

The Composition of Eta Carbide in Hastelloy N After Aging 10,000 h at 815°C

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The composition of the eta carbide in Hastelloy N containing 0.7 wt pct silicon in the alloy, approaches $M_{12}C$, rather than M_6C as indicated in the alloy literature. The silicon content of the eta phase in this case was ~25 at. pct, much higher than has been observed in less highly alloyed material. The data do not permit a definition of the limiting compositions of the phases.

THE composition, location, morphology, and kinetics of formation of precipitates, in relationship to their matrix, can all be important in determining properties of interest of a particular alloy. However, inadequate data exist to establish the exact nature of the relationships in general. For example, Fine¹ wrote, in regard to one aspect of the problem several years ago, "It is very difficult to ascribe quantitatively the hardening (by precipitates in crystalline solids) to specific sources in specific alloys at the present time." The eta carbide precipitates studied here are important contributors to the mechanical property behavior of nickel-base alloys. For example, Clarke and Titus² found that "morphological changes in the carbide precipitation (of Hastelloy X) appeared to be the most important contributor to room-temperature mechanical property changes, particularly for the shorter exposure times. A dense intragranular network of secondary M_6C carbides precipitate after exposure at 1300 and 1450°F, which weakens the solid solution matrix and causes a severe loss of ductility."

In this laboratory, Gehlback and McCoy³ investigated another nickel-base alloy (Hastelloy N) containing the eta phase. They wrote, "The microstructure is characterized by stringers of massive primary precipitates of the Ni_3Mo_3C type." These are not the only examples; there are copious references to M_6C in the literature of these alloys.

Fraker and Stadelmaier⁴ investigated the Mo-Ni-C ternary system at 1000°C and found that there were two eta carbides, both with narrow carbon content ranges. They indicated the carbides were $M_{12}C$ and M_6C ; a two phase region was reported to exist between them. However, in none of the literature on nickel-base alloys, as compared to relatively pure ternary systems, was it indicated that the eta type carbide was other than M_6C . Even in the simple ternary, not until one gets to about 20 at. pct Mo do the eta carbides become stable at 1000°C in the diagram reported by Fraker and Stadelmaier.⁴ Thus, there was no particular reason to suspect the stated formula,

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M_6C , as the eta carbide in nickel-base alloys.

The present paper describes the analysis of precipitate extracted from Hastelloy N (Ni-16 Mo-7 Cr-4 Fe), which had been aged for 10,000 h at 815°C. Electrolytic extraction of the alloy yielded more than twice the amount of precipitate expected as M_6C . This fact tends to indicate that the eta phase precipitate in Hastelloy N approximates $M_{12}C$, rather than the M_6C stated in the alloy literature.

The discrepancy of a factor of two between the amount of precipitate expected in the Hastelloy N and that extracted led to the present investigation. As it became clear that the precipitate was not M_6C , but approximated $M_{12}C$, the level of analytical effort on the relatively small sample was increased, to demonstrate as well as possible the composition of this precipitate. Further efforts of an even more extensive nature will be necessary if one hopes to explain the relationship between properties and structure on a quantitative basis.

EXPERIMENTAL

The Hastelloy N sample used in this work was aged at 815°C for ~10,000 h by Mr. David Gosler at Hittman Corp., Md. At the conclusion of that program the sample was transferred to J. P. Hammonds at this laboratory, who performed mechanical property tests.⁵ One of the specimens was used for this analysis. The composition of the metallic sample is given in Table I.

Pieces of the specimen were extracted anodically

Table I. Composition of Hastelloy N

Element	Content (wt pct)
Mo	16.50
Cr	6.96
Fe	3.67
Si	0.70
Mn	0.56
V	0.26
W	0.26
Al + Ti	0.13
Co	0.11
C	0.081
Cu	0.01
B	0.008
S	0.008
P	0.001
O	0.007
Ni	Balance

(1.5 V) to separate the precipitate from the matrix. The precipitate was then X-rayed on a diffractometer especially designed to detect small amounts of second phases. The precipitate was also carefully analyzed chemically to determine its composition. More complete details of the extraction procedure, the X-Ray procedure, and the chemical analysis are available in Ref. 6.

RESULTS

Three independent examinations indicate that the carbon content of eta carbide in Hastelloy N after aging 10,000 h at 815°C is much less than that corresponding to M_6C . Two of the examinations, weight of extracted precipitate and X-ray lattice parameter, are qualitative. The examination by chemical analysis is quantitative. (The elaborate care used to establish confidence in the chemical analysis is covered in Ref. 6.) We record the three results separately.

X-Ray Lattice Parameter

The lattice parameter was determined on precipitates from two different extractions of the material. The values were both 1.089 ± 0.001 nm. In the pure Mo-Ni-C ternary Fraker and Stadelmaier⁴ indicate the phase $M_{12}C$ has the lattice parameter 1.0894 nm (no error stated), while M_6C varies between 1.1161 and 1.1255 nm, depending on the estimated Ni-Mo content. The eta carbide can be easily distinguished from the tau carbide ($M_{23}C_6$) in that the (420) X-ray peak has zero intensity for the eta carbide while that intensity in the pattern of the tau carbide is appreciable.

Quantity of Precipitate

Extraction results for five experiments are given in Table II. There is found 5.55 ± 0.24 wt pct precipitate from four of the five extractions. It appears that the third extraction is in error. Further, the scatter in the data is larger than has usually been experienced, suggesting that the samples are inhomogeneous. One can estimate the amount of precipitate expected for M_6C in a Ni-base alloy containing 0.081 wt pct carbon (from Table I): From Fraker and Stadelmaier⁴ the nickel-rich end of the M_6C phase is 48 at. pct Ni, 40 at. pct Mo, and 12 at. pct C. If all the carbon is assumed to react at 815°C, one calculates 3.82 wt pct precipitate could be extracted. Considerably more

Table II. Extraction Results from Hastelloy N aged 10,000 h at 815°C

Extraction	Precipitate extracted (mg)	wt pct	Remarks
1	40.87	5.65	X-Rayed
2	149.61	5.53	Analyzed for metal, N and O
3	31.61	4.80 ^a	X-Rayed
4	27.96	5.78	Analyzed for Carbon
5	16.22	5.23	Analyzed for Carbon
Average		5.55 ± 0.24	

^aNot counted in average or in error. There was probably an error in weighing.

precipitate than this was obtained, tending to indicate a lower carbon content in the precipitate phase than indicated by the formula M_6C .

Chemical Analyses

The previous two paragraphs tended to indicate the eta carbide in Hastelloy N can be less rich in carbon than indicated by the formula M_6C . A reasonable objection to this possibility might be that oxygen is contained in the precipitate giving both a low lattice parameter and additional wt pct precipitate. Alternatively, one might suppose that at 815°C more nickel could dissolve in the eta phase giving the lower lattice parameter, and, further, a second phase was present in the extracted precipitate giving the additional weight percentage found. The answer to these objections is, of course, an accurate chemical analysis of a single-phase material.

The precipitate was demonstrated to be a well-crystallized, single phase by X-ray diffraction of two different extracted samples. Figure 1 is a reproduction of a portion of a pattern from the diffractometer. Note the extremely low background, relative to the eta phase peak intensities. (The TaC is added as an internal, calibrating standard for lattice parameter measurements. In this case the TaC (200) peak overlaps the (422) X-ray peak of eta phase.) Figure 1 shows that any phase with a peak giving a diffraction intensity of 50 counts (5 pct) would be easily seen. Twenty counts above background probably would be seen. Moreover, this area of the spectrum, near the eta (333) peak, is the least sensitive region of the spectrum because of the high intensity of the eta (333) peak. Thus, it is clear that the specimen on which the chemical analysis was done is single phase.

Analytical data on chemical compositions are given in Table III. The raw data are given in the second column. The third column is included so that easy comparisons can be made by the reader between atom ratios. The fourth column normalizes the moles of

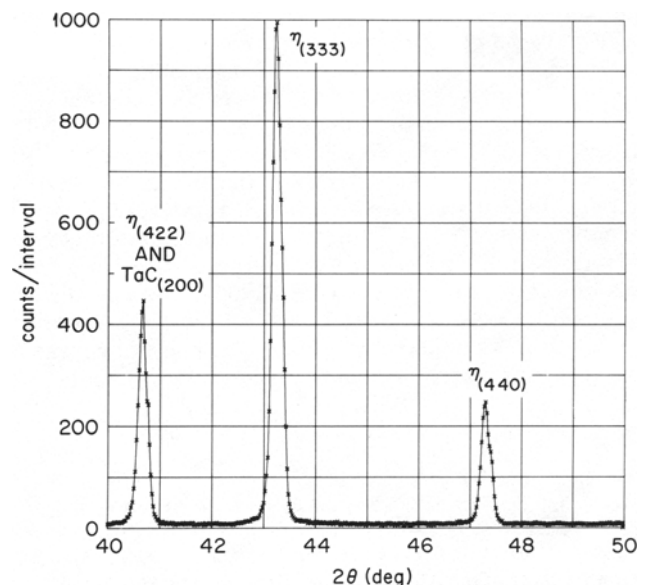


Fig. 1—Diffraction plot of region (40 to 50 deg 2θ) where most second phases would occur in Hastelloy N.

Table III. Composition of Precipitate Extracted From Hastelloy N aged 10,000 h at 815°C

Element	wt pct	Moles/100 g	Normalized ^a	Normalized Uncertainty
Cr ^b	1.2	0.0231	1.48	0.3
Ni ^b	28	0.4769	30.65	1.5
Mo ^b	59	0.6150	39.53	2.0
Si ^b	10.3	0.3667	23.57	1.2
C ^c	1.35	0.1133	7.28	0.07
O ^d	0.26	0.0075	0.48	0.08
N	0.11	0.0079	0.51	0.05
Al ^e	0.05			
Co ^e	0.2	0.0034	0.22	0.2
Fe ^e	0.08			
Hg ^e	0.02			
Mg ^e	0.02			
Mn ^e	0.01			
Nb ^e	0.2	0.0021	0.13	0.1
Sn ^e	0.3	0.0025	0.16	0.2
Ti ^e	0.005			
V ^e	0.2	0.0039	0.25	0.2
W ^e	<0.1			
Zr ^e	0.02			

^aNormalization was done, as explained in the text, by multiplying each mole/100 g by 64.27.

^bPhotoelectric analysis for which standardization curves are precise to ± 5 pct (2 σ). Uncertainty of individual values are estimated to be the same except for chromium, for which 10 pct must be assigned at this low level.

^cThe uncertainty (2 σ) is ± 1 pct, based on the 610.3 Leco instrument reading which has a standard deviation of 3.8. The weight of precipitate burned was 39.10 mg, and the uncertainty in weight should be ~ 0.05 mg. An unknown amount of atmospheric contaminants were absorbed on the surface, but the resulting uncertainty should not be as large as 1 pct (0.4 mg in weight).

^dThe precision stated for oxygen by the Analytical Chemistry group is ± 5 pct. The moles of oxygen per 100 g is calculated via the assumption that the oxygen in the precipitate was that in the steel. Additional oxygen was assumed to be absorbed on the precipitate surface.

^eSemiquantitative values. The errors could be as large as a factor of two in the quoted value.

metal so that the summation of *metal* atoms is 96. The reason for this is that there are 96 *metal* atoms in the unit cell of the eta diamond cubic structure plus additional sites for carbon. These additional sites might be occupied by C, N, O, or could be vacant. The final column is the uncertainty in the normalized composition. The methods by which these were obtained are given in detail in Ref. 6.

The results of Table III sustain quantitatively the qualitative indications of 1) extracted wt pct precipitate and 2) X-ray lattice parameter. The composition of the eta phase is not M₆C, as it has been referred to extensively in the literature but is considerably less rich in carbon than indicated by the formula.

DISCUSSION

There are two aspects of this work which deserve discussion: the implications of the measured composition and the consequences to the mechanical properties. Hammond⁵ found that the Hastelloy N used in this study fractured intergranularly. He ascribed the reason to massive and continuous precipitates arrayed at the grain boundaries. This finding points up the importance of two aspects of the composition study: 1) the high metal-to-carbon ratio and 2) the high silicon content of the precipitate.

Table I reveals 0.081 wt pct C was contained in the alloy. Table II reveals 5.55 wt pct precipitate was extracted. Table III reveals the precipitate contained 1.35 wt pct C. A simple calculation reveals 0.075 wt pct C was recovered of the 0.081 wt pct C in the alloy. Additional carbon would, obviously, have produced more precipitate or less carbon would have produced less. Thus, if one wishes to avoid the massive grain boundary precipitates seen by Hammond, the quantity of carbon available to react must be reduced. This can be done either by reducing the quantity of carbon or by tying it up with an active element, such as titanium.

The silicon content of the precipitate is higher than has been reported in any such study. The lattice parameter indicates the silicon did not deposit on the carbon sites. That is, the lattice parameter with low carbon is lower than with high carbon.⁴ If the silicon had filled a carbon site one would not unreasonably assume the lattice parameter would increase since silicon is a bigger atom than carbon; such an increase was not observed. It is more reasonable to assume, as did Mukherju and Dyson,⁷ that silicon is on the metal lattice. The amount of silicon is much higher than they indicated, however.

It is interesting to compare the silicon content in this alloy with that in low alloy steels, for which Godden and Beech⁸ show that 12 at. pct silicon is in the residue after 1000 h heating at 700°C when 1 wt pct silicon is in the original steel. In the high alloy specimens discussed here, a larger fraction of the precipitate, ~ 25 at. pct, is made up of silicon. The direction is the correct one. That is, the higher concentration of Mo in our alloy (16 wt pct vs 3.5 wt pct in Godden and Beech's steel) would be expected to drive the reaction with silicon in the direction observed.

The observed, qualitative effect of eta carbides on mechanical properties of nickel-base alloys was noted.^{2,3} Also noted was the difficulty in ascribing quantitative numbers to the effects.¹ The present work should be of assistance, indicating the wt pct of eta carbide which can be formed with a given carbon content in the alloy. Obviously, this is only a start, even though a necessary one. Techniques are becoming available to determine, quantitatively, the relationship between microstructure and properties of an alloy. In cases where precipitates are important, the determination of the nature of the precipitate and its relationship to the matrix is also important.

CONCLUSIONS

- 1) The composition of the eta carbide phase in Hastelloy N is near M₁₂C rather than M₆C, as has been reported in the literature.
- 2) The silicon content of the eta phase can be higher, relatively, than in low alloy steels.
- 3) The relationship of mechanical properties of microstructure can be assisted by these data, but additional work is needed.

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