Solubility Product for Niobium Carbide in Austenite

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The solubility product for $NbC_{0.87}$ has been experimentally determined between 950° and 1250 °C by gas equilibration and extraction methods. The new relation $\log_{10}[\text{pct Nb}]\,[\text{pct C}]^{0.87} = 3.4 - 7920/T$ on a weight percent basis has been evaluated from the data. This is in good agreement with a compendium of measurements from the literature. The data do not yet justify an analysis which takes account of a variable stoichiometry.

I. INTRODUCTION

As part of a comprehensive thermodynamic examination of the equilibrium of niobium carbonitrides with alloyed austenite[1] we have experimentally determined the solubility product for $NbC_{0.87}$ in unalloyed austenite between 950 and 1250 °C. This expands, and to a large extent bridges and confirms, the extensive data set already available in the literature.[2-11] The principal methodology involved mutual equilibration of encapsulated Fe-C and Fe-C-Nb alloy samples in hydrogen. Solubility product determinations and precipitate identifications were also carried out on two high purity vacuum-melted steels using chemical and electro-chemical methods to isolate the precipitated phases.

II. THE GAS EQUILIBRIUM EXPERIMENTAL METHOD

The sealed capsule technique, employed by Källstrom and Omsen,[12] Heckler and Winchell,[13] Zupp and Stevenson,[14] Nishizawa,[15] and Uhrenius and Harvig[16] was chosen for the present study. This consists of a series of diffusion-isolated Fe-Nb alloys and Fe-C alloys enclosed in an evacuated, H_2 back-filled, thick-walled quartz tube, annealed at the desired temperature. Carbon is selectively transferred between the Fe-C and the Fe-Nb alloys which are not in physical contact. The carbon activity obtaining in the capsule is determined from the final carbon content of the binary Fe-C alloy samples *via* the results of Ban-ya *et al.*[17]

The main experimental considerations in this method were:

(1) High purity Ferrovac electrolytic iron and ferro-niobium with an oxygen content less than 0.0012W pct has been used in this study (Table I). Samples were prepared by melting ferro-niobium and electrolytic iron under an argon atmosphere. High purity H_2 gas with a very low H_2O content has been used in the equilibration. We therefore conclude that the oxygen contamination of the $NbC_{0.87}$ precipitates is negligible.

(2) Accurate temperature control and establishment of a uniform temperature zone (± 4 °C for $T < 1100$ °C; ± 6 °C for $T > 1100$ °C).

(3) Prevention of leakage of H_2 from the thick-walled quartz tube *via* a 1 atm external H_2 bath.

(4) Establishment and assessment of equilibrium with respect to carbon content (0.5 mm sheet annealed for times up to 120 hours).

(5) Investigation of the possibility of transfer of niobium between the samples or of silicon contamination from the quartz capsule.

(6) Carbon analysis (Leco conductometric apparatus for low concentrations).

Full details are to be found in References 1 and 12 to 16.

III. STUDIES ON PRECIPITATES EXTRACTED FROM NIOBIUM-BEARING STEELS

Effective electrochemical means for isolating precipitates have been discussed by Blickwede and Cohen,[18] Andrews and Hughes,[19] Walz and Bloom,[20] and Gurry *et al.*[21] The principle in all these techniques is the same, *viz.*, anodic dissolution of the heat treated steel specimen under suitable conditions. Mandry and Dornelas[22] have successfully used a citrate cell for extracting carbonitrides of niobium. The advantage of an electrochemical technique is that it is conducive to the extraction of large amounts of precipitates in a short time.

The small amounts of niobium normally found in steels and the need for an evaluation of the fixed and free niobium to calculate the solubility limits of the interstitial phases has led to the development of chemical dissolution techniques for isolating these phases and accurate procedures for analyzing the residues.[23-26]

Mori *et al.*[10,27] have made extensive studies on niobium compounds precipitated in steel using a simple chemical dissolution method to extract the precipitates quantitatively. The chemical analysis is by the Kawamura spectrophotometric technique.[23] Numerous other chemical procedures are available and have been reviewed by Bhargava and Donovan.[28] These authors have also given new and accurate procedures for niobium analysis.

In the present investigation, a few solubility product determinations and precipitate identifications have been made

Table I. Compositions of the Fe-Nb and Fe-C Alloys for Gas Equilibrium Studies

Fe-Nb (Wt Pct)	
0.012 ± 0.0010	0.108 ± 0.0040
0.032 ± 0.0010	0.315 ± 0.0050
0.056 ± 0.0010	0.402 ± 0.0060
0.073 ± 0.0024	0.510 ± 0.0070
0.091 ± 0.0030	0.605 ± 0.0080
Fe-C: 0.1 to 0.4 pct C	

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Table II. Composition of Steels Used for Precipitate Isolation Studies

Steel No.	Composition, Wt Pct				
	Nb	C	N	S	O
S1	0.180	0.030	—	0.004	0.0010
S2	0.026	0.175	0.0026	~0.01	~0.0018

using chemical and electrochemical methods to isolate the precipitated phases. Two high purity vacuum melted steels, S1 and S2, whose compositions are given in Table II, were used for the study. They were analyzed particularly for nitrogen, oxygen, and sulfur. About 200 gm specimens were used for each electrolysis to yield adequate quantities of the precipitated carbides after isolation. The samples in the form of thin sheets of 4 cms × 2.5 cms × 0.3 cms were first solution treated at 1200 °C and 1300 °C, respectively, and quenched into brine. Isothermal heat treatments were then carried out at 1000 °C for more than two weeks. The specimens were all sealed in highly evacuated and argon-back-filled quartz capsules, and the argon gas at an atmospheric pressure was passed continuously through the furnace tube, around the sealed quartz tubes. The heat treatments were then interrupted by quenching in brine. The specimens always had a clean surface at the end of the heat treatments. They were then cleaned in 6 N HCl for a few minutes and were then ready for electrolysis or chemical dissolution.

A full account of the chemical and electrochemical treatments is given in Reference 1.

X-ray diffraction of the residues from steels S1 and S2 was carried out in a Debye-Scherrer 114 mm cylindrical camera using a Cu-target for the X-ray source and a Ni filter. Helium was flushed through the camera throughout the exposure period. Because of the long coarsening treatments, the precipitates were adequately sized to yield the desired high angle resolution. Standard extrapolation procedures were used to measure lattice parameters to better than 0.001 Å accuracy, this being adequate to identify the nonstoichiometric compounds.

IV. EXPERIMENTAL RESULTS

Figures 1 and 2 give examples of the raw gas equilibration data from which the solubility limits were extracted. Each point represents the average of two independent equilibrations and at least 8 carbon determinations on pure iron samples used to check for equilibration (equal to the final carbon contents of the Fe-C samples). Points on each isoactivity line correspond to the alloy compositions within the same capsule.

Each alloy sample was metallographically checked for the presence of precipitated carbides, and the samples in the single phase and two phase regions could clearly be delineated.

The point at which each isoactivity line changes slope corresponds to the $\gamma/\gamma + \mathrm{NbC}_x$ equilibrium and represents the maximum amounts of niobium and carbon that can remain in solution in austenite at that carbon activity before precipitation of NbC_x begins. The uncertainties in both the niobium and carbon contents have been used to estimate the errors in the tie lines. At each carbon activity, the possible changes in slopes of the straight lines that represent the best linear least squares fit of the points in the two phase and the single phase regions have been taken into account in arriving at the solubility products indicated in Table III. In some cases, however, horizontal lines have necessarily been drawn in the single phase region corresponding to the binary carbon level. The uncertainty recorded for each of the solubility limits represents the maximum deviation and thus corresponds approximately to a 95 pct confidence limit.

The results of the chemical analysis of carbides extracted from steel S1 are shown in Table IV. The carbide present in this steel at 1000 °C was identified as $\mathrm{NbC}_{0.9}$. The soluble niobium and carbon were calculated from the total amounts of niobium and carbon in the steel S1 and the mean value of niobium present as carbide.

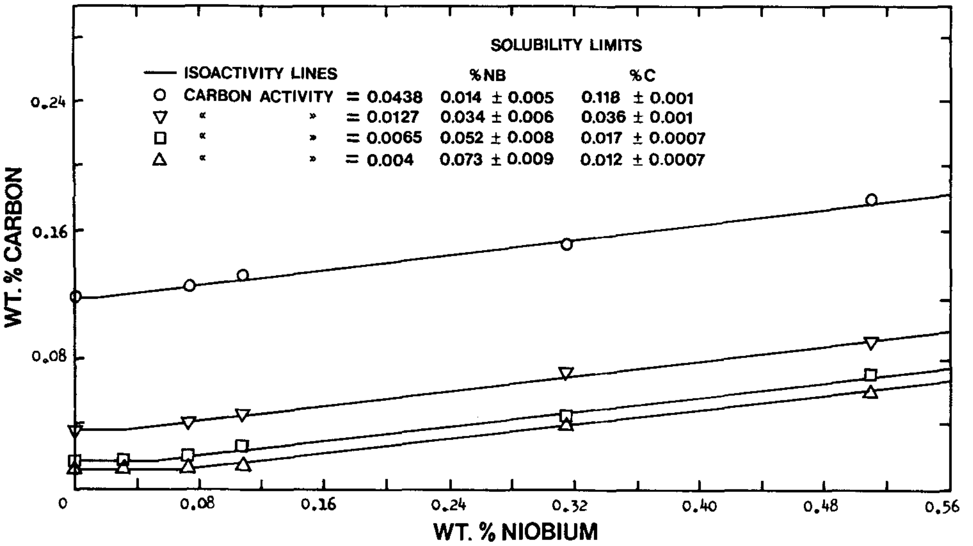

Fig. 1—Carbon content of Fe-Nb alloys, equilibrated at 1000 °C. Standard state of carbon activity referred to graphite.

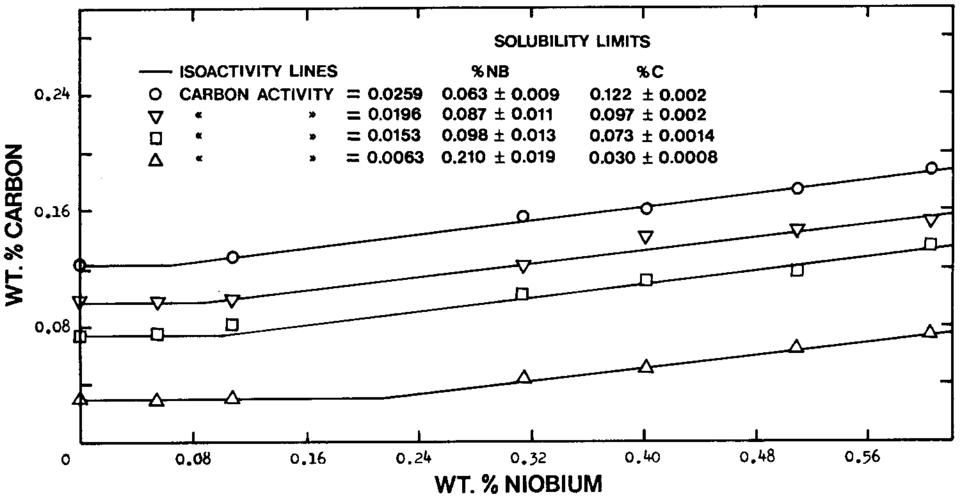

Fig. 2—Carbon content of Fe-Nb alloys, equilibrated at 1200 °C. Standard state of carbon activity referred to graphite.

Table III. Solubility Products from Equilibration Studies

T°C	Solubility Limits Pct Nb	 Pct C	$\log_{10}$ [Pct Nb][Pct C]$^{0.87}$
1000	0.014	0.118	−2.66 ± 0.19
	0.034	0.036	−2.72 ± 0.12
	0.052	0.015	−2.85 ± 0.07
	0.073	0.010	−2.88 ± 0.06
1050	0.057	0.031	−2.56 ± 0.06
1100	0.031	0.125	−2.29 ± 0.09
	0.047	0.064	−2.37 ± 0.08
	0.091	0.032	−2.34 ± 0.05
	0.110	0.024	−2.35 ± 0.06
1150	0.110	0.035	−2.23 ± 0.05
	0.185	0.020	−2.21 ± 0.06
1200	0.063	0.122	−2.00 ± 0.07
	0.087	0.097	−1.94 ± 0.06
	0.098	0.073	−2.00 ± 0.06
	0.210	0.030	−2.00 ± 0.05
1250	0.180	0.065	−1.78 ± 0.05

The results of X-ray analysis of the precipitates extracted from steels S1 and S2, held at 1000 °C, are given in Table V. The lattice parameters of the precipitates are also given along with their respective uncertainties.

The lattice parameter of the precipitate in steel S1 was compared with the results of Kempter *et al.*[29] and identified as $NbC_{0.9}$. The data of Brauer and Lesser[30] have been utilized to identify the carbonitride in steel S2 as $NbC_{0.91}N_{0.04}$.

Table V. X-Ray Analysis of Precepitates

Steel	Extrapolated Lattice Parameter	Compound
S1	4.465 ± 0.001 Å	$NbC_{0.9}$
S2	4.469 ± 0.001 Å	$NbC_{0.91}N_{0.04}$

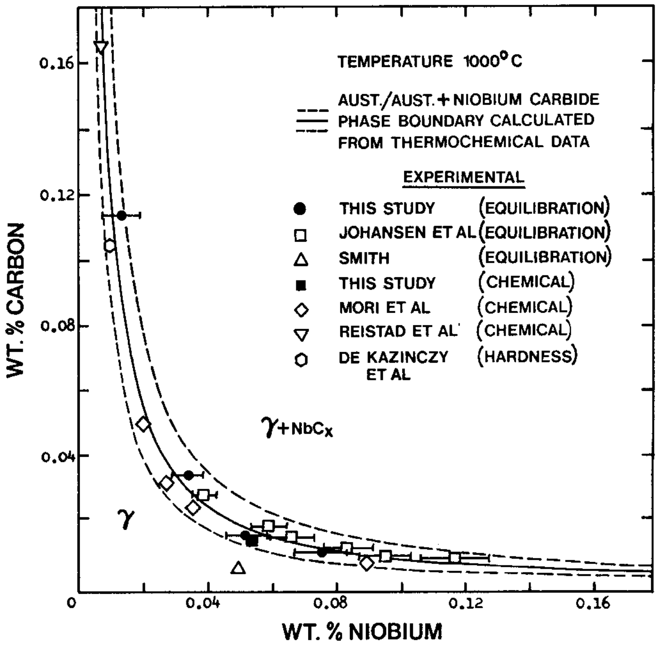

Fig. 3—γ/γ + NbC_x phase boundary at 1000 °C.

Table IV. The Details of Residuum Analysis for Steel S1

Temp. of austenitization, °C	950	1000	1050	1100	1150	1200
Holding time (hours)	120	100	94	48	48	12
Wt pct Nb in solution in austenite (total Nb-fixed Nb)	0.045	0.065	0.085	0.128	0.158	0.180
Wt pct C in solution (total pct C-fixed Nb × 0.87 × 12.01/92.91)	0.015	0.017	0.019	0.024	0.028	—
Log[pct Nb][pct C]$^{0.87}$	−2.93	−2.73	−2.57	−2.30	−2.15	—

$$\log_{10} K = 2.7 - \frac{6900}{T} \pm 0.12$$

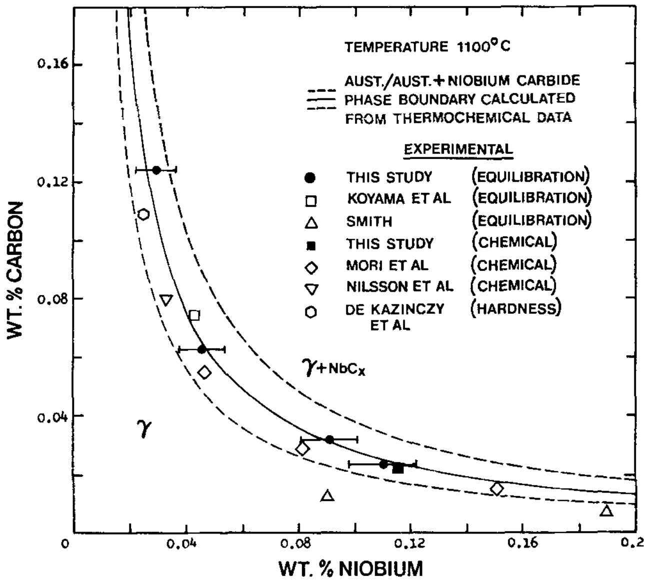

Fig. 4—γ/γ + NbC$_x$ phase boundary at 1100 °C.

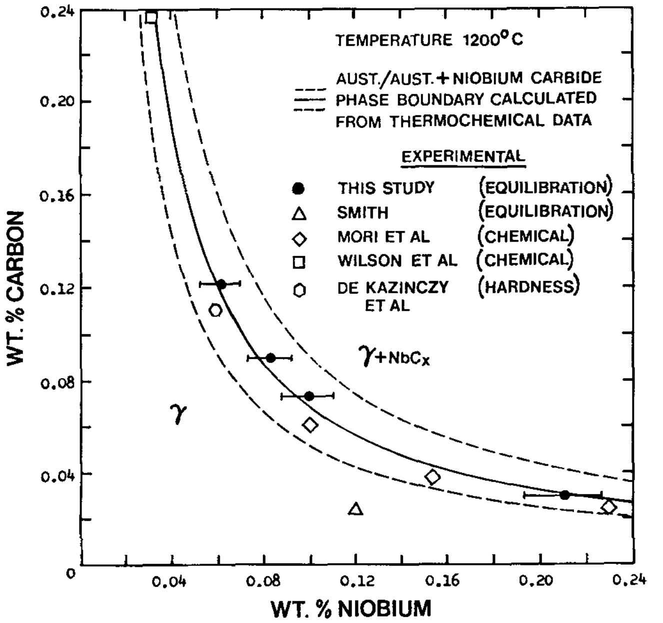

Fig. 5—γ/γ + NbC$_x$ phase boundary at 1200 °C.

A selection of γ/γ + NbC$_x$ phase boundaries calculated from thermochemical data[1] along with the present experimental information (including that of Nillson *et al.*[31]) and the reported solubility data are summarized in Figures 3 through 5.

The average solubility product generated by the results of the present equilibration experiments (Table III) is

$$\log_{10}[\text{pct Nb}]\,[\text{pct C}]^{0.87} = 3.4 - \frac{7920}{T} \qquad [1]$$

This is to be compared with an empirical and thermodynamically self-consistent formula developed by Sharma *et al.*[32]

$$\log_{10}[\text{pct Nb}]\,[\text{pct C}]^{0.87} = 2.81 - \frac{7019.5}{T} \qquad [2]$$

The latter, which includes the data leading to [1] is recommended as a reliable summary formula.

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