The Solubility of Carbon in High Purity α Iron Measured by Electrical Resistivity at 4.2 K

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The solubility of carbon in iron was studied using high purity ($RRR \approx 3000$) α iron samples carbon-doped by levitation melting. Various methods of analysis were used and the results were compared to the target values. After quenching from 1000 K the obtained results show that the variation of residual resistivity at 4.2 K as a function of the carbon concentration in solid solution is not monotonous. For carbon addition up to 50 mass ppm, the resistivity increment is $46.6 \text{ n}\Omega \text{ m/mol\%}$, and for higher carbon addition the resistivity increment $31.4 \text{ n}\Omega \text{ m/mol\%}$. The obtained results show that, for pure iron, carbon contents are low, at about one tenth of a ppm. The variations of carbon solubility in α iron, as determined in this study, are close to those obtained by diffusion methods, but lower than those determined by internal friction.

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1. Introduction

The solubility of carbon in α iron has been studied mainly in the sixties,¹⁾ by various methods, *i.e.* diffusion,²⁻⁴⁾ internal friction measurement,⁵⁻⁷⁾ calorimetric method,⁸⁾ thermodynamic method.^{9,10)} These generally deal with the solubility of carbon in α iron in equilibrium with cementite Fe_3C . These experiments were conducted on relatively pure irons with impurities such as Mn, Cr, Ti, O, and N. Carbon contents were assessed by analysis, per conventional combustion methods, or through calibration curves. Carbon addition was often performed in the austenite region in carburizing atmosphere (CH_4/H_2 , CO/CO_2). Several studies have shown that carbon solubility in α iron is influenced by grain size,¹¹⁾ the state of stress induced by volume variations related to precipitate growth⁷⁾ and magnetic transition.⁴⁾

Some previous results plotted in Fig. 1 show some degree of dispersion. The results obtained by internal friction are higher than those obtained using the other methods.

Fig. 1 The solubility of carbon in α iron in equilibrium with cementite.¹⁾ Comparison of the present results with some previous ones. Results of Dijkstra⁵⁾ and Swartz⁷⁾ were obtained by internal friction measurements.

The purpose of this study is to determine the solubility of carbon in α iron using alloys prepared from very high purity iron and graphite. After heat treatment, the evolution of carbon in the specimens was monitored through measurements of residual resistivity ratio $RRR = \rho(293 \text{ K})/\rho(4.2 \text{ K})$, under a longitudinal magnetic field of 80 kA/m.

2. Experimental Technique

The starting iron was zone melted in hydrogen. The RRR of the metal was between 3000 and 4000.¹²⁾ Glow Discharge Mass Spectrometry (GDMS) analysis results are listed in Table 1. The total metallic impurity contents are close to 5 mass ppm, and the major impurity is nickel of 1.5 mass ppm. The carbon, nitrogen and oxygen contents are low. The results obtained for these elements and through this method are of the same order of magnitude as those obtained using nuclear methods,¹²⁾ in particular for carbon, at about 0.1 mass ppm.

Carbon was introduced during levitation melting under helium, the purity of which was controlled by chromatography

Table 1 GDMS analysis results of high purity iron ($RRR = 3000$) used in this study (mass ppm).

Metallic impurities			
Ni=1.4	Cr=0.53	W=0.22	Cu=0.15
Ti=0.098	Mn=0.06	Co=0.07	
Ta<1	Nb<0.1	Mo<0.5	
Concentration <0.01			
Al-As-Br-Ca-Cl-Na-Se-Sn			
Concentration <0.05			
Au-Cd-Ge-Hg-K-Zr			
Concentration <0.005			
Ag-Ba-Bi-Ca-Os-Pb-Pd-Pt-Rb-Rh-Ru-Sb-Sr-Sn-Zn			
Concentration <0.001			
Other impurities			
Non-metallic impurities			
C=0.22	N=0.60	O=3.1	
Si<0.05	Br, Cl<0.01	S, B, P<0.005	

Table 2 Carbon analysis results (mass ppm) obtained by different methods.—A and B are different laboratories.

Sample Target carbon content	GDMS	Combustion A	Combustion B	Resistivity
After zone-melted	0.22	20	34	<0.1
5	2.6	27	53	3
10	10		43	12
30	25			27
40	27	52		30
50	45		64	50
100		130		100
150		160	160	155
180	165	170		185
250	163–410	200		
300				

at the enclosure outlet ($O < 0.5$ vol ppm, $N < 1$ vol ppm, $H_2O < 2$ vol ppm). We used a 1 mass% carbon master alloy doped with spectrographic purity graphite (2 mass ppm ash content). The alloys were shaped into 1.5 and 0.6 mm dia. wires, etched and then recrystallized by 24 hour annealing at 1023 K and furnace cooling under ultra-high vacuum (7×10^{-7} Pa) to avoid pollution and decarburization. The grain size of the annealed alloys decreased when the carbon content increased. The samples of pure iron had three or four grains in the section. Low carbon additions gave samples with grain size of about 200 μm , whereas for samples with 250 mass ppm carbon the grain size was about 80 μm .

Carbon solution treatment was performed by heating the specimens at 1000 K in helium for 15 minutes, followed by quenching in mercury at 273 K. Increasing heating time did not change the solution-treated quantities. The specimens were aged under ultra-high vacuum. Annealing times ranged from 500 h at 528 K to 96 h at 723 K, 24 h at 873 K and 15 min at higher temperatures. We verified that these times indeed correspond to equilibrium by making intermediate measurements. Note that these times were longer than those calculated by Swartz⁷⁾ to achieve equilibrium under the same conditions. For aging temperatures lower than 873 K, air quenching was adequate to preserve the equilibrium of solid solutions.

The carbon contents of specimens were checked by various analysis methods. We compared the target carbon contents with the analysis results obtained through GDMS, conventional combustion and electrical resistivity from the calibration curve. The results are given in Table 2. For low carbon contents, the results obtained by GDMS are very close to both the target contents and the contents evaluated by resistivity. In this respect, the values obtained by combustion methods are significantly higher. For higher contents, the results obtained by conventional analysis are more consistent.

3. Results

3.1 Contribution of carbon to the electrical resistivity at 4.2 K of iron

The amount of carbon in solid solution was estimated by the measurement of the electrical resistivity ratio $RRR =$

$\rho(293 K)/\rho(4.2 K)$. Using $\rho(273 K) = 98.7 \text{ n}\Omega \text{ m}$ as the iron resistivity value at ambient temperature, we obtained the residual resistivity at 4.2 K sensitive to the carbon in solid solution. After quenching, knowing the carbon quantity introduced by melting, we can deduce the residual resistivity increment per mol% carbon. The measurements were made using a stabilized power source and a 10 nV sensitivity voltmeter. In the case of pure iron and also carbon-doped specimens it is necessary to measure the resistivity in an applied longitudinal magnetic field of 80 kA/m for eliminating the magnetic contribution to resistivity.^{13,14)}

Figure 2 shows the residual resistivity of specimens quenched from 1000 K, as a function of the added carbon quantity. The obtained diagram shows that the contribution of carbon to $\rho(4.2 K)$ is larger for low carbon contents. The specific increment of the residual resistivity is $46.6 \text{ n}\Omega \text{ m/mol\%}$ for carbon contents less than 50 mass ppm, and $31.4 \text{ n}\Omega \text{ m/mol\%}$ for more carbon. These results are somewhat different from those published by Wagenblast and Arais¹⁵⁾ who suggested a contribution of $49 \text{ n}\Omega \text{ m/mol\%}$ carbon for the whole range studied up to 0.1 mol% carbon in high purity iron.

This difference may result from several causes. In their

Fig. 2 Influence of carbon on residual resistivity $\rho(4.2 K)$ of α iron. Each point corresponds to a sample whose carbon content was determined by weighing before melting.

publication, these authors discuss the validity of the results of dosages they used, which leads them to think that the variation could not be linear. Note that for a given carbon content, the residual resistivity difference observed between their results and ours increases as the carbon content rises. This suggests increasing specimen contamination during gas-phase carburizing, as time and temperature increase as the added quantity increases. The effectiveness of quenching from 1000 K can also be a contributor. We conducted quenching tests on wires with different diameters, *i.e.* 1.5 and 0.6 mm. These tests are non conclusive as the results obtained on thin wires were either higher or lower than those obtained on thicker wires, to a small extent. The use of thin wires with diameters of about 0.6 mm poses decarburization and pollution problems. Thus the alloy at 5 mass ppm after mercury quenching exhibits a resistivity lower than after air quenching. Although the oxygen content of the helium used as protective atmosphere for quenching is very low (<0.5 vol ppm), a decarburization of a few ppm is detected. Smaller diameters sometimes result in significant pollution of the wires, which results in abnormally high resistivity values of some specimens after annealing. The difference of result is also possibly due to a purity difference, as Wagenblast and Arajs¹⁵⁾ showed that the effect of carbon on resistivity decreases as iron purity increases.

The comparison between the values of resistivity at 4.2 and at 77 K show that the solid solution α Fe-C do not obeyed the Matthiessen's rule. Beyond 50 mass ppm the contribution of carbon to the resistivity is 31.4 n Ω m/mol% at 4.2 K and 38.4 n Ω m/mol% at 77 K. This difference agree with the Arajs's result.¹⁵⁾ This behaviour is mainly observed with solid solution of transition element in iron.^{16,17)}

The change in slope of the residual resistivity curve as a function of the carbon content, when the content is lower than 50 mass ppm, corresponds to the range where the magnetic field of 80 kA/m have a strong effect on result. This phenomena remain without explanation.

The origin of the curve, for zero additions, shows that the carbon content of high purity iron is low, probably less than a tenth of a ppm. Quenching pure iron, where carbon and nitrogen are solution-treated, produces a resistivity increase of 30 to 39 $\times 10^{-3}$ n Ω m which corresponds to a solution of a few tenths of a mass ppm carbon. To the effect of carbon should be added that of nitrogen maintained in solid solution, of about one mass ppm (N = 0.6 mass ppm), whose effect on resistivity is larger than that of carbon¹⁸⁾ and which further reduces the carbon content. A carbon atom trapping effect at grain boundaries may also be observed. According to Hasebe *et al.*,⁴⁾ the quantity of carbon trapped at the grain boundaries would be 1 mass ppm for a grain size of 200 μ m and a single layer of carbon at the boundary. Such a content should be detected by analysis. The analysis results (GDMS and activation) C $\approx$ 0.1 mass ppm heavily lean toward a carbon content of pure iron of about 0.1 mass ppm. These conclusions are in agreement with the results obtained by Albert in his study on decarburization of iron with C₁₄.¹⁹⁾

3.2 Solubility of carbon in α iron

Using the resistivity increment at 4.2 K per mol% carbon in iron we can find the quantity of carbon in solid solution in the

specimens for each aging temperature. The values are plotted in Fig. 1.

At lower aging temperatures of 528 and 589 K, the measurements taken on several samples whose contents vary from 10 to 100 mass ppm show equilibrium values corresponding to 4 and 5.5 mass ppm carbon in solid solution, respectively. As there is no significant difference as a function of initial carbon content, the effect of the presence of cementite precipitate on resistivity must be low. We can therefore conclude that this is the real solubility of carbon in α iron at these temperatures. This shows that it is difficult to obtain a material fully free of carbon in solution by simple heat treatment.

At 773 K, carbon solubility would be close to 16 mass ppm. In this temperature range, the results are comparable with those obtained using the solid state diffusion bonding method used by Hasebe *et al.*⁴⁾ At 773 K these authors obtain a solubility of 14 mass ppm, which is equivalent to our values.

After quenching from 1000 K samples doped at 250 and 300 mass ppm we obtain equivalent resistivity values which correspond to the maximum solubility in α iron, *i.e.* 230 mass ppm. This value is slightly greater than that obtained by previous work.

Between 773 and 873 K the solubility of carbon in α iron can be written in the form

$$\log[\text{C}] \text{ mass\%} = 2.553 - 4182/T.$$

We can deduce a 80.7 KJ/mol heat of solution of cementite in α iron which is close to the value obtained by Chipman,⁹⁾ but much lower than Swartz's.⁷⁾

The overall results obtained through this study are clearly consistent with the results of Smith,³⁾ Hasebe *et al.*⁴⁾ The results of Borelius⁸⁾ are low at high temperature. The internal friction results are too high in the temperature range. These differences can be attributed to annealing times too short to achieve equilibrium.

4. Conclusions

The solubility of carbon in α iron has been determined from high purity ($RRR \approx 3000$) iron samples doped with carbon by levitation melting. The target contents are between 5 and 300 mass ppm by weight. Various analysis methods were used and the results compared with the target values. At low contents of 5 to 50 mass ppm, the GDMS analysis results are consistent with the target values.

The evolution of carbon in iron during heat treatments under ultra-high vacuum is monitored by RRR measurements under a magnetic field of 80 kA/m. After quenching from 1000 K, the obtained results show that the residual resistivity variation at 4.2 K as a function of the quantity of carbon in solid solution is not monotonous. For additions of up to 50 mass ppm, the carbon's resistivity contribution is 46.6 n Ω m/mol% and 31.4 n Ω m/mol% for larger additions.

The overall results obtained seem to indicate that the carbon content of high purity iron is low, at about one tenth of a mass ppm.

The variation of carbon solubility in α iron is obtained by RRR measurement on specimens aged at different temperatures. The values determined in this study are close to those

obtained by diffusion, but much lower than those determined by internal friction.

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