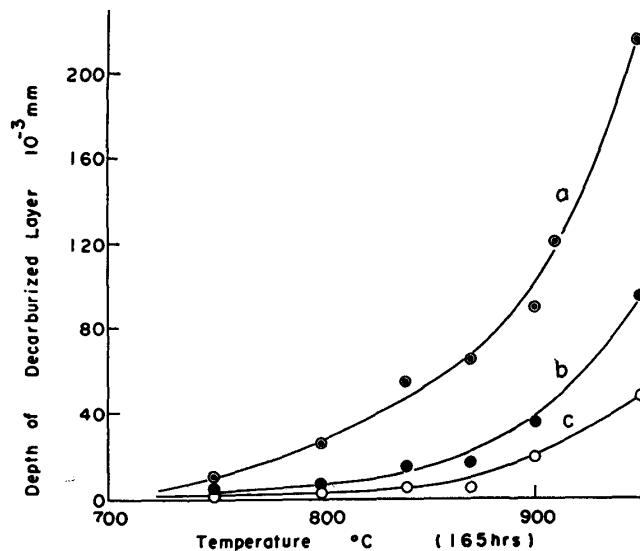


Fig. 11. Depth of decarburized layer versus temperature
 a: Fe-0.20% C-0.89% Cr b: Fe-0.21% C-1.83% Cr
 c: Fe-0.25% C-2.80% Cr

which it is seen that the depth decreases considerably as the chromium content increases. In the case of 10 per cent of chromium, the depth became very small and was difficult to measure. Fig. 11 shows the thickness of decarburized layer after immersion at various temperature ranges of austenite, indicating that the logarithm of the thickness has an approximately linear relationship to the reciprocal of the absolute temperature. From this result and that on the thickness vs. immersion time, the activation energy for the decarburization was obtained as shown in Fig. 12. In carbon steels, the value is 36 kcal/mol, being in good correspondence to that for the diffusion of carbon in austenite. The activation energy increases with increasing chromium content, being 45 kcal/mol at 2~3 per cent of chromium. Beyond 3

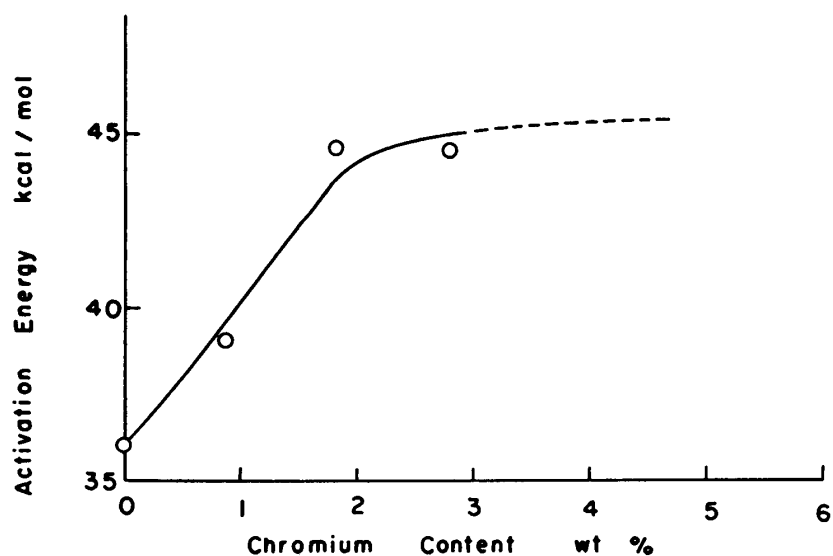


Fig. 12. Activation energy for the decarburization in temperature ranges of austenitic phase in Fe-0.2%C-Cr alloys.

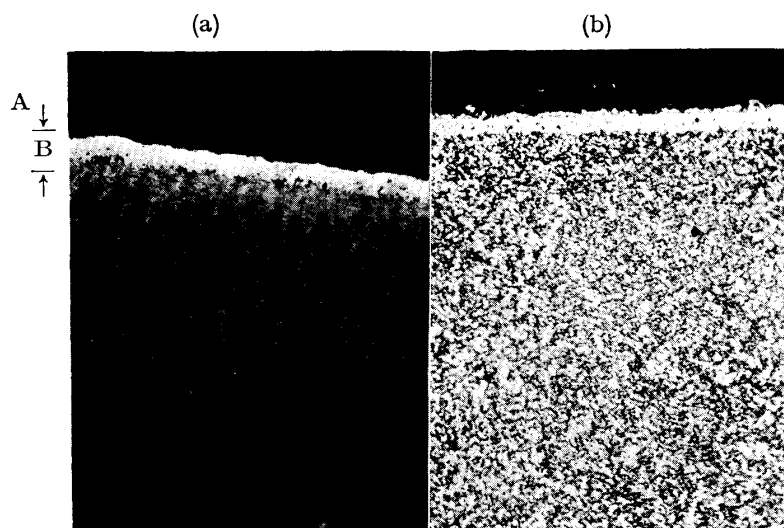


Fig. 13. Microstructures of carburized iron alloys after immersion in Bi at 800°C for 165 hours ($\times 700$).

(a) Fe-14.05%Cr (b) Fe-4.24%W
 A: Surface B: Carbide film

per cent, although the thickness of decarburized layer is very small, and is difficult to measure, it is presumed that the activation energy is considerably high.

(3) Carburization and corrosion of iron base binary alloys

It may be evident that the inhibiting effect is due to the film of ZrC formed at steel surface. To know whether the carburization is effective for the inhibition or not, the corrosion characteristics of iron base alloys were studied after carburization at 950°C for 15 hours. Fig. 13 shows the microstructures of the surface layers of Fe-Cr and Fe-W alloys carburized and then immersed in liquid bismuth. The carbide film seemed to be hardly attacked by liquid bismuth. The results on

Table 2. Corrosion loss (d) of iron base binary alloys carburized at 950°C for 15 hours and then immersed in liquid bismuth at 800°C for 165 hours.

Conc.	5.0% Cr	14.1% Cr	2.4% Mo	3.0% Ti
d, 10 ² g/cm ²	0.008	0.01	0.01	0.03
Conc.	3.1% V	3.0% Zr	4.2% W	10.2% W
d, 10 ² g/cm ²	0.01	0.03	0.01	0.01

corrosion loss are summarized in Table 2, where it reveals that the corrosion loss is very small, and that thus the carbide film formed at the surface has almost no solubility in liquid bismuth.

III. Consideration

There has been little study on the diffusion of carbon in the temperature ranges of austenite in chromium steel. It is, however, probable that the decarburization of chromium steel is attributable to the diffusion of carbon. The rate of diffusion of carbon in steel at high temperatures is 10⁴ times higher than that of chromium, and also probably 10²~10³ times higher than that of zirconium. In accordance, it may be said that the rate of formation of ZrC films is controlled by diffusion of carbon in steel. In chromium steel, the rate of diffusion of carbon is considerably lower than that in carbon steel,⁽⁵⁾ and so the rate of formation of ZrC film is also lower. As the over-growth of ZrC film may bring about the easy separation from the steel surface, chromium steels may be favorable from the practical point of view. If, however, the rate of growth is lower than that of corrosion or dissolution, the inhibiting effect would not be expected.

Summary

The static corrosion of chromium steels by liquid bismuth at 600~950°C was studied, and the results obtained may be summarized as follows:

(1) The corrosion loss increases with increasing chromium content, while, when zirconium is added in liquid bismuth, the corrosion loss of high chromium steels becomes very small in the case of the carbon content being beyond a critical value. The critical amount of carbon increases with increasing chromium content.

(2) The inhibiting effect of zirconium is due to the formation of ZrC film at steel surface. The growth of the film seems to be controlled by the diffusion of carbon in steel. The over-growth is unfavorable since the separation of the film from the steel surface easily occurs. In this regard, chromium steels is favorable because the diffusion resistance of carbon is considerably high compared with that in carbon steel. Instead of the addition of zirconium in liquid bismuth, carburization is an effective method for the inhibition of corrosion.

(5) R.W. Balluffi, M. Cohen and B.L. Averbach, Trans. ASM, **43** (1951), 497.