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# Corrosion and Erosion of Ferritic Steel by Liquid Bismuth\*

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## Synopsis

Static corrosion of Fe-C-Cr alloys and erosion of Fe-C and Fe-Cr alloys due to the contact with liquid bismuth were studied. For the static corrosion test, magnesium as a deoxidant and zirconium as an inhibitor were added into liquid bismuth prior to the immersion of specimens. The erosion test was carried out by applying an ultrasonic oscillation of  $20 \pm 2$  kc in frequency and 15 microns in amplitude. The results obtained were as follows. (1) In Fe-C alloys, when the carbon content increases the degree of static corrosion becomes less. In Fe-C-Cr alloys, the chromium content enhances the degree of static corrosion. For the inhibition of corrosion the increase of carbon content in the alloy may be necessary. (2) From the erosion test it was found that the surface pits are not due to a chemical corrosion but to a mechanical attack, and that the degree of erosion chiefly depends on the hardness of the alloy.

## I. Introduction

The proposed application of bismuth in liquid metal fuelled reactors has focused attention on corrosion. Though low chromium steels ( $2 \frac{1}{4}$  Cr-) are generally resistant to bismuth containing zirconium as an inhibitor<sup>(1)-(7)</sup>, little attention was paid to the effects of alloying elements in the steels. So, the present experiments were made chiefly with Fe-C-Cr system by the static corrosion method.

While high velocity circulation of liquid bismuth is desirable from the viewpoint of the thermal efficiency in the heat exchanger, there is a possibility of the occurrence of cavitation, due to which the container is liable to suffer a heavy erosion<sup>(8)(9)</sup>. From this standpoint, the erosion resistivity of binary alloys of Fe-C and Fe-Cr to liquid metals was studied by using an ultrasonic oscillator, by which it might be possible to obtain a condition similar to high speed flow.

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## II. Specimens and experimental methods

The alloys listed in Table 1 were obtained by melting in a high frequency induction furnace and by forging followed by annealing. For the static corrosion test were used the Fe-C (A and B), Fe-Cr (C) and Fe-C-Cr (D, E, F and G) alloys, while for the erosion test Fe-C (H) and Fe-Cr (I) alloys were used. Contents of

Table 1. Chemical analyses of specimens

Alloy	Group	No	C wt %	Cr wt %	Total N <sub>2</sub> wt %	Soluble N <sub>2</sub> wt %
pure Iron	A		0.011		0.008	0.001
Fe-C Alloy	B	1	0.175		0.011	0.001
		2	0.29		0.008	0.002
		3	0.49		0.007	0.001
		4	0.75		0.009	0.003
		5	0.98		0.008	0.002
		6	1.11		0.010	0.003
Fe-Cr Alloy	C	1	0.011	0.85	0.010	0.004
		2	0.022	1.89	0.008	0.002
		3	0.008	2.31	0.015	0.003
		4	0.011	4.35	0.011	0.003
		5	0.035	9.52	0.020	0.013
		6	0.025	14.02	0.056	0.056
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-10% Cr Alloy	G	1	0.071	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
Fe-C Alloy	H	1	0.12		<0.01	
		2	0.28		<0.01	
		3	0.51		<0.01	
		4	0.78		<0.01	
		5	1.00		<0.01	
		6	1.21		<0.01	
Fe-Cr Alloy	I	1	0.033	3.33	0.004	
		2	0.022	6.85	0.011	
		3	0.033	9.55	0.038	
		4	0.033	14.58	0.014	
		5	0.038	17.29	0.068	
		6	0.011	21.62	0.015	
		7	0.022	24.45	0.026	

impurities in these alloys were as follows: Si, 0.008~0.20%; Mn 0.10~0.50%; P, 0.003~0.011%; S, 0.01%~0.02%. With regard to the effect of the heat-treatment of steel on the corrosion, the situation is yet confused<sup>(6)(10)</sup>. In the present experiments, however, the testing temperatures were relatively high and so, on the assumption that there would be little effect, the specimens were all annealed for 1 hour at higher temperatures above  $A_3$  or  $A_1$  point by 50~70°C, and then furnace-cooled.

The procedure of the static corrosion test was as follows. The specimens were prepared in a cylindrical disc (12 mm dia.  $\times$  3 mm) and supported by a silica tube and graphite ring, and immersed in an alumina crucible containing 900~1000 g of bismuth of 99.9% in purity. The degree of corrosion is greatly affected by the presence of oxygen in the atmosphere. It was ascertained from the experiments on pure iron that the degree of corrosion at 700°C for 100 hours was 10~12 times larger in the presence of oxygen than in the absence. So, the best attention was paid to the content of oxygen in the atmosphere to minimize the corrosion, that is, the bismuth was heated up to 450°C in argon atmosphere, and followed by the addition of about 500~700 ppm of magnesium as deoxidant, and then specimens were immersed in it. The addition of magnesium was carried out by using Bi-47% Mg alloy. For inhibited tests about 700~800 ppm of zirconium was added prior to the immersion of specimens. Prior to each test the specimens were abraded down to 3/0 grade emery paper and degreased with benzol and alcohol. Tests were carried out at various temperatures for a week. Weight loss of the specimens was then measured after removal of adhering bismuth with hot mercury (270~290°C).

For the erosion test, the procedure was as follows: Specimens in a cylindrical form (7 mm dia.  $\times$  130 mm) were immersed in liquid bismuth of 300 g sealed in the atmosphere of argon, and oscillated for 1 hour, the testing temperature being maintained at various values over the range of 300~500°C. The oscillation was generated with the ultrasonic oscillator of  $20 \pm 2$  kc, the amplitude at the top part of the specimen being about 15 microns. Neither magnesium as a deoxidant nor zirconium as an inhibitor were added in order to minimize the inclusions in the liquid bismuth. The degree of erosion was estimated from the weight decrease.

### III. Results

#### 1. Static corrosion test

##### (i) Corrosion of Fe-C alloys

Fig. 1 shows the relation between the degree of corrosion and the carbon content in Fe-C alloys in the cases with and without the addition of zirconium (curve a and curve b, respectively), wherein it will be seen that the corrosion decreases, in every case, with increasing carbon content, and that its tendency is considerably remarkable when the zirconium is present. This may lead to the

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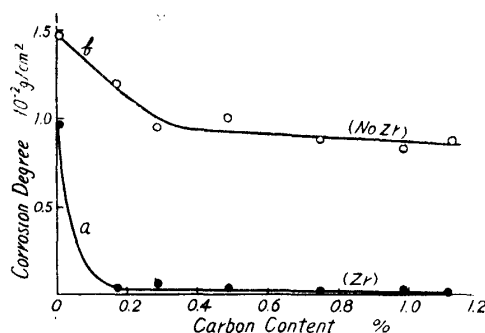


Fig. 1. Corrosion degree versus carbon content in Fe-C alloys (A, B1 ~ 6). ( $700^{\circ}\text{C} \times 165$  hrs.)

presumption that the presence of carbon in the alloy is necessary for the inhibition of corrosion. In curve (a) in Fig. 2 is shown the degree of corrosion at various temperatures in an Fe-0.175% C alloy, the degree increasing exponentially with the rise of temperature. Curve (b) shows the change in the depth of decarburized layer on the surface region of specimen after tests, and it will be seen that the depth increases similarly to the case of corrosion degree. Fig. 3 shows the depth of decarburized layer after the immersion for 165 hours plotted against reciprocal of the absolute temperature, the linearity being apparent in two ranges of temperature. The higher temperatures are in austenitic range and the lower in ferritic range, and the activation energies calculated from these linearities were 36,000 and 18,000 cal/mol, respectively. These values are generally coincident with those of the diffusion of carbon in respective phases. Thus, since the decarburization is considered to be due to the formation of ZrC film, it follows that the corrosion is controlled by the diffusion of carbon.

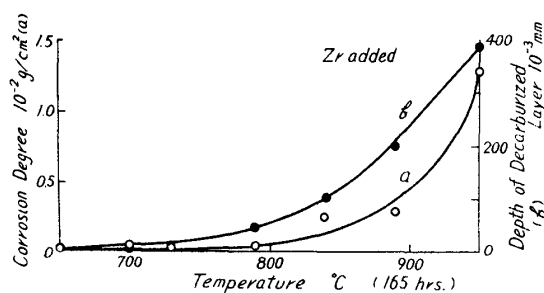


Fig. 2. Corrosion degree and depth of decarburized layer versus temperature in an Fe-0.175% C alloy (B1).

Fig. 4 shows the relation between the degree of corrosion or the depth of decarburized layer and the carbon content in the temperature range of austenite phase in Fe-C alloys. From the fact that the higher the carbon content the less the degree of corrosion and the thinner the decarburized layer, it may be pertinent to mention that the decarburization is due rather to the formation of ZrC film than to the presence of oxygen in the atmosphere.

(ii) Corrosion of Fe-C-Cr alloys

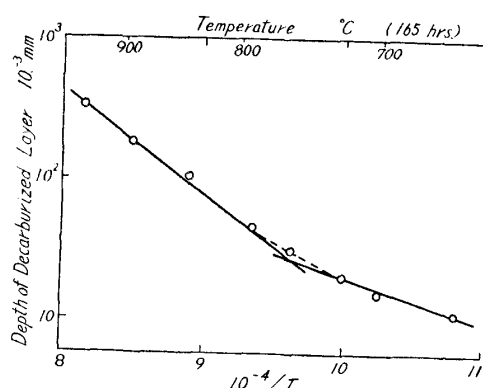


Fig. 3. Depth of decarburized layer versus temperature in an Fe-0.175%C alloy (B1).

850 ~ 950°C . . . .  $Q = 36,000 \text{ cal/mol}$

650 ~ 720°C . . . .  $Q = 18,000 \text{ cal/mol}$

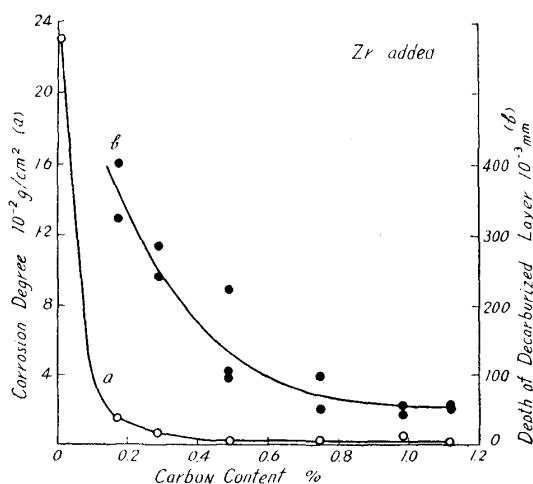


Fig. 4. Corrosion degree and depth of decarburized layer versus carbon content in Fe-C alloys (A, B1~6). (950°C × 165 hrs.)

In Fig. 5 is shown the relation between the degree of corrosion and the chromium content in Fe-C-Cr alloys in the case of the absence of zirconium in liquid bismuth. Curves (a) and (b) are the results on the alloys containing less than 0.03% and 0.2% carbon respectively. Two features are immediately obvious. First the higher the chromium content becomes, the more the degree of corrosion is enhanced which probably originates from the circumstances that chromium is dissolved into liquid bismuth much more than iron. Second, when the carbon content is increased, the degree of corrosion is reduced; this is probably due to the circumstances that the dissolution of chromium is decreased owing to the retardation of its diffusion by the presence of carbon or by the formation of chromium carbide.

Fig. 6 shows the relation between the degree of corrosion and the chromium content in Fe-0.2%C-Cr alloys tested at various temperatures for a week. In this test zirconium was added to liquid bismuth as an inhibitor. The degree of corrosion increases with the increase of chromium content and with the rise of

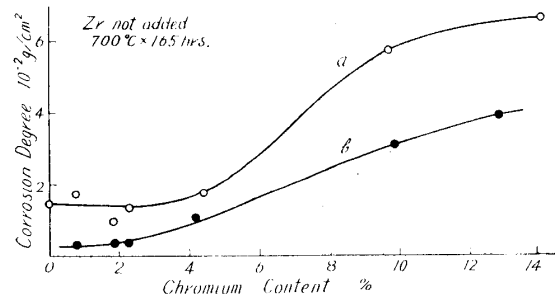


Fig. 5. Corrosion degree versus chromium content in Fe-C-Cr alloys.  
a: Fe-Cr alloys (C1~6) b: Fe-0.2%C-Cr alloys (E1~6)

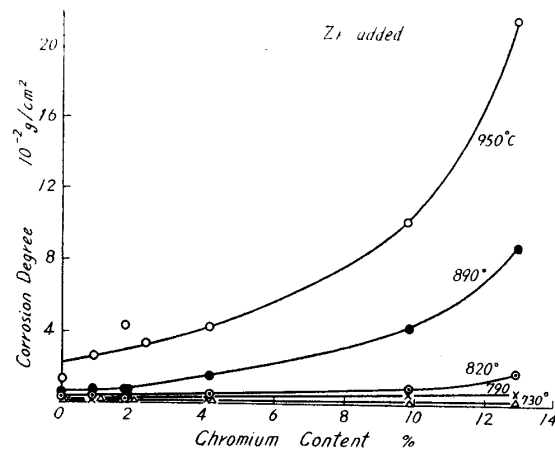


Fig. 6. Corrosion degree versus chromium content in Fe-0.2%C-Cr alloys (E1~6). (Time: 165 hrs.)

testing temperature, although it is far less than the case of zirconium being absent. The above figure relates to the case in which the carbon content is maintained at about 0.2%, while Figs. 7 and 8 relate to the case in which the chromium content is maintained nearly constant. From both figures it is apparent that the degree of corrosion varies widely with the carbon content, and that as the chromium content increases, the amount of carbon for the inhibition of corrosion increases.

With regard to the diffusion of carbon in Fe-C-Cr alloys, its velocity may roughly be seen from the results shown in Fig. 9, which shows the relation between the depth of decarburized layer and the chromium content in Fe-0.2%C-Cr alloys tested at 700° and 900°C for a week. It will be seen from this figure that the more the chromium content is the thinner the decarburized layer becomes, in other words, the presence of chromium hinders appreciably the carbon from diffusion.

## 2. Erosion test

In Fig. 10 is shown the change in weight decrease with the carbon content in Fe-C alloys in the case tested by the oscillation method at various temperatures for 1 hour, wherein it is evident that the weight decrease is reduced with the increase of carbon content, although it is considerably large compared with the degree of corrosion shown in Fig. 1. The dotted curves concern the hardness at room temperature, which will be stated later. The change with the chromium content in

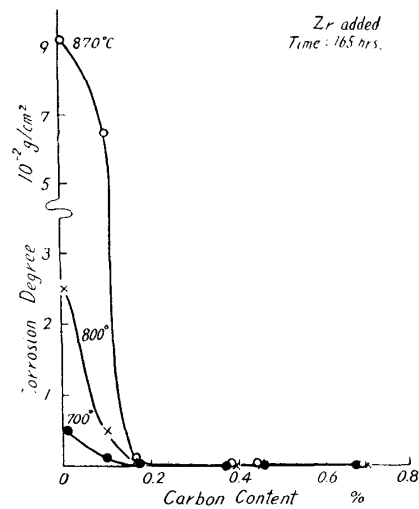


Fig. 7. Corrosion degree versus carbon content in Fe-2% Cr-C alloys (F1~6).

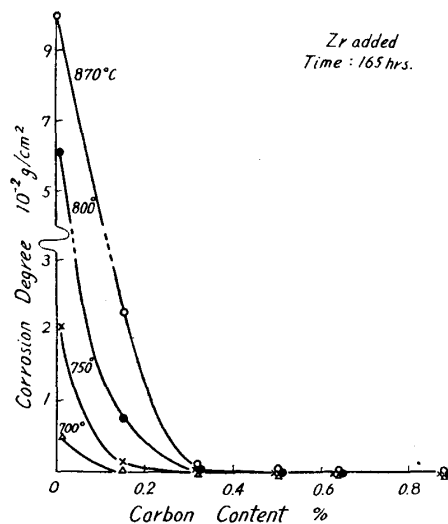


Fig. 8. Corrosion degree versus carbon content in Fe-10% Cr-C alloys (G1~6)

Fe-Cr alloys is shown in Fig. 11, which was obtained by the same method as stated with reference to Fig. 10. The weight decrease is reduced by the increase of chromium content contrary to the results on corrosion test (curve b in Fig. 5), leading to the suggestion that the weight decrease does not originate merely from chemical corrosion.

A close relationship seemed to be present between the weight decrease and the hardness, as seen in Figs. 10 and 11. Anomalies in the hardness of Fe-Cr alloy in the range of chromium content of 8~10% and 20~22% seem to relate to the martensitic transformation and the 475° embrittlement, respectively. The relation between the hardness at room temperature and the weight decrease is shown in Fig. 12, being a simple curve in the case either of Fe-C or of Fe-Cr alloy.



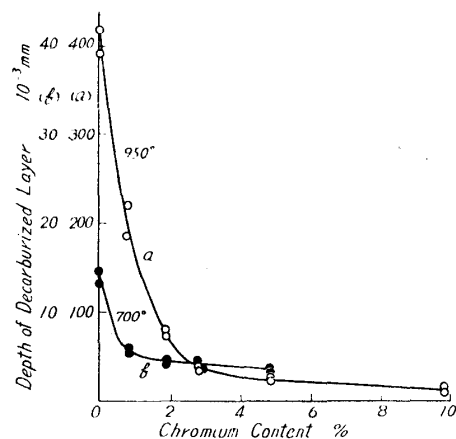


Fig. 9. Depth of decarburized layer versus chromium content in Fe-0.2% C-Cr alloys (E1 ~ 6).

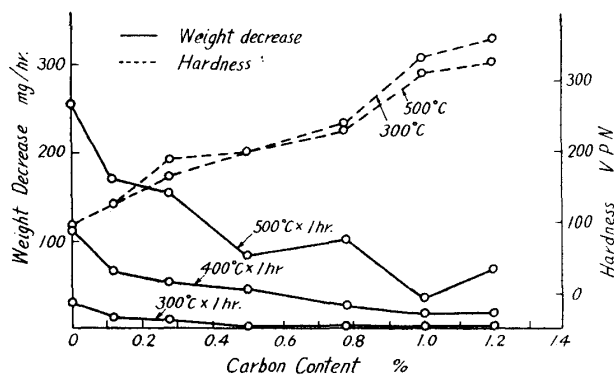


Fig. 10. Weight decrease and hardness versus carbon content in Fe-C alloys (H1 ~ 6).

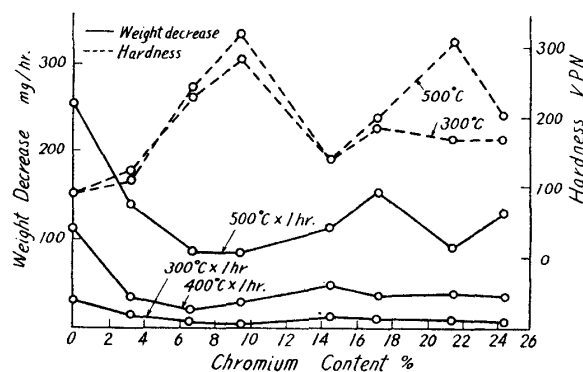


Fig. 11. Weight decrease and hardness versus chromium content in Fe-Cr alloys (H1 ~ 7).

To obtain a further information on this relationship, erosion tests were carried out with Fe-0.3%C and 0.8%C alloys having various values of hardness. The hardness was controlled by tempering at various temperatures after water quenching. The results are shown in Fig. 13, from which it may be said that there is a linear relationship between the hardness and the weight decrease.

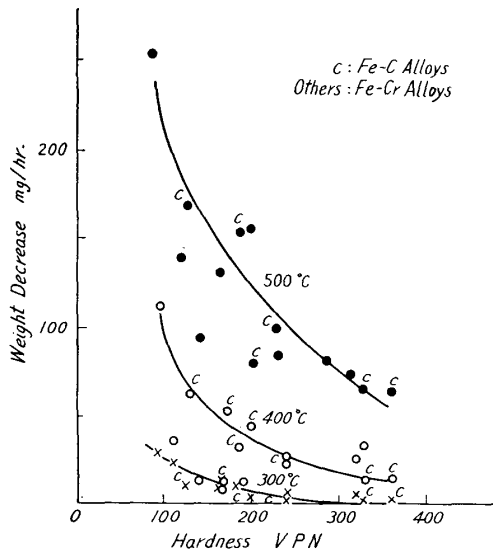


Fig. 12.

Fig. 12. Weight decrease versus hardness of Fe-C and Fe-Cr alloys (H1~6, I1~7).

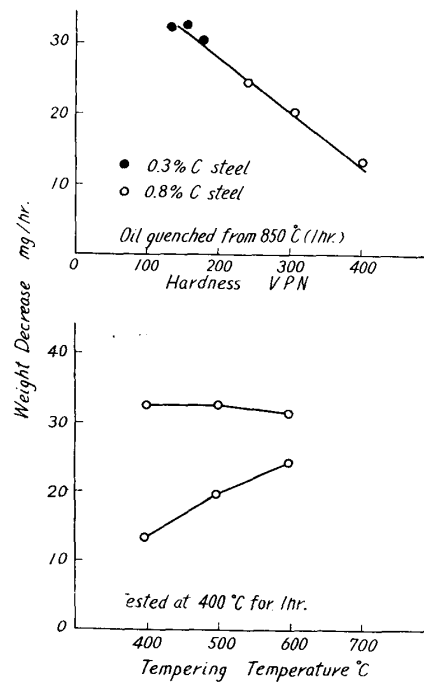


Fig. 13.

Fig. 13. Weight decrease versus tempering temperature or hardness of tempered Fe-C alloys (H2, H4).

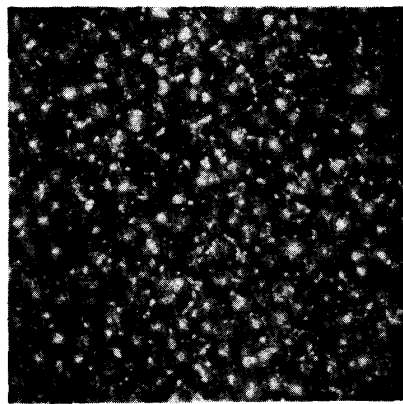


Fig. 14. Macrostructure of surface of pure iron attacked by liquid bismuth ( $500^{\circ}\text{C} \times 1 \text{ hr.}$ ).

From the above results it was confirmed that the weight decrease shown in the erosion test was governed rather by the hardness than by the alloying element or by the structure. According to the macroscopic observation of the specimen surface eroded, a number of pits formed during erosion test as shown in Fig. 14 seems to result not from a chemical corrosion but from a mechanical attack. Fig. 15 shows the results of carburized steels having various values of hardness tested at  $500^{\circ}\text{C}$  for 1 hour. The hardness was controlled by varying the duration of carburization. It seems highly possible that the weight decrease plotted against hardness lies on the curve obtained by extrapolating the curve in Fig. 12,

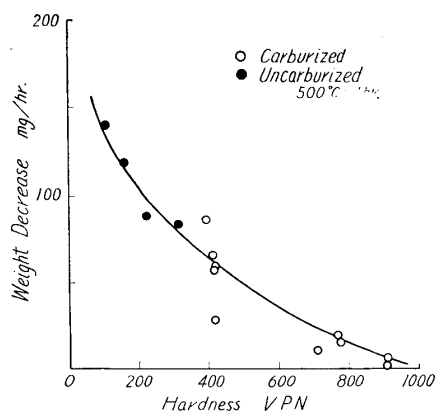


Fig. 15. Weight decrease versus hardness of carburized steels.

leading to the confirmation that the weight decrease depends chiefly on the hardness.

#### IV. Consideration

1. It has been reported that when zirconium is present in liquid bismuth as an inhibitor, films of ZrN and ZrC are formed at the surface of steels<sup>(3)(5)(10)</sup>. With regard to the inhibition effect of ZrN film, the situation is yet confused. When the content of nitrogen is large amounting to about 1%, it seems to inhibit the corrosion<sup>(4)</sup>, but its effect is appreciably slight compared with that of carbon.<sup>(7)</sup> It may be supported from the present investigation that nitrizing treatment of high chromium steels results in only a few per cent of the improvement against corrosion. In this regard, it is presumed that the ZrC film covers uniformly throughout the surface of steel specimens, whereas the ZrN film is easy to globulize, reducing its inhibiting effect.

2. Inhibiting effect of zirconium is considered to be due chiefly to the formation of ZrC film. In Fe-C alloys it was found that the depth of decarburized layer was controlled by the diffusion of carbon. The presence of chromium in steels hinders the progress of decarburization, causing a growth of the protective film difficult. If the film becomes too thick, it is liable to break off by a slight mechanical or thermal shock. It may be allowable to say that the prevention of the film from growth may, to some extent, be necessary for the inhibition of corrosion. From this standpoint, chromium steels may be preferable to plain carbon steels.

3. High velocity circulation of liquid bismuth, at least of 5~10 m/sec, is desirable from the viewpoint of the thermal efficiency in the heat exchanger, leading to the presumption that there is a possibility of the occurrence of cavitation similar to the case of aqueous solution<sup>(8)</sup>. This has already been pointed out by the test of a disc rotation in liquid bismuth<sup>(9)</sup>. To obtain further informations on this point, some observations were made with various liquid metals (Hg, Pb, Bi) by the ultrasonic oscillation method, and a cavitation effect was seen in mercury at room

temperature as shown in Fig. 16, in which vapor pressure was very low, and an erosion damage was also induced.<sup>(11)(12)</sup> In accordance with this, it may be allowable to say that also with bismuth there is a possibility of the occurrence of cavitation when the testing temperature is sufficiently high.

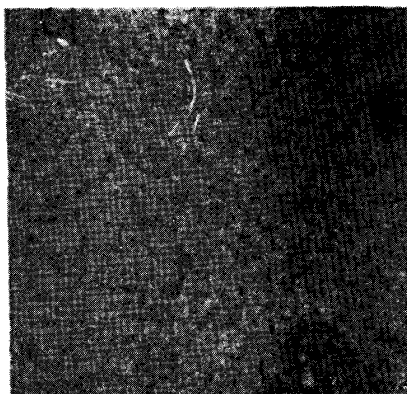


Fig. 16. Macrostructure of attacked surface of pure iron by mercury. (room temperature  $\times$  1 hr)

### Summary

Corrosion of Fe-C-Cr alloys and erosion of Fe-C and Fe-Cr alloys were studied with liquid bismuth, and the following results were obtained.

1. In Fe-C alloys, the more the carbon content is the less the degree of corrosion becomes. In Fe-C-Cr alloys, the more the chromium content is the more the degree of corrosion becomes. For the inhibition of corrosion the increase of carbon content in the alloy may be necessary.

2. From the erosion test it was found that surface pits were not due to chemical corrosion but to the mechanical attack, and that the degree of erosion was depend chiefly on the hardness.

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