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J. C. Franklin,* and W. R. Laing*

The composition of the eta carbide in Hastelloy N containing 0.7 wt % Si 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 about 25 at. %, 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.

INTRODUCTION

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, Fine[1] 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 precipitate studied here is an important contributor to the mechanical property behavior of nickel-base alloys. For example, Clarke and Titus[2] 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 weaken the solid solution matrix and cause a severe loss of ductility."

In this laboratory, Gehlback and McCoy[3] investigated another nickel-base alloy (Hastelloy N) containing the eta phase. They wrote, "The microstructure is characterized by stringers of massive primary precipitates

*Analytical Chemistry Division.

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 Stadelmaier[4] investigated the Mo-Ni-C ternary system at 1000°C and found two eta carbides, both with narrow carbon content ranges. They indicated that the carbides were $M_{12}C$ and M_6C; a two-phase region was reported to exist between them. However, none of the literature on nickel-base alloys, as compared with relatively pure ternary systems, indicated that the eta-type carbide was other than M_6C. Even in the simple ternary, not until one gets to about 20 at. % Mo do the eta carbides become stable at 1000°C in the diagram reported by Fraker and Stadelmaier. Thus, there was no particular reason to suspect the stated formula, 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) that had been aged for 10,000 hr 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 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 even more extensive efforts 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 about 10,000 hr by David Gosler at Hittman Corporation, Maryland. At the conclusion of that program the sample was transferred to J. P. Hammond at this laboratory, who performed mechanical property tests. One of the specimens was used for this analysis. The vendor's stated composition of the metallic specimen is given in Table 1. Additional carbon and oxygen

Table 1. Composition of Hastelloy N (Vendor's Analysis)

Element	Content (wt %)	Element	Content (wt %)
Mo	16.50	Co	0.11
Cr	6.96	C	0.06
Fe	3.67	Cu	0.01
Si	0.70	B	0.008
Mn	0.56	S	0.008
V	0.26	P	0.001
W	0.26	Ni	balance
Al+Ti	0.13		

determinations were performed on the metal, and carbon, oxygen, nitrogen, and metals were determined in the precipitate extracted electrolytically.

Extraction Procedure

The sample was anodically extracted at 1.5 V with a platinum cathode in a 10% HCl—90% methanol solution. Precipitation adhering to the sample was removed by ultrasonic vibration in ethanol, and the sample was then dried and weighed. The precipitate was centrifuged from the supernate. It was washed with ethanol, centrifuged again to separate it from the alcohol, dried in a vacuum desiccator, and weighed. The actual weights are precise to 0.03 mg. Possible errors are (1) loss of precipitate through dissolution or inadequate centrifuging and (2) inadequate cleaning of tube or precipitate. Results on carefully prepared alloys have been very consistent, indicating reproducibility within 0.05 mg. We have never demonstrated that very small precipitate particles are not being dissolved, but extraction of carbides appears to be a quantitative procedure, within experimental error. The samples extracted for metallic element determination were large and were in the extraction solution nearly 8 hr before separation of the precipitate from the supernate was completed.

X-ray Procedure

Extracted precipitate samples were completely dispersed in ethyl alcohol, and the alcohol was removed by dropping the dispersion slowly onto a piece of glass at room temperature. 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.) A small amount of TaC was dusted on the drying paste as an internal standard. Copper radiation was used; the beam leaving the sample was passed through a graphite monochromator 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.

From 3 to 4 mg of precipitate is sufficient for an x-ray sample, and from steel it is easy to detect 5% of $M_{23}C_6$ dispersed in M_6C.

The x rays were detected in a scintillation counter, the counts were averaged electronically over a period of 6 s, and the result was printed. Since 1° is scanned in 8 min, 80 points were counted and tabulated for each degree (in 2θ).

Analysis for Metals in Precipitate

A sample of 15.5 mg was dissolved by mixed HCl-HNO_3 in a plastic vessel to avoid dissolution of SiO_2 from glass. Drop by drop, HF was added until the solution cleared, and the solution was diluted to a volume of 10 ml. The elemental analysis of the solution was determined by emission spectrometry. We used a 6.4-m Paschen mount grating spectrometer having a reciprocal linear dispersion of approximately 0.126×10^{-6} at 320 nm. Excitation was by high-voltage spark into which a rotating graphite electrode introduced the sample. Nominal spark conditons were 2 1/2 breaks per half cycle at 20,000 V and 10 A rf, with an air gap in the secondary circuit. The analytical lines used for the determination of the metallic elements are shown in Table 2.

Table 2. Lines Used for Spectrographic Analysis

Element	Analytical Lines (nm)	Concentration Range (g/m^3)
Molybdenum	281.615	100–1100
Chromium	284.325	20–200
Silicon	288.160	25–150
Nickel	310.155	100–1000

Strontium (407.771 nm) was used as an internal standard for all elements. The concentrations of each individual element was determined from a plot of the response ratio of the analytical line to the internal standard line versus concentration. Background corrections were made automatically with a background correction circuit[5] at 440.1 nm.

Figure 1 compares the instrument response for the four elements reported in the extracted sample with a plot of the response to NBS standards and reference alloys. Although no standard is identical to the extract, the analysis of standard materials made under these identical conditions indicates an uncertainty (2σ) of 5% of the reported value for Mo, Cr, Ni, and Si.

Metallic elements other than the Mo, Cr, Ni, and Si were determined by optical emission spectrographic analysis with photographic detection. The analysis was made on a dual spectrograph using 3.4-m Ebert and Wadsworth mounts. Excitation was 250 V dc, 7.5 A for 3 min using a National Spectrographic Laboratories power supply. Aliquots (1 mg) of the sample were mixed with LiF-graphite buffer[6] for excitation. Concentrations were determined by visual comparison with a set of synthetic standards made by adding 0.01 and 0.1% of the metals to a matrix composed of 60% MoO_3, 30% NiO, and 10% SiO_2. The data for elements other than Mo, Cr, Ni, and Si are semiquantitative and should be accurate within a factor of 2.

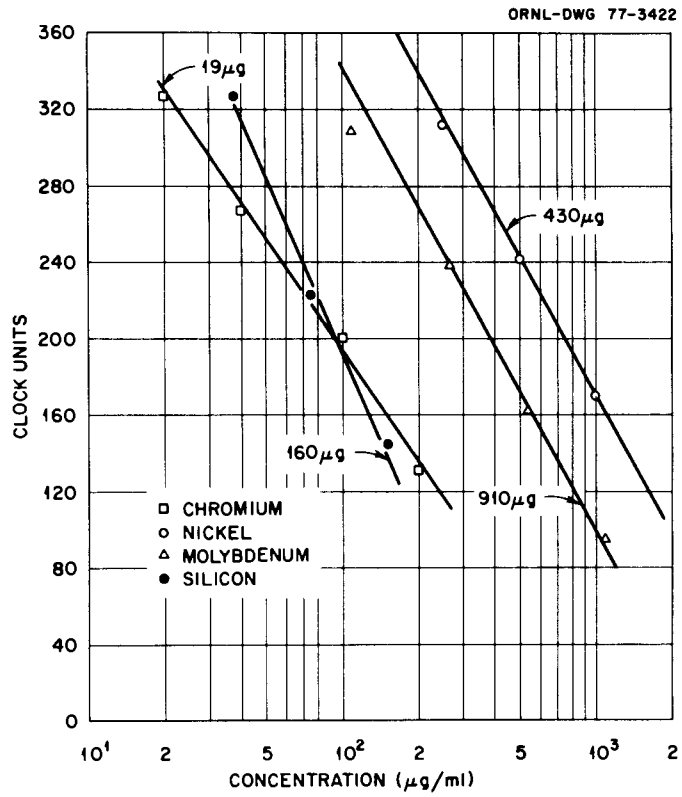

Fig. 1. Instrument Response as a Function of Concentration for Spectrographic Determination of Major Metallic Elements. Plotted points are for known standard samples. Arrows indicate readings of concentrations in the precipitate from the calibration lines.

Carbon Determination

A Leco apparatus was used to determine the carbon contents of both the precipitate and the alloy. The procedure finally developed for precise results involves use of NBS Standard Reference Material 19E (0.197 wt % C) to calibrate the apparatus over the range 150 to 900 μg C. Within this range the data could be fitted with a straight line with precision of a few micrograms. However, the line did not pass through zero instrument reading at zero carbon, even with a blank subtracted. Thus the instrument is nonlinear.

The procedure was to weigh an amount of sample into a prefired ceramic crucible. Two level scoops of cupric oxide wire, which had been fired 2 to 3 hr at 1000°C in air, were added to cover the sample and act as a promoter, along with 1 scoop of tin granules (approximately 0.75 g) to aid in coupling with the induction heater and melting the

mass. The carbon dioxide released on heating in oxygen was passed through manganese dioxide to remove sulfur, then passed through CuO to ensure complete oxidation of any CO, and finally collected on a molecular sieve. After combustion was complete, the molecular sieve was warmed and the CO_2 was eluted by helium through a gas chromatograph. The CO_2 peak was integrated electronically, and the integral was used to calibrate against the known amount of carbon or to determine, alternatively, the amount of carbon in the sample.

The instrument response to carbon level was not constant with time. The instrument was calibrated at the start of a day with five standard samples, the desired analyses were run, and the samples were interspersed with standards to prevent instrument drift. In general the instrument was stable during the period of one 8-hr day.

Different equations describe the instrument response to given amounts of carbon on different days. Thus, on the day the alloy was analyzed the equation was

$$\text{carbon } (\mu g) = 0.9175(\text{instrument reading minus blank}) - 20.93 ,$$

a typical blank was an instrument reading of 24.5. Over the range 160 to 750 μg C one standard deviation of an individual measurement was 8.6 μg C. The carbon in the precipitate was determined on a day for which the equation was

$$(\mu g) \text{ carbon} = 0.9545(\text{instrument reading minus blank}) - 27.39 .$$

It was valid over the range 260 to 800 μg C, with one standard deviation of 3.8 μg C.

Nitrogen and oxygen were determined in the precipitate, and oxygen was measured in the alloy. No special precautions were taken since these elements were considered as relatively minor impurities, a view that was subsequently substantiated.

RESULTS

Extraction data are given in Table 3. Of the five extractions, one appears to contain an error in weighing. The rest have more variation than is usual in extractions where the material is known to be homogeneous. Sample 5, for example, is below the average by an amount corresponding to 1 mg of precipitate. As mentioned in the experimental section, the precision of weighing is a factor of 30 better than this; inhomogeneity in the sample is the most likely explanation.

Table 3. Extractions Results from Hastelloy N Aged 10,000 hr at 815°C

Extraction	Precipitate Extracted (mg)	Proportion (wt %)	Analysis Done
1	40.87	5.65	X-ray diffraction
2	149.61	5.53	Analysis for metal, N, and O
3	31.61	4.80[a]	X-ray diffraction
4	27.96	5.78	Analysis for carbon
5	16.22	5.23	Analysis for carbon
Average		5.55 ± 0.24	

[a]Not counted in average or in error. There was probably an error in weighing.

Two of the samples extracted were examined by x-ray diffraction. Both examinations revealed only the presence of the eta phase. The measured lattice constant was 1.089 ± 0.001 nm. The eta carbide can easily be distinguished from the tau carbide ($M_{23}C_6$) because eta has a zero intensity for the (420) peak and tau does not. Figure 2 shows diffraction peaks in the region where most intense impurity peaks are likely to occur. Only TaC, used as an internal standard, occurs in addition to the eta phase. The eta phase is exceedingly homogeneous; one can detect the widening due to $K\alpha_1$-$K\alpha_2$ splitting in the (440) peak, Fig. 2.

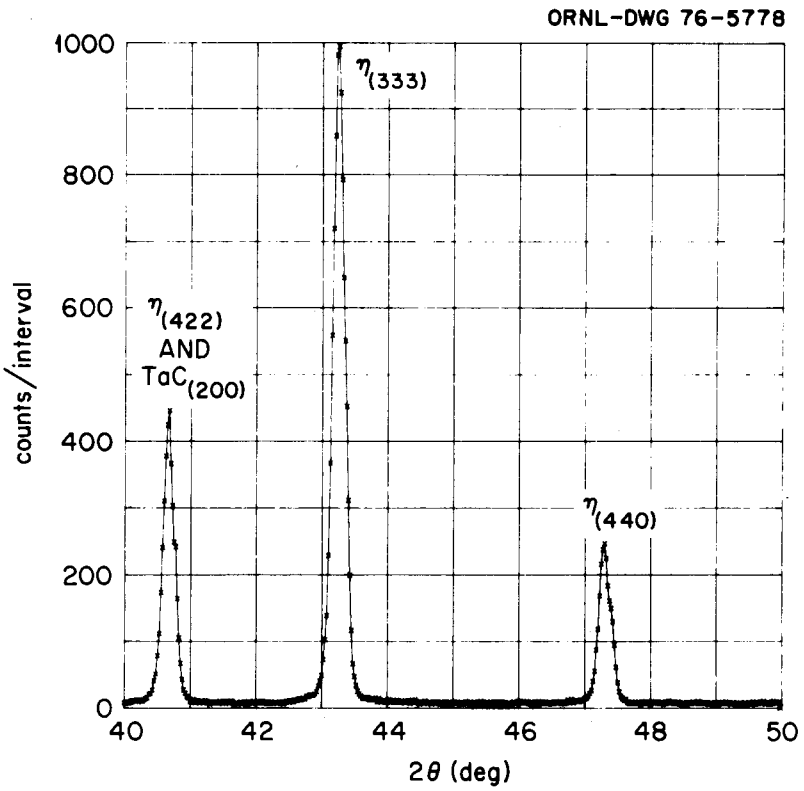

Fig. 2. Diffraction Plot of Region (40–50° 2θ) Where Most Second Phases Would Occur in Hastelloy N.

The contents of carbon and oxygen determined in the alloy are given in Table 4. Note that the amount of carbon found in the sample is substantially greater than that given in Table 1. We believe sufficient care was used in the present analysis and that the vendor's result was in error. The specimen for this determination was a 0.189-g residue from an extraction, taken in this way to ensure that any decarburization of the surface had been eliminated. The precision of our carbon determination is ±10% (2σ), because the amount of carbon was only 154 μg. Additional material was not available for a more definitive measurement. The possibility that some free carbon is present in the precipitate is discussed in an Appendix.

Concentrations of the elements determined in the precipitate are reported in Table 5. In subsequent calculations all metallic elements below 0.2 wt % are ignored. The uncertainty of the standardization values for the major metallic elements are precise (2σ) within 5%, and

Table 4. Carbon and Oxygen Content of Hastelloy N

Element		Content, wt %
Carbon		0.081[a]
Oxygen		0.0078
		0.0061
	Average	0.0069

[a]Based on 0.189-g sample yielding 153.8 μg carbon. Note that the error (one standard deviation) is 8 μg C, or 0.004 wt % C, which is about 5%.

the carbon standardization is precise (2σ) to <1%. The precision of the nitrogen and oxygen determinations is stated by the Analytical Chemistry group to be ±10%. Note that Table 5 shows that 0.26 wt % of the precipitate is oxygen. If the result for oxygen in the alloy itself in Table 4, 0.0069 wt %, is used for comparison one finds that only 0.12 wt % (rather than 0.26 wt %) of the precipitate could be oxygen if all the oxygen found by analysis in the alloy were in the precipitate. The assumption that *all* the oxygen in the alloy is in the precipitate of interest is incorrect by an unknown amount. The additional oxygen in the precipitate is assumed to be present via oxidation of the precipitate and adsorption of atmospheric contaminants. No correction is made for possible nitrogen adsorption on the precipitate.

The amount of silicon found in the precipitate seems rather high, translating to about 25 at. %. The amount was not only determined carefully as described above, it was substantiated semiquantitatively by the optical emission spectrographic analysis. Careful comparison of the plate from the precipitate (for trace elements) with a standard plate also indicated that the precipitate contained slightly more than 10 wt % S. Andrews and Hughes[7] briefly discuss the problem of precipitation of gelatinous silica during extraction in citrate-thiocyanate solutions. We could not perform experiments directly on Hastelloy N samples, but did do so on a highly alloyed steel sample containing

Table 5. Composition of Precipitate Extracted from Hastelloy N Aged 10,000 hr at 815°C

Element	(wt %)	Content (mol/kg)	Normalized[a]	Normalized Uncertainty
Cr[b]	1.2	0.231	1.48	0.3
Ni[b]	28	4.769	30.65	1.5
Mo[b]	59	6.150	39.53	2.0
Si[b]	10.3	3.667	23.57	1.2
C[c]	1.35	1.133	7.28	0.07
O[d]	0.26	0.075	0.48	0.08
N	0.11	0.079	0.51	0.05
Al[e]	0.05			
Co[e]	0.2	0.034	0.22	0.2
Fe[e]	0.08			
Hg[e]	0.02			
Mg[e]	0.02			
Mn[e]	0.01			
Nb[e]	0.2	0.021	0.13	0.1
Sn[e]	0.3	0.025	0.16	0.2
Ti[e]	0.005			
V[e]	0.2	0.039	0.25	0.2
W[e]	<0.1			
Zr[e]	0.02			

[a]Normalization was done, as explained in the text, by multiplying each content in mol/kg by 6.427.

[b]Photoelectric analysis for which standardization curves are precise to ±5% (2σ). Uncertainties of individual values are estimated to be the same except for Cr, for which 10% must be assigned at this low level.

[c]The uncertainty (2σ) is <1%, 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 about 0.05 mg. An unknown amount of atmospheric contaminants was adsorbed on the surface, but the resulting uncertainty should not be as large as 1% (0.4 mg in weight).

[d]The precision stated for oxygen by the Analytical Chemistry group is ±5%. As noted in the text, the moles of oxygen per 100 g is calculated via the assumption that the oxygen in the precipitate was that in the steel.

[e]Semiquantitative values. The errors could be as large as a factor of 2 in the quoted value.

0.98 wt % Si (versus 0.7 wt % Si stated to be in the nickel-base alloy). Extractions of samples (1) as annealed and (2) aged successive periods of time at 650, 750, and 850°C indicated that no significant amount of gelatinous SiO_2 precipitated during the time of extraction. Thus, while the amount of silicon is higher than reported elsewhere,[8] we have no other basis for doubting the result.

The silicon in the precipitate should be counted as a metallic element. While one might assume, because it is in the fourth column of the periodic chart along with carbon, that it replaces carbon, Godden and Beech[8] show that the lattice parameter of the precipitate decreases with increasing silicon. The conclusion that the silicon was on the metal lattice then followed from size considerations of carbon, metal, and silicon. The specific site(s) of the silicon is less certain. From compositional considerations Mukherjee and Dyson[9] argue that the silicon replaces the iron atoms at sites labeled *d* in their Fig. 4, of which there are 16 of a total of 96 in the unit cell.

The metal concentrations of the precipitate reported in Table 4 were not normalized to 100%, but were those determined from the calibrations. The total metal plus metalloid sums to 101.1 wt %, excluding those below 0.1 wt %. The statistical error in the total analysis can be calculated from

$$\text{Error} = [\sum_i (\sigma_i)^2]^{1/2} , \qquad (1)$$

where σ_i is the individual uncertainty. The total uncertainty in the analysis (2σ) is thus 3.4 wt %, most of which arises from the 5% uncertainty in the determination of molybdenum. The total material found by analysis is thus well within the statistical uncertainty.

So that one could compare the data easily with the accepted crystal structure of the eta phases[10] we have normalized in Table 5 the amount of the elements found as follows. The total number of moles of metallic elements per kilogram alloy whose determined content was 0.1 wt % or greater was added, yielding 14.936. We required that the sum be 96, which

is the number of metallic atoms in a unit cell of $M_{12}C$ or M_6C. The factor 6.427 (96/14.936) must then be used to normalize the contents.

The metal-to-metalloid ratio is 96 ± 2.8 to 8.27 ± 0.12, or 11.6.

DISCUSSION

There is virtually no doubt that the metal-to-carbon ratio of the eta phase in Hastelloy N after long-term aging is not 6 but a value approaching 12. Not only is there the evidence of the direct analysis, but the weight of precipitate extracted also clearly signals a metal-to-carbon ratio considerably greater than 6. The metal-to-carbon ratio one calculates from the weight of precipitate extracted depends on what is assumed to be the elemental composition.

It is interesting to compare the silicon content in this alloy with that in low-alloy steels. Godden and Beech[8] show that 12 at. % Si is in the residue after 1000 hr heating at 700°C when 1 wt % Si is in the original steel. In the high-alloy specimens discussed here, a larger fraction of the precipitate, about 25 at. %, is silicon. The direction is the correct one. That is, the higher concentration of molybdenum in our alloy (16 wt % versus 3.5 wt % in Godden and Beech's steel) would be expected to drive the reaction with silicon in the direction observed.

The possibility of an $M_{12}C$ is not new. Stadelmaier[10] has discussed the eta carbides and their structures for a variety of systems. However, the alloy literature includes no definitive examples of such compositions. Even in the pure ternary systems the phase relationships at temperatures of 800°C and below are quite unknown.

In Table 5, compositions are normalized so that the number of metal atoms adds up to 96, the number of atoms thought to exist on the metal lattice of a unit cell of eta phase. In Table 6 we tabulate the positions and numbers of atoms on these positions for the eta phase. With the assumption of $M_{12}(C,N,O)$, the metalloid position is quite likely on *a*. In Table 5 the normalized number of nickel atoms is 30.7 ± 1.5, which might well be assumed to take up position *e*, since there are 32 places available. Molybdenum is usually assumed to be on the *f* position, but

Table 6. Positions and Compositions for a Number of Ni-Mo-C Eta Phases[a]

Position	Atoms Per Unit Cell	Assignment for		
		Ni_3Mo_3C	Ni_6Mo_6C	Ni_2Mo_2C
f	48	Mo	Mo	Mo
e	32	Ni	Ni	Ni
d	16	Ni	Ni	Ni
c	16	C		C
a	8		C	C

[a]Adapted from Stadelmaier, ref. 10.

Table 5 reveals that only 39.5 ± 2.0 atoms are available to fill the 48 positions listed in Table 6. Silicon could fill not only the 16 *d* positions but also fills some of the *f* positions "usually" occupied by molybdenum.

Godden and Beech[8] indicate that as the silicon contents of their alloys change from 0.06 to 1.0 wt %, the lattice constant of the eta phase changes from 1.10365 to 1.10140 nm. The lattice constant of Mo_6Ni_6C was found to be 1.0894 nm by Fraker and Stadelmaier,[4] while $Mo_{42}Ni_{45}C_{13}$($\sim Mo_3Ni_3C$) is 1.1143 nm. The lattice parameter reported here for $M_{12}C$, 1.089 ± 0.001 nm, is very near that reported for $M_{12}C$ by Fraker and Stadelmaier, whose sample was without silicon.

Fraker and Stadelmaier[4] also show that increasing the Mo/Ni ratio tends to raise the lattice constant of the eta phase(s). Note that our sample has a high Mo/Ni ratio, tending to raise the lattice constant, and a low carbon content and high silicon content, both of which tend to lower the lattice constant. Thus, our data do not seem to be inconsistent. However, one cannot deduce the location of the silicon atoms — and the presumption that nickel atoms are on the *e* position does not seem very firm.

It is interesting to speculate on the reason for the high molybdenum-to-nickel ratio in the precipitate. Note that the nickel activity in the matrix is high, yet the molybdenum-to-nickel ratio is about 1.3,

considerably higher than that shown in the phase diagram of the ternary by Fraker and Stadelmaier.[4] Bradley[11] finds that chromium increases the activity of molybdenum in these nickel-base alloys. But the effect of silicon cannot be negligible. Elucidation of these effects must wait for further work.

In the Introduction section, 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 values to the effects.[1] The present work should be of assistance, indicating the content of eta carbide that 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. A start has been made in this direction, but only a start.

CONCLUSIONS

1. The composition of the eta carbide phase in Hastelloy N is near $M_{12}C$, rather than M_6C 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 to microstructure can be assisted by these data, but additional work is needed.

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11. D. J. Bradley, Oak Ridge National Laboratory, unpublished data.

APPENDIX

Related work[1] found in nickel base alloys that elemental carbon precipitates from solid solution on quenching from high temperatures. The precipitation stops at about 500°C because the rate of migration of carbon becomes too small for agglomeration. Any carbon precipitating from solution during cooling would measured in the Leco apparatus and assumed to be present as carbide. The purpose of this Appendix is to demonstrate, with reasonable approximations, that the solubility of carbon in Hastelloy N at 815°C is negligible within a reasonable experimental error. We approach the problem as follows:

1. The solubility of carbon in pure nickel is described, and the activity coefficient obtained.
2. The influence of the alloying elements in nickel on the activity coefficient of carbon in nickel is ascertained.
3. The influence of the alloying elements in nickel on the activity of carbon in solution is ascertained.
4. The solubility of carbon at 815°C is calculated and shown to be small.

The solubility of carbon in nickel is subject to some uncertainty, of course, whose resolution is not the purpose of this paper. Consider the reaction

$$\mathrm{C(graphite)} \rightleftharpoons \mathrm{C(sol'n\ in\ Ni)}\ . \tag{A1}$$

If graphite is chosen to be the standard state for both solid carbon and carbon in solution, the free energy change, ΔG, for Reaction (A1) will be given by

$$\Delta G = RT\ \ln f_{\mathrm{C(sol'n)}} - RT\ \ln f_{\mathrm{C(graphite)}} = RT\ \ln \frac{f_{\mathrm{C(sol'n)}}}{f_{\mathrm{C(graphite)}}} \tag{A2}$$

$$= RT\ \ln a_{\mathrm{C(sol'n)}}\ ,$$

[1]D. J. Bradley, Oak Ridge National Laboratory, unpublished data.

where the f's are the thermodynamic fugacities and a_C is the activity of carbon. Equation (A2) is on a firm thermodynamic base. If one wishes to extend data into the low-activity range of carbon in nickel, as we do, some extrapolation function is needed.

Dunn et al.[2] reviewed data available in 1968 and concluded that carbon in solution in nickel obeyed Henry's law from the equilibrium with graphite down to zero concentration; that is

$$a_C = \gamma_C N_C \quad (0 \leqslant a_C \leqslant 1) \ , \tag{A3}$$

where N_C is the mole fraction of carbon in solution and γ_C is the activity coefficient. Wada et al.[3] disagreed with this conclusion. However, in looking at the actual data of Wada et al. for pure nickel, there does not appear to be a firm denial of the conclusion of Dunn et al. In pure iron, carbon activities depart significantly from Henry's law, and in iron-nickel alloys these carbon activity departures are also seen.[3] It is not clear that the departures from ideality extend all the way to pure nickel. Thus, for the present, data for the solubility of carbon in nickel from Dunn et al. are taken for pure nickel, and the conclusion that carbon in nickel obeys Henry's law from its equilibrium with graphite to infinite dilution is adopted.

To describe the data of Dunn et al.[2] over a range of temperatures the following formalism is used:

$$\Delta\bar{G} = RT \ \ln a_C = \Delta\bar{H}_C - T \ \Delta\bar{S}_C \ , \tag{A4}$$

where bars over the thermodynamic symbols have been used to indicate the reaction (A1) for a mole of carbon, the "partial molal" quantity. The entropy is separated into an "ideal" entropy, $-R \ \ln N_C$, and an "excess" entropy, ΔS_{exs}. Then

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[2]W. W. Dunn, R. B. McLellan, and W. A. Oates, "The Solubility of Carbon in Cobalt and Nickel," *Trans. Met. Soc. AIME* 242: 2129–32 (October 1968).

[3]T. Wada et al., "Thermodynamics of Fcc Fe-Ni-C and Ni-C Alloys," *Metall. Trans.* 2: 2199–2208 (August 1971).

$$RT \ln a_C - RT \ln N_C = \Delta\bar{H}_C - T\,\Delta\bar{S}_{exs} \tag{A5}$$

and

$$RT \ln \frac{a_C}{N_C} = RT \ln \gamma_C = \Delta\bar{H}_C - T\Delta\bar{S}_{exs} \ . \tag{A6}$$

Equation (A6) can be rearranged to

$$R \ln \gamma_C = \Delta\bar{H}_C/T - \Delta\bar{S}_{exs} \ , \tag{A7}$$

and this is true for all the results at constant carbon content of an alloy. Further, if the carbon in the alloy obeys Henry's law throughout the solubility range, then Eq. (A7) is valid throughout the solubility range because the left-hand side of Eq. (A7) is independent of carbon content. That is, with this assumption, the solubility data of Dunn et al. can be used to obtain $\Delta\bar{H}_C$ (the partial molal enthalpy) and $\Delta\bar{S}_{exs}$ (the excess partial molal entropy) of carbon in nickel. Plotting $R \ln 1/N_C$ versus $1/T$ of data from Dunn et al. yields a curve from which both $\Delta\bar{H}_C$ and $\Delta\bar{S}_{exs}$ can be obtained. If no experimental error is present, curvature in the plotted data indicates a significant ΔC_p for Reaction (A1). A plot of the data of Dunn et al. did indicate some curvature, but we did not attempt to ascribe it to a ΔC_p. Rather, a straight line was put through the data, yielding (for R = 8.314 J/K mol)

$$R \ln \gamma_C = 51{,}000/T - 4.39 \ . \tag{A8}$$

At 815°C (1088 K), where our samples were aged, γ_C = 167, so the computed solubility of pure graphite (a_C = 1) in nickel is thus 6.0×10^{-3} atom fraction or 0.124 wt %.

In related work,[11] we have shown that neither chromium nor molybdenum affects the activity coefficient of carbon in nickel as much as 20% up to the composition of Hastelloy N. Thus, we assume the activity coefficient of carbon in Hastelloy N is described by Eq. (A8).

The activity of carbon in Hastelloy N will be significantly reduced by the presence of alloying elements. No data exist to indicate how much, so estimates are necessary. We estimate the standard free energy of

formation, ΔG°_{f}, of the carbide observed is more negative than 1/6 the heat of formation, ΔH°_{f}, of $Cr_{23}C_6$, by −12.6 kJ, or −68.6 − 12.6 = −81.2 kJ/mol C. The reason for this estimate is that on adding carbon to binary alloys containing both molybdenum and chromium, the eta double carbide is seen before the tau ($M_{23}C_6$) carbide. The eta carbide is thus more stable. The 12.6 kJ attempts to take the additional stability into account. The standard entropy of formation is estimated to be zero.

The activities of both nickel and molybdenum need to be estimated to complete the estimate of carbon activity. The activity of nickel is assumed to follow Raoult's law and equal the atomic fraction nickel at all temperatures. We assume that the activity of molybdenum in the alloy at 815°C is 0.5. Then, for the reaction

$$6Ni + 6Mo + C = Ni_6Mo_6C \ ,$$

$$\Delta G^{\circ} = -81{,}200 = RT \ \ell n \ a^6_{Ni} a^6_{Mo} a_C \ .$$

Putting in the above assumptions and solving for the activity of C, one finds it would be 0.043. The activity coefficient is 167, and thus the mole fraction of carbon in solution in equilibrium with Ni_6Mo_6C is calculated to be 2.56×10^{-4}, or 5.3×10^{-3} wt % C.

In Table 4 we show that the amount of carbon in the alloy is 0.081 ± 0.004 wt %. In Table 3 we show that there is 5.55 ± 0.24 wt % precipitate, which contains (from Table 5) 1.35 wt % C. Multiplication of 5.55 by 0.0135 yields 0.075. Adding the presumed 0.005 wt % C in solution yields 0.080 wt % C total, versus 0.081 wt % C found by direct analyses. While agreement this close is fortuitous, the calculation certainty indicates that no gross errors have been made in the carbon content of the precipitate.

We believe our assumptions to be conservative. Thus, we estimate that less than 10% of the carbon present in the alloy precipitates as free carbon and is counted as found in the carbide. The effect of any significant error in this approach is to over-ascribe the amount of carbon in the carbide. Therefore, the data presented in this paper really

represent an upper limit in the amount of carbon present in the eta phase in Hastelloy N. The agreement between the amount of carbon found in the alloy and the amount calculated from (1) analysis of the precipitate plus (2) calculated from the thermodynamic treatment can be used to argue that the heat of formation of $M_{12}C$ in Hastelloy N is about −81 kJ/mol.

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