The Composition of Eta Carbide Phase in $2\frac{1}{4}$ Cr-1 Mo Steel

JAMES M. LEITNAKER, RONALD L. KLUEH, AND WILLIAM R. LAING

The metal-to-carbon ratio in the eta phase in 2 1/4 Cr-1 Mo steel exposed to sodium at 566°C for 26,500 h, and probably under a variety of service conditions, approaches four, rather than six, a fact which may be influenced by the presence of Si, O, and perhaps Cr. Silicon is present in the eta phase, probably on a metal sublattice, while oxygen is probably present on the metalloid sublattice. The observation is supported by both structural and compositional data from the literature.

Low alloy steels, such as 2 1/4 Cr-1 Mo, are projected for use in the steam generator of the demonstration Liquid-Metal Fast Breeder Reactor (LMFBR). Long-term service, up to 30 years, at high temperature will have significant effect on the alloy microstructure, and hence, its mechanical properties. For design purposes, the mechanical properties of such a steel are important, and, since it is impractical to run tests for significant fractions of the life time of such vessels, extrapolation procedures are highly desirable.

For such extrapolation procedures, one important quantity is the composition and location of the carbide precipitates which normally exist in these steels. A quantity of 2 1/4 Cr-1 Mo steel, which had been heated 26,500 h at 566°C in sodium with some consequent decarburization, recently became available. During the course of a cursory examination of the composition of the precipitate and matrix, results were obtained which were in seeming contrast to some of the accepted literature. Specifically, we noted that the precipitate phases did not seem to be tending to "M_6C" (a face-centered cubic structure called eta phase, with 96 metal atoms per unit cell, $a_0 \simeq 11.08\text{Å}$) as one might deduce from the precipitation scheme described by Baker and Nutting,[1] but rather seem established by the carbon content between "M_6C" and $M_{23}C_6$. (Baker and Nutting probably did not intend to imply the endpoint of all carbide phases was "M_6C"). Furthermore, from a chemical analysis of the supernate remaining after an electrolytic extraction the metal-to-carbon ratio, (M:C), of the "M_6C" phase was calculated to be about four rather than six. Thus, a more extensive investigation of the phases seemed advisable.

The role of carbides in low alloy ferritic steels has been reviewed extensively by Woodhead and Quarrell,[2] and a further review seems unwarranted here. The carbon content of these phases has been inadequately studied, however, an oversight which appears to be a strategic error if the mechanical properties are to be understood at long aging times. Numerous authors have shown that the mechanical properties of an alloy depend in an important way on the composition of the matrix. (See, for example, references cited by Woodhead and Quarrel.[2]) Any deviation from the composition M_6C will have an important effect on the amount of solute elements and, hence, our knowledge of their effect in solution on properties of interest.

For the above reasons, a more extensive investigation of the phases present in 2 1/4 Cr-1 Mo steel seemed advisable. The present investigation involved anodic extraction of the phases and examination by X-ray diffraction. Where a substantial amount of precipitate would be obtained, it was chemically analyzed. In other cases the supernate was analyzed. The results were used to determine the carbon content of the eta phase.

EXPERIMENTAL

The specimens used were from an experiment designed and operated by MSA Research Corporation.[3] The test specimens were in the form of 0.06-in.-thick sheet tensile specimens, 7 1/4 in. long by 1 1/4 in. wide, with a gage length of 1 in. long by 1/2 in. wide. Flat plates were spot welded to the shoulder section of the specimens to strengthen them, since holes were drilled in this region to hold the specimens during tensile tests. The specimens, aged for 26,500 h at 566°C in sodium, were obtained from MSA. Two different analyses performed on the starting material are listed in Table I. Also given are analyses on two of the samples aged in sodium and partially decarburized.

Samples of the precipitate particles were anodically extracted at 1.5 v using a platinum cathode in a 10 pct HCl-90 pct CH_3OH solution. Successive extractions on the same sample (of 1/2 to 2 h duration) were done at constant voltage, within 0.1 V. Nearly complete dissolution (of up to 5 h duration) resulted in a gradual increase in voltage, up to 2.0 V. Precipitate adhering to the sample was removed by ultrasonic vibration in ethyl alcohol, and the sample was then dried and weighed. The precipitate was separated from the supernate by centrifuging it. The precipitate was washed with CH_3CH_2OH, centrifuged again to separate it from the alcohol, dried in a vacuum desicator, and weighed. The actual weights are accurate to 0.1 mg. Possible errors are (1) loss of precipitate through dissolution or inadequate centrifuging and (2) inadequate cleaning of tube or precipitate. Results have been very consistent, indicating reproducibilty with 0.2 mg. However, we have never demonstrated that very small precipitates are not being dissolved. Only the independence of the wt pct precipitate with extraction time makes it seem reasonable that any dissolu-

---

JAMES M. LEITNAKER, RONALD L. KLUEH, and WILLIAM R. LAING are respectively, Research Staff Members, Metals and Ceramics Division, and Group Leader, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

Manuscript submitted January 29, 1975.

tion of the precipitate is within the experimental error.

The X-ray procedure used has been recently described by Spruiell and Gehlbach.[4] Briefly, the procedure is as follows: Extracted precipitate samples were completely dispersed in ethyl alcohol, and the alcohol removed by dropping the dispersion slowly onto a warm piece of glass. The precipitate was scraped from the glass onto a single crystal wafer of silicon, and a drop or two of alcohol was used to make a paste which was smeared out on the silicon wafer. (The wafer serves as the substrate for the precipitate in a diffractometer and is so oriented that no silicon lines are diffracted to the detector.) Copper radiation was used; the beam leaving the sample was passed through a graphite monochrometer to remove any scattered radiation. This procedure resulted in a low background with high sensitivity for phases present in small percentages of the total precipitate.

To correct observed intensities to relative concentrations of the two carbide phases, we used the formula

$$\frac{I_A}{I_B}\,\frac{V_A^2}{V_B^2} \times \frac{(F_B)^2}{(F_A)^2} = \frac{C_A}{C_D}$$

where the I's are the measured X-ray intensities of a given peak, the V's are the unit cell volumes, the F's are the unit cell structure factors, and the C's are the molecular concentrations.

To calculate the value for $(F_{M_{23}C_6})^2$ we assumed 21 at. pct Fe, 9 at. pct Mo and 70 at. pct Cr were randomly distributed on the four atomic sublattices. For $(F_{\text{eta}})^2$ we assumed 10 at. pct Cr replaced a like amount of Mo on the Mo sublattice. There is no good basis for these assumptions, but, fortunately, the scattering factors of Fe and Cr are not too different and where Cr and Mo were interchanged, the atom fraction was small. A variety of distributions led to structure factors only slightly different than those used. For the (511)—(333) planes, we calculated

$$\frac{(V_{\text{eta}})^2}{(V_{M_{23}C_6})^2} \times \frac{(F_{M_{23}C_6})^2}{(F_{\text{eta}})^2}$$

$$= \frac{(11.09)^6}{(10.61)^6} \times \frac{98.60}{191.66} = 0.671.$$

Sample Analysis

Metal samples were prepared by dissolution in 1-1 $HCl \cdot HNO_3$, and fuming in H_2SO_4. Iron was determined by titration with standard dichromate after reduction with stanous chloride. Chromium was oxidized with persulfate, and excess standard ferrous iron solution added and back titrated with standard permanganate. Silicon was separated by acid hydrolysis and volatilized by HF. The LECO thermal conductivity apparatus was used for carbon.

Solutions resulting from anodic extraction were analyzed by spectrophotometric methods. Diphenylcarbizide was used for chromium after oxidation with silver peroxide. Iron was réduced with hydroxylamine and a color developed with O-phenanthroline. Small amounts of silicon were measured using the molybdenum blue method. Molybdenum was determined by the thiocyanate method.

Samples of the precipitate particles were treated with 1-1 $HCl \cdot HNO_3$ and fumed in H_2SO_4. Any residues were fused with Na_2CO_3. The spectrophotometric methods described for the solutions were used for the analysis of these materials. Carbon was measured using the LECO thermal conductivity apparatus.

For the direct determination of the composition of extracted precipitate, the reinforcing plates which had been spot welded onto sample shoulders were machined off one Na-aged specimen. This specimen was cut into smaller pieces and extracted electrolytically. The precipitate was analyzed for C, Cr, Mo, and Si. The supernate was analyzed for Cr, Mo, and Si. Because a total of only 0.5 g of precipitate was available, the carbon was analyzed in a LECO apparatus as follows: a laboratory control sample was first run in the apparatus; a NBS-certified steel sample was run; the unknown was run; and another control sample was run.

RESULTS

Results of the analysis on the precipitate extracted from a large sample heated in sodium at 566°C for 26,500 h are reported in Table II. From (M:C) ratio found by analysis in the precipitate and by correcting for the amount of $M_{23}C_6$ present in the precipitate, one can readily calculate (M:C) in the eta phase: 4.26, substantially richer in carbon than M_6C.

While the direct analysis is the best indication of the eta phase composition, corroboration is provided by extraction on a piece of the gage section of a sample which had been exposed in sodium, after the surface region is removed, and reported as the final sample in Table III. Appropriate calculations in Table IV reveal the overall (M:C) is 3.9, for the last extraction. Again, assuming (M:C) in $M_{23}C_6$ is 3.83 and that all the carbon is tied up in the carbide, (M:C) in eta phase is calculated to be 3.92. While this result indicates a lower (M:C) than the direct analysis, it also supports a value much lower than 6. (The difference in the two results may be related to the assumed solubility of carbon in the ferrite, an error in carbon analysis, or dissolution of some precipitate, as discussed subsequently.)

The errors in the direct analysis for metals can be estimated by observing the total material found by analyzing both the precipitate and the supernate and com-

Table I. Composition of 2¼ Cr-1 Mo Steel Specimens Used in This Study

	Element (Wt Pct)						
Analyses	Cr	Mo	C	Mn	P	S	Si
MSAR[a]	2.17	1.01	0.097	0.56	0.007	0.022	0.33
[b]	2.22	0.99	0.11	0.50	0.009	0.022	0.21
ORNL–MSA-138[c]	2.28	1.03	0.064	–	–	–	0.175
ORNL–MSA-136[c]	2.19	1.01	0.066	–	–	–	–
ORNL–MSA-He[d]	–	–	0.096	–	–	–	–

[a] Supplied by MSA Research Corporation as starting composition.
[b] Supplied by McInnes Steel Co. to MSA Research Corp.
[c] Obtained from remainder of a Na-exposed sample after electrolytic extraction of precipitates. Note decarburization which occurred.
[d] Obtained from He-aged sample.

Table II. Results on Extraction of 28.1174 g of 2¼ Cr-1 Mo Steel Aged 26,500 H in Sodium[a]

	Element				
	C	Cr	Mo	Si	Fe
Precipitate (wt pct)[b]	4.02	13.5	39.6	2.27[c]	40.61
Supernate (mg total)[d]		487	73.7	39.4	
Total found in sample (wt pct)	[e]	1.97[f]	0.974	0.181[g]	
Moles in precipitate ($\times 10^3$)	1.692	1.313	2.087	0.409	3.676

$$\frac{\Sigma(\mathrm{Cr}+\mathrm{Mo}+\mathrm{Fe})}{\mathrm{C}} = 4.182; \quad \frac{\Sigma(\mathrm{Cr}+\mathrm{Mo}+\mathrm{Fe}+\mathrm{Si})}{\mathrm{C}} = 4.424;$$

$$\frac{\Sigma(\mathrm{Cr}+\mathrm{Mo}+\mathrm{Fe})}{\Sigma(\mathrm{C}+\mathrm{Si})} = 3.368.$$

[a] Precipitate weight was 0.5056 g. Integrated intensity ratio of M_6C to $M_{23}C_6$ by X-ray analysis was 6.8; a_0 (eta) = 11.09.

[b] Carbon analysis was done by combustion; Cr and Mo analyses were done by volumetric techniques. Fe is obtained by difference.

[c] Microprobe analysis on these samples also indicates the eta phase is enriched in Si, Relative to the matrix.

[d] Cr and Mo analyses by spectrophotometric techniques.

[e] The amount of carbon calculated by assuming it is all in the precipitate is 0.071 wt pct. This is misleading as is discussed in the text.

[f] See text for discussion of this low value.

[g] The silicon analyses for the starting material is uncertain even though the total Si found is in good agreement with our analysis. There may reflect a variation within the sample or just the difficulty of analysis.

Table III. Analysis of Elements in Supernate of Successive Extractions, with X-ray Intensities of Phases, in Na-aged Sample

Sample No. (MSAC-138)	Sample Wt Loss (mg)	Precipitate Recovered (mg)	Analyzed in Supernate Cr (mg)	Mo (mg)	Si (mg)	$\frac{I_{ETA}(333)}{IM_{23}C_6(333)}$[a]
A4678-165	83.0	2.4	0.83	0.35	0.11	[b]
A4678-166-1	289.3	3.8	5.41	0.92	0.19	–
A4678-166-2	201.8	2.6	4.00	0.59	0.32	15.2
A4678-167	257.8	3.4	5.29	0.81	0.41	13.5
A6166-12	1804.9	28.0	37.7	4.98	2.60	–
A6166-13	533.3	8.4	10.9	1.40	0.88	7.5

Original Sample size: 2.85 × 1.25 × 0.57 cm; 4.5085 g.

[a] The values given are peak height ratios, rather than integrated intensities; since the peaks were quite narrow the difference for this purpose is negligible.

[b] Broad peaks and high background. Oxygen analysis on a similar sample indicated 2000 ppm O. Recognizable peaks were M_6C and $M_{23}C_6$.

paring this with the amount expected in the total sample. The error in the molybdenum analysis should be no greater than about 3 pct, and the determination may be slightly low, since less than 1.01 wt pct Mo was found. The error in the chromium analysis may be somewhat greater than this, but since the iron is found by difference and the molecular weights are similar, the error in the metal-to-carbon ratio can be neglected.

Note that the total amount of chromium found in the large extracted sample (sum of the chromium from the precipitate and from the supernate) reported in Table II is only 1.97 wt pct rather than 2.22 wt pct as is believed to be in the total sample. This is not ascribable to careless loss of precipitate or supernate, since the total amount of molybdenum found is the same as in the total sample, within experimental error. It is believed that the low chromium content is related to a region of the sample in which the chromium content was altered by spot welding. These regions showed much more rapid dissolution during electrolysis, and, in fact, a hole would frequently appear at the weld position. Two analyses for chromium on pieces of steel from a spot welded region gave 1.73 and 1.76 wt pct chromium. Thus, the total chromium found in the large extracted sample is believed to be an average resulting from regions of low and as-fabricated (before welding) chromium contents. Furthermore, the mole fraction ratios, Cr/Mo/Fe, in the gross extraction are the same as deduced from the final extractions (Table IV) after surface effects are removed, well within any experimental error.

Because of the importance of the carbon analysis, the technique described in the experimental section of analyzing known samples before and after the carbon determination was used. The error should be no greater than 5 pct of the carbon found.

The errors in (M:C) in the successive extractions are of a somewhat different sort. The molydenum analysis is probably correct to 1 or 2 pct; note the smooth change with successive extractions. The error in the chromium analysis is much greater since chromium is found by difference of two fairly substantial numbers, and the variation of chromium found in the precipitate through the sample is consequently much larger. However, again, the iron is found by difference and the contribution to a calculated (M:C) can be neglected.

One source of discrepancy in the two different results may be what is assumed for the solubility of carbon in ferrite. In the Appendix the computations are outlined which lead to the assumption that substantially all the carbon is present in the carbide phases. The principal source of error appears to be the extent to which carbon obeys Henry's law in the activity range under discussion. Back calculation reveals that if 0.0613 wt pct C were present in the precipitate with 0.0037 wt pct C dissolved in the steel the agreement would be exact: (M:C) would be 4.26 as found for the direct analysis of the precipitate.

Another source of discrepancy may be an incorrect analysis for carbon. Two analyses were performed on the aged steel for total carbon with excellent precision (Table I). Only one analysis was performed on the large extracted sample. It seems possible that the single analysis is low, despite the great care used in setting up the analysis.

A third possibility to explain the discrepancy between the two experiments is the possibility that some precipitate was being dissolved during extraction. Such an effect would result in less metal being calculated to be in the precipitate, with the same amount of carbon being assigned to the precipitate. This would indeed result in a lower calculated (M:C).

Nevertheless, although there is a small discrepancy between the results, the source of which can not be ascertained at this time, both results are concordant in that they yield a (M:C) for the eta phase considerably less than 6.

The data in Tables III and IV reveal additional information. The wt pct precipitate in the first sample is much higher than in the remainder. Analysis for oxygen in a layer about 0.003 in. thick machined from the surface of the Na-exposed material revealed about 2000 ppm oxygen, while the remainder of the material

Table IV. Calculations on Molecular Content of Precipitate (from data of Table III)

Sample No.	Wt Pct Precipitate	Elements in Precipitate[a]				Moles of Elements in Precipitate per g Steel			M/C
		Cr Wt Pct	Mo Wt Pct	Si Wt Pct	Fe Wt Pct	Cr × 10^4	Mo × 10^4	Fe × 10^4	
A4678-165	2.89	1.22	0.59	0.060	0.955	2.35	0.61	1.71	8.6
A4678-166-1	1.31	0.35	0.69	0.127	0.078	0.67	0.72	0.14	2.82
A4678-166-2	1.29	0.24	0.72	0.034	0.231	0.46	0.75	0.41	2.99
A4678-167	1.32	0.17	0.70	0.034	0.351	0.33	0.73	0.63	3.12
A6166-12	1.55	0.13	0.73	0.049	0.576	0.25	0.76	1.03	3.8
A6166-13	1.58	0.18	0.75	0.028	0.557	0.35	0.78	1.00	3.9

[a] Obtained by subtracting elements found in supernate from total in sample: Cr, 2.22 ± 0.02 wt pct; Mo, 1.01 ± 0.01 wt pct; C, 0.065 ± 0.001 wt pct; and Si, 0.193 ± 0.04. Iron is taken as the difference between (Cr, Mo, C, Si) and the total wt pct precipitate. Obviously, this is incorrect in the first sample where oxygen is a significant contaminant.

contained about 200 ppm oxygen. The calculated (M:C) is clearly incorrect for the surface region if one is ascribing the result to "carbides" for oxides are clearly present. (The X-ray patterns were much less sharp for this surface region, and examination of the surface region via electron microscopy revealed such heavy precipitation that useable micrographs were not possible.) The wt pct precipitate remains substantially constant, then, with subsequent extractions until the last two extractions when it increases markedly. Note that the chromium content in the precipitate for the first extraction is exceedingly high, and undoubtedly reflects the greater stability of the chromium oxides versus oxides of the other metals in the system. Note also that the chromium content of the precipitates in the second extraction is also high, relative to the chromium content in the rest of the extractions. This quite likely reflects an influence of increased oxygen content on the wt pct precipitate in this region of the sample. There is a hint of this effect in the third sample as well. The fact that the X-ray patterns were exceedingly sharp for the second and third extractions and contained only carbide phases for these samples strongly suggests that the oxygen present was dissolved in the "carbide" phases.

In the large extracted sample the wt pct C found, by back calculation assuming all the carbon was precipitated in the form of carbides, was 0.071 wt pct (Table II). But only 0.065 wt pct C is found by analysis in the analysis of the steel. A portion of the steel used came from the protected shoulder region of the sample. It is reasonable to suppose that this portion of the sample was not so depleted in carbon as the gage section, which started at ~0.1 wt pct C and was reduced to 0.065 wt pct C after the aging treatment. Thus, the 0.071 wt pct total represents an average between the gage section and the shoulder section.

The low results found for (M:C) in the second, third and fourth extractions (Table IV) are readily explained by a carbon gradient in the outer region of the sample. Too high a value for carbon is being used and a low (M:C) result is obtained.

The data for both the extracted precipitate and the successive extractions reveal that the carbide phases are enriched in silicon. A quantitative measure can be placed on this, subject to the error in the analysis for silicon. (The analysis for silicon is a difficult one and the error on the bulk sample could possibly be 20 pct of the silicon, but is probably not greater.) The total silicon content of the samples is about 0.19 wt pct, of which 0.15 wt pct remains in the matrix and the remaining 0.04 wt pct (total) corresponds to 2.3 wt pct Si in the precipitate. The distribution of silicon can then be expressed most reasonably by a partitioning expression

$$\text{Si (matrix)} = \text{Si (carbide)}$$

and

$$K = \frac{\text{Si (carbide)}}{\text{Si (matrix)}} = \frac{2.3}{0.15} = 15.$$

Despite the fact that we have no information on how the distribution coefficient changes with silicon content, the fact that it is greater than one indicates that silicon increases the driving force for formation of carbide phases. This result is in agreement with observations by Gehlbach several years ago, who observed that silicon "stabilized" the M_6C phase in Hastelloy.[5]

DISCUSSION

It is apparent that (M:C) in the eta carbide, where M is the sum of Cr, Mo, and Fe, is less than 6. Up to now, the influence of both silicon and oxygen have been ignored. Some discussion of their possible roles and the influence on the conclusions is appropriate.

The "pure" eta carbides have been recently reviewed by Stadelmaier.[6] The basic formula of those discussed by him can be taken as $M_6M'_6C_\chi$, where two metals, M and M′, are involved with carbon, C, and χ is 1 or 2. The difference in these two is the position of the carbon atom. When $\chi = 1$ there are eight carbon atoms per unit cell located at the center of a metal octahedra (position *a*). When $\chi = 2$ there are 16 carbon atoms per unit cell located between the metal octahedra (position *c*). Examples of eta carbides have been reported where both *a* and *c* positions are filled; *e.g.*, $Zr_8Zn_4C_3$ and $Nb_8Zn_4C_3$ by Jeitschko *et al.*[7] (See Stadelmaier[6] for a pictorial description of the lettered positions, *a*, *c*, and *d*, in the eta phase.)

For the influence of silicon on the structure, a normal assumption might be that silicon could be on a carbon lattice site, *a* and/or *c*. However, there does not appear, physically, to be enough room for a silicon atom in either position. Several silicides with the eta structure have been investigated and the conclusion has been that the silicon replaces some of the metal atoms, on position *d*. (The formulas given are

$M_3M_2'Si$ but do not include an Mo-Fe-Si structure.)

An oxide, Mo_3Fe_3O, which has the eta structure has been reported by Shönberg.[8] In view of findings by Stadelmaier and Meussner[9] as well as by Parthé, *et al.*[10] (in contrast to the report of Nevitt[11]), it is most reasonable to suppose that the structure is identical with the eta carbides.

With this background in mind, one can assess the possible influence of the silicon and oxygen on the metal-to-metalloid ratio, (M:X), by examining the various possibilities as in Table V. (The possibility that silicon can replace carbon by expanding the metal lattice is ignored.) One sees that if silicon is placed on the metal lattice (possibly in position *d*, but the location is not demanded for our treatment), (M:C) in eta phase is still significantly less than 6. If all the oxygen found by analysis in the steel is on the metalloid lattice, the (M:X) in eta is not calculable, for (M:X) overall is greater than that for $M_{23}C_6$.

Thus, not only is (M:C) less than 6; even when silicon is on the metal lattice (M:C) is considerably less than 6. Further, if oxygen is on the metalloid sublattice, (M:X) can be less than that calculated for (M:C) with silicon on the metal lattice and perhaps less than that calculated for (M:C) with only Mo, Cr, Fe, and C considered.

From data reported here, the composition of the eta phase in 2 1/4 Cr-1 Mo, expressed either as (M:C) or (M:X) is seen to be significantly less than 6, approaching 4. This finding appears to disagree with much of the published literature. The reasons for the difference can only be surmised. First, no analytical data are reported on any samples heated as long as ours at 566°C. In almost all the instances where eta phase, as M_6C, is reported X-ray evidence is used to deduce the composition. A notable exception is the work of Fraker and Stadelmaier.[12] Their samples were annealed at 1000°C for 1000 h. The difference between our work and the former may therefore lie in the effect of temperature on composition.

Alternatively, our samples contain, in addition to Mo, Fe, and C, Cr, Si, and O in apparently significant quantities. It seems possible that one or more of these elements has the observed effect on (M:C). Certainly, the presence of both silicon and oxygen will be expected to increase the amount of precipitate.

Data from a paper by Ridal and Quarrell on "The Molybdenum Carbide Transformation in Ferritic Steels"[13] add support to our conclusions. (These data have been largely ignored by those authors interested in the eta phase—and were by us until quite recently—because neither the title nor abstract suggest that data on the composition of the eta phase are included.) These authors reported that the eta carbide in 3.5 wt pct Mo steel is best represented by the formula $Fe_3Mo_3C_{1.25}$. That is, their composition is $M_{4.8}C$ while this work indicates M_4C. Their temperature, for much of the work, was about 700°C, while the present work was 566°C. Their steel contained 3.5 wt pct Mo and was quite low in Cr, while our steel contained 2 1/4 wt pct Cr and had only about 1 wt pct Mo. Both the composition and temperature may influence the results and explain the difference between their stated result and those presented here.

Ridal and Quarrell's Table III contains additionally suggestive data.[13] As their Mo/C ratio decreases from 3.02 to 2.15, the metal to carbon ratio in the eta phase also appears to decrease. (Their Fig. 8 shows that an extrapolated value was used for the wt pct of carbide in sample M20 which is actually higher than the actual experimental result. If the experimental result is taken, our deductions are further strengthened.) It is more instructive to invert the two ratios: as the carbon content increases, more carbon is deduced to be in the precipitate per gram atom of metal in the precipitate. Such a finding is consistent with the view that a range of homogeneity exists between compositions of M_6C and M_4C.

Further study of Ridal and Quarrell's Table III[13] reveals one sample, M16 is apparently "out of line." Reference to their Table I reveals this sample is rich in Si. Such a finding is consistent with our own observations that Si can participate importantly in formation of the eta phase. Viewed another way, the "effectice" M/C is higher than that revealed by the Mo-to-C ratio.

The implications of these observations are of technological importance. They indicate that the amount of precipitate, which affects the amount of strengthening elements left in solution, is a function not only of the carbon content, but also a function of the silicon and oxygen content of the steel. During operation of an LMFBR steam generator for 30 years, one would expect simultaneous decarburization via Na transport and oxidation via steam. Clearly, extrapolation of short term mechanical property measurements must be made with some care. Furthermore, mechanical properties may be expected to vary (significantly) throughout the component thickness.

One final comment concerning the phase relationships observed seems in order. The phases $M_{23}C_6$ and eta phase were observed in the samples aged 26,500 h at 566°C. The molecular concentration ratio, $M_{23}C_6$-to-eta, increased from the outside to the center of the specimen, the same direction in which the carbon increased. Considering the system as a quaternary, Fe-Mo-Cr-C, the phase rule predicts that, except at singular points as many as four phases can be in equilibrium at one time. Three are observed in this sample: α-Fe, eta, and $M_{23}C_6$. Since $M_{23}C_6$ increases with carbon content it seems reasonable to suppose that over regions extending a few microns the sample is at chemical equilibrium. If the composition remained constant, there appears no reason to suppose that

Table V. (M:X) Values Calculated Using Various Assumptions

Assumption	M:X (Gross)	M:X Eta
Only Cr, Mo, and Fe are on the metal lattices; only C is on the metalloid lattice.	4.182	4.26
Cr, Mo, Fe, and Si[a] are on the metal lattices; only C is on the metalloid lattices.	4.424	4.57
Cr, Mo, Fe, and Si are on the metallic lattices; C and the 200 ppm O contained in the sample are on the metalloid lattices.	3.61	–

[a] Note that Si is assumed to be distributed on the two carbide phases in proportion to their molar concentration. This is very liketly not true but no error results in the basic conclusions.

$M_{23}C_6$ would ever totally disappear to yield a two phase system, α-Fe plus eta phase.

CONCLUSIONS

1) The phase widely called M_6C approaches M_4C in 2 1/4 Cr-1 Mo steel at 566°C. Presently available structural information suggests that eight additional carbon atoms can be accommodated per unit cell in the structure for a total of 24 carbon atoms and 96 metal atoms. The phase should probably be referred to as the eta phase to avoid specifying a generic carbon content, since a range of compositions is probably possible.

2) Silicon in the steel is concentrated in the precipitate. Structural data on silicides in the literature suggests the Si is on the metal sublattice, an observation which is consistent with these data.

3) Oxygen and chromium may influence the value of M/C observed. Oxygen can probably replace C in the structure of the eta phase. The Cr is quite likely on the Mo sublattice of the eta phase. The presence of both oxygen and silicon will be expected to increase the amount of precipitate.

APPENDIX

To interpret a portion of these data an estimate of the solubility of carbon in 2 1/4 Cr-1 Mo after ~0.75 wt pct of the molybdenum and about 0.25 wt pct Cr have reacted with carbon (to form eta phase) is necessary. This appendix describes the auxiliary data necessary to make that estimate.

The solubility of carbon in α-Fe in equilibrium with Fe_3C in the temperature range of interest has been measured most recently by Lindstrand,[14] Petrova, *et al.*,[15] Bruk,[16] and Smith.[17] All the measurements were plotted and a smooth curve was drawn through the points. The data of Lindstrand was most closely matched in the temperature range of interest, near 566°C, the curve being about 0.0005 wt pct C below the data of Lindstrom. At 566°C the solubility of carbon used is 0.0062 wt pct or 2.88×10^{-4} at. pct.

The system α-Fe–Fe_3C is unstable; thus, the solubility must be reduced by an appropriate amount. The calculation involved for determining this amount is as follows: For the reaction

$$3\,\alpha\text{-Fe} + \text{C} = \text{Fe}_3\text{C} \tag{A-1}$$

from NBS data[18]

$$\Delta G^0 = 6000 - T(4.07) \tag{A-2}$$

at 839 K

$$\Delta G^0 = 2585 \tag{A-3}$$

The activity of carbon in this system can be obtained from the equation

$$\Delta G^0 = -RT \ln \text{K}, \tag{A-4}$$

$$\frac{\Delta G^0}{RT} = \ln A_\text{C} = 1.551, \tag{A-5}$$

or

$$A_\text{C} = 4.715 \tag{A-6}$$

Hence, the activity of carbon is a factor of 4.72 higher in the equilibrium α Fe–Fe_3C than in the equilibrium α Fe–graphite.

Even at the concentration level of 0.0062 wt pct carbon, one cannot safely assume the validity of Henry's law, since the activity of carbon relative to graphite is so high. Dividing the concentration by a factor of two may be a reasonable approximation to the solubility of graphite in α-Fe.

The solubility of carbon will be further reduced by the formation of $M_{23}C_6$ in the 2 1/4 Cr-1 Mo steel. To calculate the further reduction in solubility by the formation the equation

$$23\,\text{Cr}\,(\text{s}) + 6\,\text{C}\,(\text{graphite}) = \text{Cr}_{23}\text{C}_6\,(\text{s}) \tag{A-7}$$

is used.

The activity of chromium at 566°C may be calculated from measurements in the body centered cubic phase at higher temperatures by Mayandarany and Pehlke.[19] The logarithm of the activities were plotted *vs* $1/T$ and extrapolated to 566°C. Plotting for the several compositions $\ln \gamma_{Cr}/(X_{Fe})^2$ *vs* X_{Cr} yielded a slowly changing function which was used to calculate at 566°C (839 K) and 0.0212 atomic fraction Cr, $\ln A_C = -2.097$ for Eq. [A-7], from NBS data[18] $\Delta G^0 = -93{,}023$ cal.

Choosing the activity of $Cr_{23}C_6$ as 0.7, one can calculate the activity of carbon as 0.267 at 839 K. The system probably still does not obey Henry's law, but reducing the carbon solubility (from that calculated to be in equilibrium with graphite) by a factor of 3 is not unreasonable. Thus, the amount of carbon dissolved in 2 1/4 Cr-1 Mo when about 0.75 wt pct Mo has reacted with the carbon and about 2 wt pct Cr remains in the steel is

$$\frac{0.0062}{2 \times 3} = 0.001 \text{ wt pct.} \tag{A-8}$$

ACKNOWLEDGMENTS

Assistance from H. L. Yakel and O. B. Cavin in the X-ray procedures contributed materially to the success of this program. The use of Dr. Yakel's computer program to calculate X-ray intensities was indispensable. Assistance from numerous technical personnel in the Analytical Chemistry Division was absolutely necessary. Mr. G. Potter aided in many of the extractions made. Comments from J. O. Stiegler, D. N. Braski, and J. E. Spruiell aided the presentation of results. The able assistance of Mrs. Jo Anne J. Zody in preparing the manuscript is gratefully acknowledged. Research sponsored by the U.S. Energy Research and Development Administration under contract with Union Carbide Corporation.

REFERENCES

1. R. G. Baker and J. Nutting: *J. Iron Steel Inst.*, 1959, vol. 192, p. 257.
2. J. H. Woodhead and A. G. Quarrell: *J. Iron Steel Inst.*, 1965, vol. 203, p. 605.
3. R. H. Hiltz and L. H. Kirschler: *Effect of High Temperature Sodium on the Mechanical Properties of Candidate Alloys for the LMFBR Program*, MSAR 69-139, July 1969.
4. J. E. Spruiell and R. E. Gehlbach: *Trans. Am. Nucl. Soc. 15*, 1972, vol. 2, p. 769.
5. R. E. Gehlbach and S. W. Cook: *Molten-Salt Reactor Program Semi Annual Report for Period Ending February 28, 1970*, ORNL-4548, p. 231.
6. H. H. Stadelmaier: *Developments in the Structural Chemistry of Alloy Phases*, p. 141, Plenum Press, 1969.

7. W. Jeitschko, H. Nowotny, and F. Benesovsky: *Monatsh. Chem.*, 1964, vol. 95, p. 156.
8. N. Schonberg: *Acta Chem. Scand.*, 1954, vol. 8, p. 932.
9. H. H. Stadelmaier and R. A. Meussner: *Monatsh. Chem.*, 1965, vol. 96, p. 228.
10. E. Parthé, W. Jeitschko, and V. Sadagopan: *Acta Crystallog.*, 1965, vol. 19, p. 1031.
11. M. V. Nevitt: *Electronic Structure and Alloy Chemistry of the Transition Elements*, P. A. Beck, ed., p. 101, John Wiley & Sons, New York, 1963.
12. A. C. Fraker and H. H. Stadelmaier: *Trans. TMS-AIME*, 1969, vol. 245, p. 847.
13. K. A. Ridal and A. G. Quarrell: *J. Iron Steel Inst.*, 1962, vol. 200, p. 359.
14. E. Lindstrand: *Acta Met.*, 1955, vol. 3, p. 431.
15. E. F. Petrova, M. I. Lapshina, and L. A. Shvartsman: *Dokl. Akad. Nauk, SSSR*, 1958, vol. 121, p. 1021.
16. B. I. Bruk: *Dokl. Akad. Nauk, SSSR*, 1959, vol. 128, pp. 709-12; *Sov. Phys.*, vol. 4, p. 1093.
17. R. P. Smith: *Trans. TMS-AIME*, 1962, vol. 224, p. 105.
18. *National Bureau of Standards Technical Notes*, 270-3, 270-4.
19. F. N. Mazandarany and R. D. Pehlke: *Thermodynamic Properties of Solid Alloys of Chromium with Nickel and Iron*, COO-1791-4, Final Report, April 1, 1968–June 30, 1972.