Solid Solubility of Cementite

In Alpha Iron

by Charles A. Wert

By the use of the internal friction of carbon in α-iron the solubility of cementite in α-iron has been measured down to a temperature of 150°C. The yield strength of ingot iron containing small amounts of cementite has also been determined as a function of carbon concentration.

THE solid solubility of cementite in α-iron has been investigated a number of times and there is now general agreement on the solubility of about 0.018 wt pct at the eutectoid temperature, 720°C. With decreasing temperature, the solubility falls off so rapidly and to such a low value that no data obtained by standard metallurgical methods are available below 500°C. Using a new technique, however, Dijkstra[1] has obtained apparently accurate solubilities down to 400°C; which data agree well with previously measured solubilities in the 600° to 700°C temperature range.[2] The present paper has in part the purpose of extending his work to still lower temperatures.

Earlier work of Low and Gensamer[3] on iron has

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established that the presence of a relatively small amount of carbon can play a tremendous role in affecting the mechanical properties. In particular they found that the yield point remained high as they reduced the amount of carbon in the iron; the yield point dropped only after the carbon content had fallen to something less than 0.003 wt pct, the point where their carbon analysis failed. It seemed desirable to the present author to see if some means could not be found to extend this part of their work. This investigation has then the additional purpose to determine the range of carbon concentration in which the major change occurs.

Solubility

The method used in the present work to measure small percentages of carbon in α-iron utilizes internal friction. Since this method may not be familiar to the reader, the following explanation will be given (a part of this procedure is from unpublished results of Dijkstra): It is known that the internal friction associated with the diffusion of

carbon in α-iron is linearly dependent on the amount of carbon present in solid solution; i.e., wt 0/0 C = $K\ Q^{-1}$. In this expression Q^{-1} is the internal friction and K is a constant. To measure amounts of carbon, one needs only to determine the magnitude of the internal friction appropriately; if one knows the proportionality constant K, one can compute the carbon concentration. Dijkstra measured K by the following method: He first measured the increase in weight and the increase in electrical resistivity at room temperature caused by adding carbon to a bar of iron.[4] Hence he was able to find an equation wt 0/0 C = $A_1\ \Delta R/R$, where A_1 is determined empirically. Then on an iron wire he measured Q^{-1} and $\Delta R/R$ for various carbon concentrations, obtaining an equation $\Delta R/R = A_2 Q^{-1}$ where A_2 is also determined empirically. Hence, he could say that wt 0/0 C = $A_1 A_2 Q^{-1}$ where $A_1 A_2 = K$. He found that if internal friction was expressed in units Q^{-1}, then (by chance) the constant K was about unity for polycrystalline iron, so that

$$\text{wt } 0/0 \text{ C} = Q^{-1} \qquad [1]$$

To measure solid solubilities the specimens were in the form of wires 0.03 in. in diam and 1 ft long. The specimens were swaged and drawn from a ⅜ in. bar of Puron iron with appropriate intermediate vacuum anneals. They were then freed from carbon and nitrogen by a 4-hr treatment in wet hydrogen at 750°C. These wires were carburized to about 0.02 wt pct C, and, after they were quenched, they were tempered at the desired temperatures for varying periods of time. During this time the internal friction decreased for a time as the carbon precipitated into Fe₃C, but it finally reached a stable value. The background damping (i.e., the damping due to air, etc.) was then measured. The difference between these two values represented the damping due to carbon in equilibrium with Fe₃C at that temperature. Use of eq 1 then gave the equilibrium concentration of carbon.

The solubilities obtained in this way are shown in fig. 1. Here is also given the work of Stanley[3] and Dijkstra,[1] showing the relatively good agreement between the two methods at the higher temperatures. This good agreement provides an independent check on the accuracy of calibration of the present method. The present work has extended the measurements down to 150°C where the equilibrium value is of the order of 4×10^{-5} wt pct. The most striking fact to be noted about this plot is the extremely low value that it indicates for the solid solubility at room temperature. If the straight line of log C vs. 1/T is extrapolated to 20°C, the solubility there is of the order of 10^{-7} wt pct. This estimate is orders of magnitude lower than previous estimates. It means that without extreme care, one may never have a piece of iron at room temperature which is not supersaturated with carbon.

The Puron iron used in this investigation contains oxygen as the major impurity, which is present to the extent of about 0.04 pct, according to the Westinghouse Corp. The solubility of oxygen in iron in the range 200° to 500°C is not known, but most of the oxygen present is assumed to be in the form
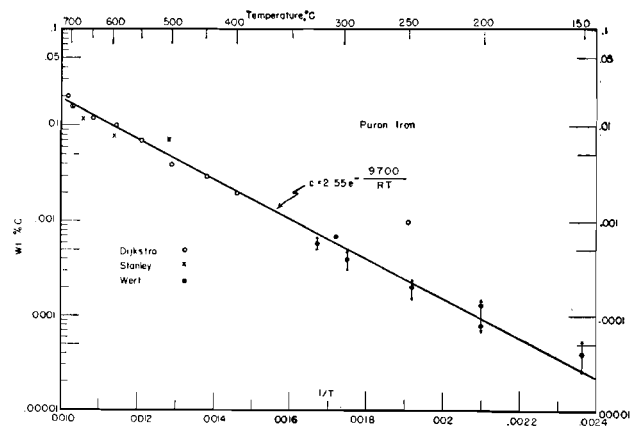

Fig. 1—Plot of solid solubility of carbon in α-iron vs. 1/T.

of oxides. No large amount of metallic impurities is believed to be present, spectrographic analysis failed to disclose any significant impurities after treatment. It is possible that the oxide present, as well as some lattice imperfections, may bind some of the carbon to particular regions of the lattice. The present method of internal friction does not measure these particular carbon atoms but rather measures those which are situated in the normal regions of the lattice. Those carbon atoms which are bound to particular sites, however, are not in solid solution in the same sense as those which are free to move about in the normal lattice. In this paper, it is these latter atoms which are referred to when the solubility limit is stated.

Yield Strength

For the type of specimens used in this part of the work, a compromise was found necessary. For the determination of carbon concentrations by the
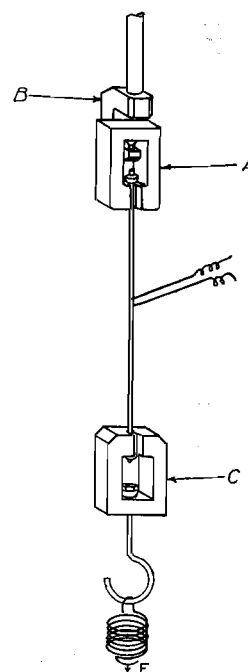

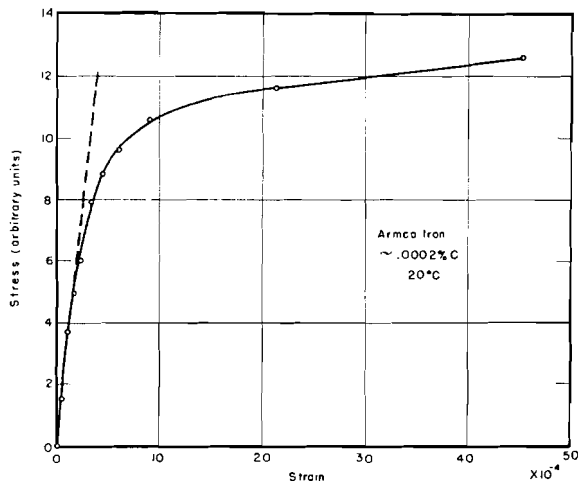Fig. 2—Schematic drawing of apparatus used to determine yield points.

Fig. 3—A typical stress-strain curve.

method employed here, it is desirable that the specimens be thin wires. Unfortunately, good yield strength determinations are rather uncertain on such wires; during the preparation of the samples they are unavoidably bent somewhat; during tensile runs the straightening of the wire during the loading complicates matters to some extent. For these measurements, one would like specimens of somewhat larger dimensions than wires. In spite of these difficulties, by the method described here, it was found possible to obtain data consistent enough to show the desired effect.

The tensile specimens were Armco iron wires about 0.05 in. in diam and about 6 in. long. They had been swaged and drawn from a piece of ½ in. rod with appropriate intermediate vacuum anneals. The nitrogen and carbon were then removed by a wet H_2 treatment at 750°C for 4 hr. A measurement by means of internal friction showed no measureable amount of either nitrogen or carbon present (this means that nitrogen and carbon were surely present in the normal lattice in amounts less than 0.0001 wt pct). The samples were then carburized slightly and homogenized. After this treatment the carbon content was measured in the manner de-
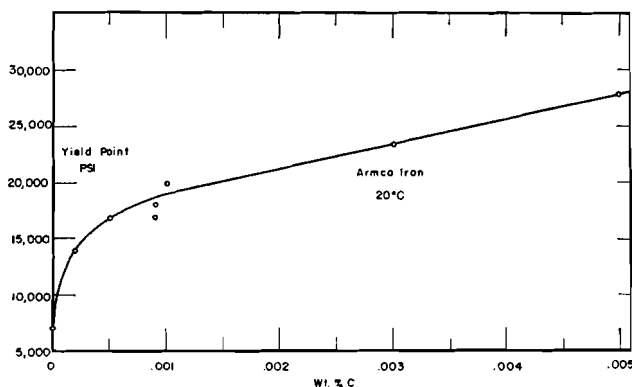
scribed in the previous section. The yield strength measurements were then made.

For these tests a soft tensile machine was used. The wires were suspended vertically as shown in fig. 2. On each end of the wire was soldered a spherical ball which rested in conical seats cut in the members A and B. Appropriate slots and holes were cut in these pieces to permit easy assembly. The top piece A was in turn supported on a 1/16 in. ball bearing fastened securely to A and resting in a slight depression in part C. The force was applied by means of a water load through a spring which was calibrated to read the load directly. All these parts were made in such a manner that the wire was under as nearly a purely tensile force as possible. The loading was done at about 500 psi per min.

The strain was measured using a strain gauge composed of a single 1 in. loop of 0.001 in. wire cemented to the central part of the specimen.

This strain gauge was one arm of a Wheatstone bridge whose state of unbalance was continuously recorded by a Brown potentiometer. A typical stress-strain curve is given in fig. 3. From such curves the yield strength was determined by noting the stress at which the strain had deviated 0.02 pct from a straight line extended from the elastic position of the curve. Because of the unbending of the wire it was not always possible to draw this line with great accuracy. Such difficulties give rise to an inaccuracy of only about 1000 psi in measured yield strength, however, so they are not considered too serious. This spread, too, is about the same as that found for different wires of the same composition.

The yield strengths determined as a function of carbon concentration are given in fig. 4. These data show that the most striking increase in yield strength occurs in the range zero to 0.0002 wt pct C. For high carbon concentrations, the magnitude is of the same order as those values obtained by Low and Gensamer.[3] The effect of impurities, again oxygen and other metals, can again not be ascertained in detail. The important fact is that for this iron the yield strength depends on carbon concentration in the way shown in fig. 4.

Summary

The two chief findings of this investigation are: (1) The solid solubility of cementite in α-iron in equilibrium with Fe_3C decreases to extremely low values with decreasing temperature. From these data the room temperature extrapolated value is much lower than had previously been supposed. (2) The amount of carbon necessary to affect the yield strength of ingot (Armco) iron is very small, about 0.0001 wt pct.

References

[1] L. J. Dijkstra: Trans. AIME, 185, 252; Journal of Metals (March 1949) TP 2540E.

[2] J. K. Stanley: Trans. AIME, 185, 752; Journal of Metals (Oct. 1949) TP 2679E.

[3] J. Low and M. Gensamer: Trans. AIME (1944) 158, 207.

[4] D. J. Dijkstra: Philips Research Report. (1947) No. 2, 257.

Fig. 4—Yield point vs. percent carbon (in all cases the C is in solid solution).