The Distribution of Carbon Between the Zirconium and Ferrite Phases[1]

W. P. Fishel, John C. Hayes[2], Vanderbilt University

A previous investigation by Rhoad (1), on the distribution of carbon between the zirconium and ferrite phases, confirmed the existence of zirconium carbide (ZrC) as a crystalline constituent, which could be identified microscopically, and which could be separated by the solution method. It also indicated that in some iron-carbon-zirconium alloys, part of the zirconium occurred in some form which was soluble in dilute acids. This work is concerned mainly with the carbide forming tendency of zirconium, and the effect of zirconium on the carbon content of the eutectoid mixture.

Zirconium in iron-carbon alloys is capable of reacting with carbon to form zirconium carbide (ZrC), and with iron to form iron zirconide (Fe_3Zr_2). Its distribution between these two phases must depend upon the affinities of zirconium for iron and carbon, and the relative atomic ratios of these elements present in the steel. Indications are that both are practically insoluble in solid iron. Hence, they could not contribute to precipitation hardening, and should be considered as inclusions.

In order to be a part of the Ar_1 transformation, zirconium carbide must separate from the austenitic solid solution at the Ar_1 temperature. If zirconium does take part in this transformation, the percent of carbon in the eutectoid mixture will be increased or decreased, depending upon the effect of zirconium on the Acm and A_3 transformations.

Zirconium occurring as a solid solution with ferrite should be found in the solution of the reagent used to dissolve the steel sample. If zirconium is an avid carbide former, it would be expected that in steels whose atomic ratios of carbon to zirconium are less than one, all of the carbon would form zirconium carbide, and the remaining zirconium would form a solid solution with ferrite. If the atomic ratio of carbon to zirconium is greater than one, all the zirconium would form zirconium carbide. However, if zirconium is not a strong carbide former, then the presence of other elements would influence the distribution of carbon to a greater extent. Some relation similar to the mass law would apply.

The iron-carbon system of Vogel and Loehberg (2) which is approximated from their data shows that the carbon content of the iron-carbon (carbide) eutectoid increases progressively with zirconium. Shapiro and Strauss (3) have interpreted this diagram to mean that the carbon content in the eutectoid mixture is increased with increasing

zirconium. This may be true, but it does not take into account the fact that zirconium forms a carbide. If zirconium forms a carbide, the amount of carbon necessary for this formation is removed from solution, and more carbon is then necessary for the formation and separation of the eutectoid mixture. If zirconium does increase the carbon content in the eutectoid mixture, then zirconium must take part in the eutectoid separation and must be a part of it.

Experimental Procedure

Several zirconium steels were prepared by melting pure materials in an induction furnace, fitted with a silica tube for vacuum melting. An evacuated system was used due to the ease with which zirconium unites with oxygen and nitrogen. The alloying agents used were Armco iron, graphite, zirconium carbide, and ferro-silicon-zirconium. The Acheson graphite crucibles were lined with a mixture of four parts sintered and ground magnesium oxide to one part unsintered magnesium oxide, moistened with a saturated solution of magnesium chloride. The lined crucibles were baked at 120°C. for several hours and then baked in the induction furnace for 10-15 minutes before the charge was added. The ingots were turned down on a lathe to sound metal, and then turnings were collected for chemical analyses. A section was cut from the sound metal of each alloy for microscopic analysis.

Analytical Procedure

The method used to separate zirconium occurring in the carbide phase from that occurring in some other phase was by digesting the ingot turnings in hydrochloric acid (sp. gr. 1.1) and then determining the amount of zirconium dissolved and that undissolved. The zirconium found in the residue was considered to be zirconium carbide, and that soluble in the acid to be zirconium occurring in some other phase. Zirconium was determined by precipitation with phenylarsonic acid, according to Rhoad (1).

Carbon was determined by the standard combustion method, using 2.0 gm. samples.

No determination was made for the silicon present in any alloy.

A summary of the analysis of the alloys of this study is given in Table I.

Discussion

By plotting the atomic ratios of zirconium to carbon against the percent of the total carbon existing as zirconium carbide, figure I is obtained. The carbon united with zirconium was calculated from the zirconium found in the residue. This diagram shows that all the carbon exists as zirconium carbide if the atomic ratio of zirconium to carbon

TABLE I

ALLOY	% C.	% Zr	% Zr / % C	% of Total Zr. in Res	At. % Zr. / At% C	C as ZrC / % of Total
2	0.14	0.13	0.93	100.00	0.12	12.24
3	0.16	0.071	0.44	100.00	0.06	5.85
5	1.11	0.254	0.23	25.66	0.03	3.02
6	0.56	0.086	0.15	86.03	0.02	2.02
7	2.92	0.923	0.32	78.76	0.04	4.17
11	0.168	1.62	9.65	100.00	1.32	100.0
12	0.16	1.58	9.75	87.00	1.28	100.0
Rhoad's Samples						
9	0.75	1.315	1.75	61.75	0.23	23.12
13	0.86	0.958	1.11	94.5	0.15	14.69
14	0.56	1.246	2.22	56.8	0.29	29.3
15	0.86	0.306	0.36	44.0	0.05	4.8
18	1.52	1.993	1.31	79.8	0.17	17.2

is greater than one. Data for atomic ratios of zirconium to carbon between .3 and 1.28 is lacking. The points for atomic ratios below .3 form almost a straight line, which seems to indicate that a distribution law must apply in this case.
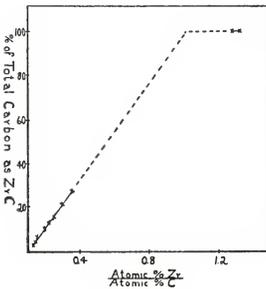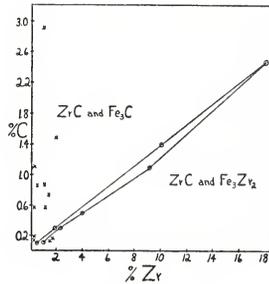

Figure I

Figure II

The data obtained from the alloys of this study and from those of Rhoad (1) agree with the inferences of figure II, which is approximated from the data of Vogel and Loehberg (2). All alloys above the curve show zirconium carbide, and iron carbide, as pearlite or as pearlite and cementite. In this area the ratio of zirconium to carbon is less than one. The two points below the curve are alloys No. 11 and No. 12, which showed zirconium carbide, and a lacy network which is probably iron zirconide, but no iron carbide was present. In this area, the ratio of zirconium to carbon is greater than one.

The preparation of a group of zirconium steels, whose atomic ratios of zirconium to carbon varied widely, was difficult. Zirconium carbide and ferro-silicon-zirconium were the only available sources of zirconium. The quantity of zirconium carbide was very limited, and when alloys were prepared with this compound, the percent of zirconium to carbon could not be varied. The ferro-silicon-zirconium contained about one-third zirconium and about one-half silicon, so that a large amount of silicon was necessarily present.
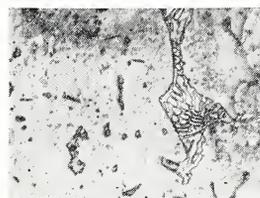

Figure III

Figure IV

Figure V

Figure VI

Fig. 3. Alloy #7, unetched. X750. Zirconium Carbide Crystals. Zr. = 0.923% (0.732% insol.) C = 2.92%.

Fig. 4. Alloy #7. Etchant: sodium picrate. X750 Zirconium carbide crystals and cleavage planes cementite.

Fig. 5. Alloy #12. Etchant: nital. X750 abundance of crowfoot structure.

Fig. 6. Alloy #11. Etchant: nital. X750. Lacy network and absence of pearlite.

Zirconium and the Eutectoid Mixture

In order to show that zirconium does not take part in the eutectoid transformation, three of the samples (Nos. 5, 7, and 12) which showed an abundance of zirconium carbide crystals and crowfoot structure, were held at 400°C. for two hours, then quenched in ice water. If zirconium takes part in the Ar_1 transformation, it must go into solution on heating and reprecipitate at the Ar_1 temperature. A section from each of the quenched samples was polished and examined. This examination revealed the presence of the crowfoot structure, characteristic of ZrC. The form and the amount of ZrC had not been changed by the heating and the quenching. Since the ZrC structure is still present at 900°C., its formation must occur at a higher temperature. According to

Vogel and Loehberg, the temperature of this formation is about 1330°C. for alloys rich in Zr, and about 1145°C. for those poor in Zr. (figure 7.)
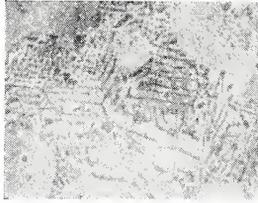

Fig. 7. Alloy #5. Unetched. X700. 900° for two hours, water quenched.

Conclusions

1. All the carbon in a steel whose atomic ratio Zr:C is greater than 1, will be united with the Zirconium.

2. If the ratio Zr:C is less than 1, there is a fairly direct ratio between this and % of Total carbon as ZrC.

3. Fe_3C appears only if Zr:C is less than one.

4. Zirconium does not enter Ar_1 transformation because ZrC separates in the crystalline or crowfoot structure at a temperature well above the Ar_1; *therefore zirconium* does not increase the carbon content of the eutectoid, as stated by Strauss.

However in order to have a matrix of pearlite, the steel must contain more than 0.85% C. The excess carbon unites with zirconium, and is in no way connected with the eutectoid separation.

5. ZrC particles in steels function as inclusions *only*.

Bibliography

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