Absorption of Nitrogen by Zirconium and Iron

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Zirconium is one of the elements which are said to have good effect of denitrogen, deoxygen, etc., when added in steel. It is used, also, as a getter in the vacuum-tube. These are owing to its great affinity to metalloid atoms.

It is the object of the present papers to investigate in detail the characateristics of the nitrides formation of zirconium, ferro-zirconium and pure iron, which will make a contribution to the problems concerned to the use of this element.

Experimental

The increase of the weight of the samples (zirconium-metal, ferro-zirconium and pure iron) which was resulted from the progress of the nitrogen absorption with the samples, was measured.

The dish containing the sample was hanged vertically with a spring balance and the whole was settled in a tube. All of the equipments, the dish, the spring balance and the tube, were made of fused silica. The stream of the purified nitrogen was sent into the tube which was heated in an electric furnace.

As the sample absorbed nitrogen at some temperature, the balance stretched and the stretched length was measured with the telescope of the cathetometre, and then temperature was gradually raised. Increase of 1 mg. in weight corresponded to 0.628 ± 0.002 mm. of

the stretched length, Δl.

Results

Samples Zr-metal: amorphous, black powder made in Japan.
Fe-Zr: „ „
Iron: powder of reduced iron made by Kahlbaum Co.

In Table 1 the compositions of the samples are given.

Table 1

Sample		Zr cont. (total %)	Zr % (as carbides)	Zr % (as oxides)
Zr-metal	No. 114	94.0	4.9	6.0
	103	84.0	49.3	—
	131	96.7	7.3	21.2
	133	96.5	3.9	29.9
Fe-Zr	40	28.1	2.8	0.4
	44	29.9	4.0	3.1

Experiments Expt. No. 1—Zr-metal No. 114. Sample taken: 100.5 mg. The reaction between Zr and nitrogen began in the range of 265°-290°C and then continued linearly as the temperature was raised and the time passed. The temperature was raised up to 1000°C during 6 hours. (Table 2).

Table 2

Expt. No. 1			Expt. No. 2		
T°C	t min.	Δl mm. (×1/100)	T°C	t min.	Δl mm. (×1/100)
265	85	0	470	120	0
290	96	25	520	130	20
400	199	235	620	186	85
450	240	350	〃	220	205
520	250	390	〃	260	465
650	298	515	700	265	490
760	323	589	760	275	565
870	330	679	850	281	620
920	365	870	940	290	640
1020	368	919	950	310	740

Expt. No. 3			Expt. No. 4		
T°C	t min.	Δl mm. (×1/100)	T°C	t min.	Δl mm. (×1/100)
100	10	0	250	67	0
400	35	75	280	77	35
〃	100	100	300	164	175
〃	295	340	〃	307	315
〃	518	765	〃	407	425
600	559	780	500	542	555
770	576	740	800	557	585
790	616	〃	850	602	620
880	626	720	900	610	605
900	636	690	〃	620	595
940	645	725	〃	627	585
910	655	750	1030	632	595
900	677	780	〃	662	625
〃	685	790			
〃	725	〃			
950	733	750			
1010	744	750			

T°C .....temperature where the experiment was carried out
t min. ...the time since the start of the experiment
Δl mm....stretching of the spring balance

Expt. No. 2—Zr-metal No. 103. Sample taken: 109.0 mg. It is strange that the beginning-temperature of the reaction lies between 470°C and 520°C and differs from those of the other samples (No. 114, 131, 133) which react at 265°-290°C.

This would be due to the special condition of the sample, because, while all the other samples were produced through reduction with carbon or sodium metal, the present one was made by alumino-thermit method and would have been affected by aluminium in some way.(1)

Expt. No. 3—Zr-metal No. 131. Sample taken: 111.5 mg. In this case, the decomposition occured at 600°C and the decrease of the weight of the sample was observed. This decreasing tendency continued up to 900°C. Just above 900°C, the length of the spring balance once increased and then the decreasing tendency began again (Table 2).

Similar decreasing tendency at 900°C was also observed in the case of the sample, Zr-metal No. 133, in Expt. No. 4.

The present author has found by chemical analysis that the decomposition or the transformation of carbides into nitrides occur at 700°C and 900°C in the researches concerning the metalloid compounds of zirconium and hafnium.(2) The results found here seem to correspond to that phenomenon.

Expt. No. 4—Zr-metal No. 133. Sample taken: 76.6 mg.

Expt. No. 5—Fe-Zr No. 44. Sample taken: 115.2 mg.

Expt. No. 6—Fe-Zr No. 40. Sample taken: 131.1 mg.

The most distinctive character of the Fe-Zr that makes it different from Zr-metal is the temperature where the absorption of nitro-

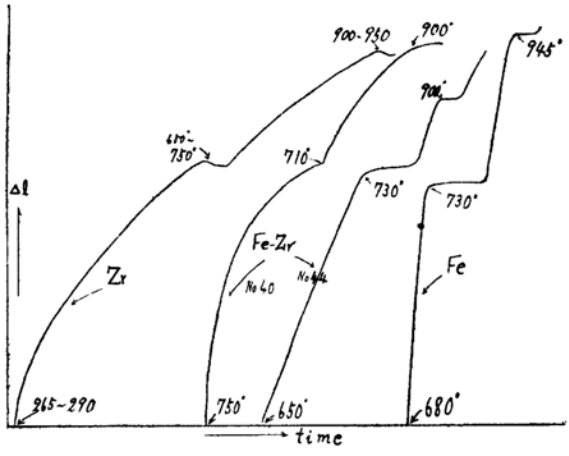

Fig. 1

(1) Aluminium begins to absorb nitrogen at 600°~700°C. (K. Iwase, *Sci. paper. Tohoku Univ.*, **15**, 531 (1926))
(2) S. Fujiwara, *J. Chem. Soc. Japan*, in press.

gen begins; it is 650°~750°C which is far higher than 265°~290°C, at which Zr-metal bagins to absorb nitrogen.

Moreover, in this case the absorption curve shows the breaks at 700°C and 900°C as shown in Fig. 1.

It must be emphasized that these temperatures where the absorption begins and the breaks occur exactly coincide to those for the pure metal of iron except that the curvature for Fe-Zr is greater and the figure of the absoption curve for iron is rather steep.

Expt. No. 7—Pure Iron. Sample taken: 163.0 mg. In the earlier stages of heating, the weight of the sample decreases as seen in Table 3. It would be due to the desorption of the moisture contained in the sample.

Table 3

Expt. No. 5			Expt. No. 6			Expt. No. 7		
T °C	t min.	Δl mm. (×1/100)	T °C	t min.	Δl mm. (×1/100)	T °C	t min.	Δl mm. (×1/100)
630	165	0	700	114	0	200	16	−185
550	172	15	〃	131	130	〃	44	−215
700	191	65	〃	170	215	250	50	−255
〃	220	165	710	191	230	300	55	〃
740	245	185	〃	222	250	〃	76	〃
730	258	245	910	235	275	670	130	0
〃	290	〃	〃	250	295	680	144	20
820	308	〃	〃	275	325	730	169	347
960	330	310	920	302	370	〃	179	372
970	345	〃	920	310	〃	〃	184	〃
〃	353	〃	〃	320	〃	〃	219	〃
〃	368	345				800	226	372
〃	380	360				940	244	457
						945	254	492
						〃	259	517
						〃	274	〃
						〃	284	〃
						〃	294	542

The absorption of nitrogen begins at about 650°C and then the weight of the sample increases rapidly. The absorption goes on straight up to 730°C, where the increasing tendency of the weight stops and the equilibrium comes.

After this equilibrium is passed, the rapid increase in the weight of the sample begins again and then comes the equilibrium at 945 °C. These circumstances are shown in Fig. 1.

The nitrides formation of the γ-iron in the range of 620° and 700°C has been found only by K. Iwase[1] among many workers. The results of the present author that the absorption begins at 650°C and the equilibrium is obtained at 730°C seem to coincide to those of K. Iwase.

Conclusion

The characteristic temperatures are summarized in Table 4 and in Fig. 1. Fe-Zr and

Table 4

	Zr-metal	Fe-Zr	Iron
Temp. where N_2 absorption begins	265 ~290	650 ~750	650
Temp. where 1st equilibrium begins	600 ~700	730	730
Temp. where 2nd equilibrium begins	900 ~950	900 ~960	945

iron coincide exactly both in the beginning temperature and the equilibrium temperature. These features may be attributed to the nitrogen absorption by α- and the γ-iron. The effect of zirconium in Fe-Zr may be seen in the gentle slope of the absorption curve for Fe-Zr No. 40, but it is not so distinct.

As zirconium has great affinity to the metalloid atoms, it begins to absorb nitrogen at as early as 260°C. Two breaks are observed in the absorption curve of Expt. No. 3 (Sample 131) and one in Expt. No. 4 (Sample 133). These breaks would represent some equilibrium, but the reactions occurring here would be different from those for pure iron and Fe-Zr, and as it could be found in the former case, the decrease of the weight was due to the decomposition of the samples.

The absorption curve goes on linearly with the rise of temprature in the case of Zr metal and is far less steep than those for iron and Fe-Zr. It may be concluded from all these results that the nitrogen absorption of the former is different from the latter.

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