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STUDIES OF THE CARBON DISTRIBUTION IN HASTELLOY N

H. E. McCoy

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METALS AND CERAMICS DIVISION

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

A small heat of Hastelloy N was prepared in which a portion of the carbon atoms were tagged as carbon-14. The response of this alloy to heat treatment was studied in an effort to determine whether the changes in mechanical properties could be correlated with the observed changes in the carbon distribution. Although marked segregation resulted, the changes in mechanical properties did not appear to be related.

A second objective of this study was to determine whether the relatively large precipitates in this alloy were carbides. These precipitates, in both their stringer (low-temperature) and lamellar (high-temperature) forms, were found to be as low or lower in carbon than the matrix. It is hypothesized that the other alloying elements reduce the solubility of molybdenum in nickel so that the precipitates are basically nickel-molybdenum intermetallic compounds.

INTRODUCTION

Previous studies[1] of Hastelloy N have shown that the fracture ductility of this alloy at elevated temperatures is very sensitive to the thermal history of the alloy. Although numerous metallographic changes have been observed, it has not been possible to correlate these changes with the changes in the properties. Most of the metallographic changes involve the fairly coarse precipitate particles (0.1 to 1 mil in diameter) which are normally present as stringers. As the alloy is taken to temperatures above 1260°C, these precipitates transform to a lamellar phase. Quite early in the development of this alloy, these

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[1]H. E. McCoy, Influence of Several Metallurgical Variables on the Tensile Properties of Hastelloy N, ORNL-3661 (August 1964).

precipitates were reasoned to be carbides.[2] However, more recent
studies indicate that these particles may not be carbides.

      In order to help clarify this problem, a small heat of Hastelloy
N was made in which part of the carbon atoms were carbon-14. Samples
of this alloy were given the various heat treatments, which were
observed to alter the mechanical properties and subsequent autoradio-
graphic studies were carried out. It was felt that this approach would
provide the answers to two important questions: (1) are the coarse
precipitates and the lamellar phase in Hastelloy N carbides, and (2) how
does the carbon distribution in the alloy change with heat treatment and
can the changes in mechanical properties be correlated with the carbon
distribution? The following report will present the details of this
study.

EXPERIMENTAL DETAILS

      A small heat of Hastelloy N was prepared from a charge of
commercial air-melted Hastelloy N and a small amount of nickel that had
been carburized by heating in a mixture of graphite and $BaCO_3$ (carbon
atoms present as carbon-14). The charge was nonconsumably arc melted
and cast into a 3/8-in.-diam mold. The ingot was sheathed in stainless
steel, swaged to 1/4 in. in diameter at 1177°C, and swaged to 1/8 in.
in diameter at ambient temperature. The chemical analysis of the
resulting heat is given in Table 1. The composition is within the
specified limits[3] for Hastelloy N.

      The resulting 1/8-in.-diam rod was cut into small pieces that
were given various heat treatments in argon. The specimens were then
prepared for metallographic examination. Eastman NTB Liquid Emulsion
was used for the autoradiographic studies and was applied directly on

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[2]T. K. Roche, The Influence of Composition Upon the 1500°F
Creep-Rupture Strength and Microstructure of Molybdenum-Iron-Nickel-
Base Alloys, ORNL-2524 (June 24, 1958).

[3]J. T. Venard, Tensile and Creep Properties of INOR-8 for the
Molten-Salt Reactor Experiment, ORNL-TM-1017 (February 1965).

Table 1. Analysis of Experimental Material

Element	Content (wt %)
Nickel	73.4
Chromium	6.34
Iron	3.11
Molybdenum	15.5
Silicon	0.71
Manganese	0.50
Carbon	0.058

the surface of the polished specimen. In order to obtain high resolution, very thin layers of emulsion were used. The emulsion was left undisturbed until the desired exposure was obtained, after which the emulsion was developed in situ. The carbon distribution was determined by microscopic examination of the specimen-emulsion composite.

One problem associated with the interpretation of autoradiographs was the fact that when viewed at about 250X, the emulsion was always exposed in "spots" rather than uniformly. The reported grain size for the emulsion is of the order of 1 μ and the type of exposure expected would be a uniform darkening even when the developed emulsion is viewed at 1000X. This apparent inconsistency is as yet unresolved, but the "uniform" exposure has never been observed in any material studied. It is felt that the small spots represent a uniform carbon distribution and that these spots arise because all the material in the emulsion is not capable of being exposed.

EXPERIMENTAL OBSERVATIONS

Figure 1a shows the microstructure of the material in the as-worked condition. Figure 1b shows an autoradiograph of the material in the as-worked condition. The carbon seems to be inhomogeneously
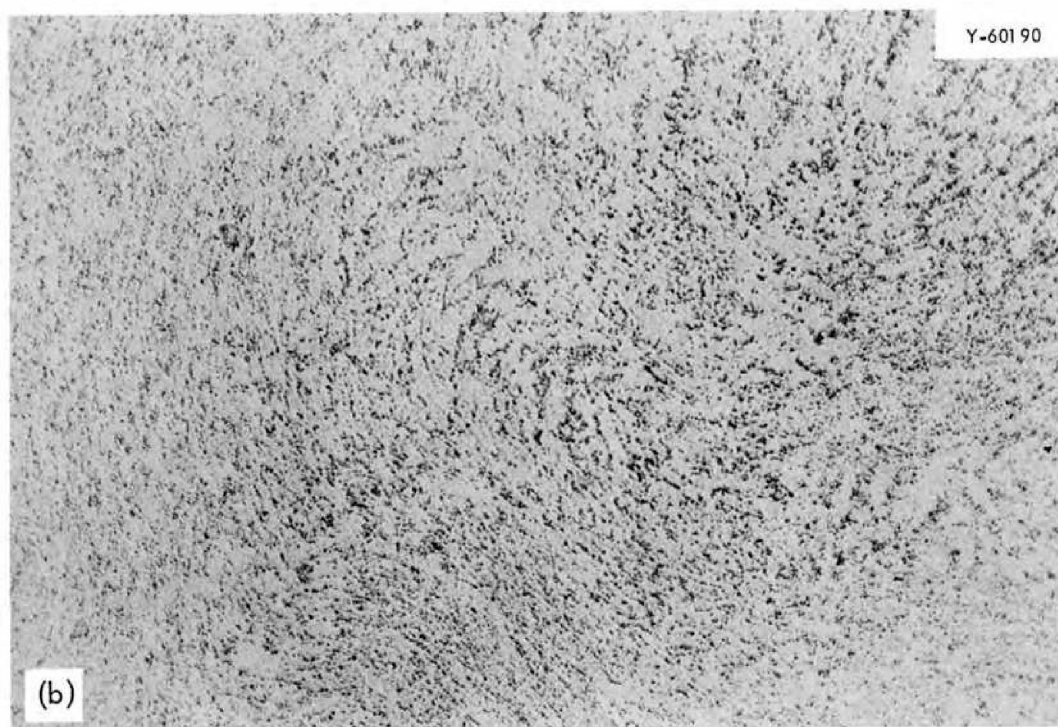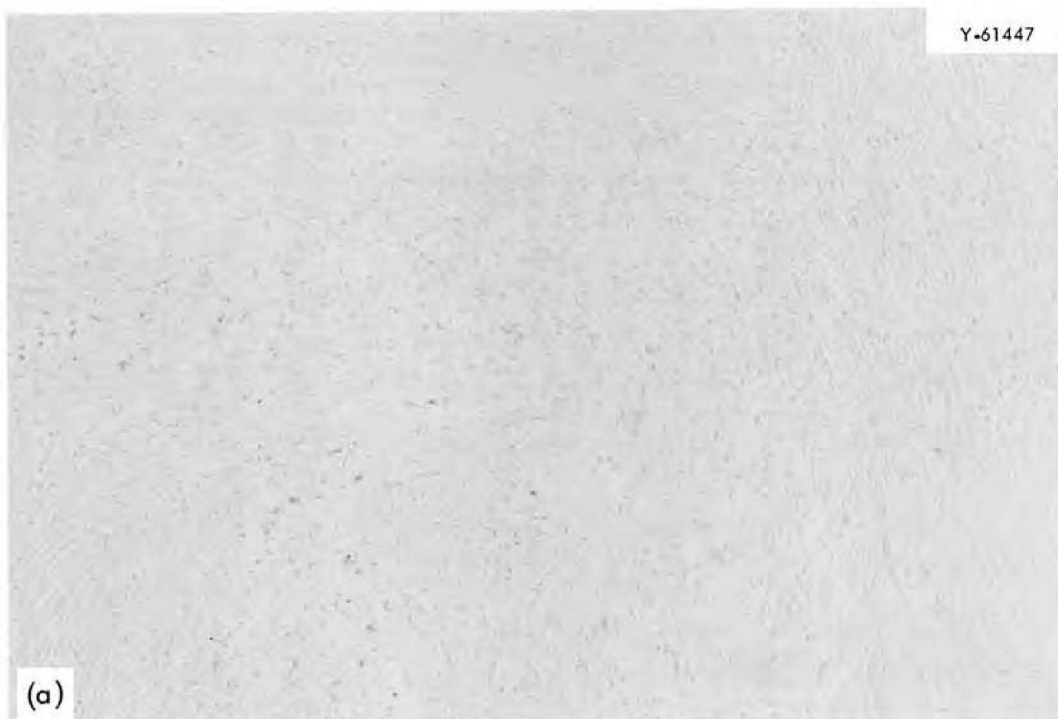
Fig. 1. Hastelloy N in the As-Worked Condition. (a) Photo-micrograph of specimen etched with aqua regia. (b) Autoradiograph of specimen in the as-polished condition, 16-hr exposure. 100X.

distributed on a microscale. Figure 2a shows the material after a 1-hr
anneal at 1177°C, followed by rapid cooling. Figure 2b is an autoradio-
graph of the same specimen. This anneal distributes the carbon almost
uniformly in the material, although there does seem to be enough
grain-boundary segregation to delineate the grain structure. Figure 3a
shows the alloy after a 1-hr anneal at 1232°C. This photomicrograph is
at high enough magnification to resolve the large precipitates that are
characteristic of this alloy. The autoradiograph of this specimen is
quite similar to that shown in Fig. 2b. However, Fig. 3b shows the
autoradiograph at a high magnification. The light spots are the
precipitate particles in the alloy. Note that the autoradiograph does
not show any darkening above these particles, indicating that they are
low in carbon.

Figure 4a shows the microstructure which results from a 1-hr
anneal at 1260°C. Many of the precipitates become associated with grain
boundaries so that an almost continuous network results. Figure 4b shows
an autoradiograph of this specimen which has a 48-hr exposure. The
importance of the exposure time will be shown later. There is a definite
segregation of carbon to the grain boundaries.

Figure 5a shows the microstructure of a specimen annealed 1 hr
at 1316°C. The precipitate particles have transformed almost entirely
to the lamellar phase. Figure 5b illustrates the microstructure in
greater detail. Figure 6a shows that one constituent of the lamellar
product is quite low in carbon and the the other constituent contains
about the same amount of carbon as the matrix. Figure 6b shows the
grain-boundary phase in a somewhat different morphology, but again, one
constituent is low in carbon and the other contains about the same amount
of carbon as the matrix.

As shown in Fig. 7a, a 1-hr anneal at 1371°C increases the con-
centration of the intergranular phase. Figure 7b is an autoradiograph
with a 72-hr exposure which indicates that the grain boundaries are
enriched in carbon. However, a shorter exposure and the use of a higher
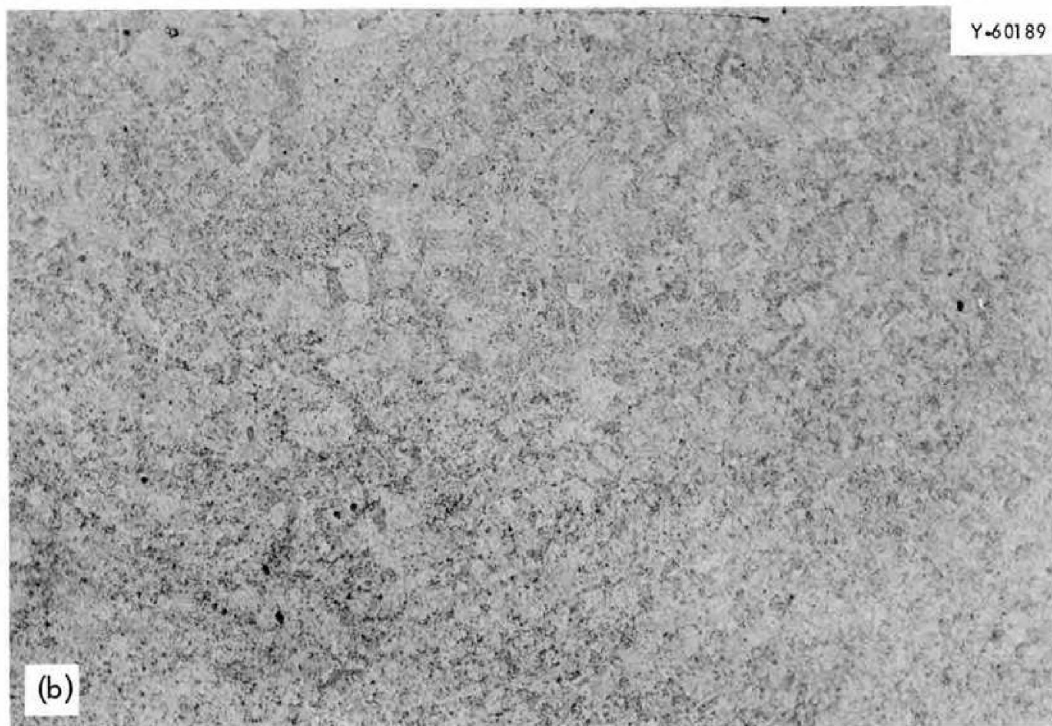magnification help delineate the actual location of the carbon.

Fig. 2. Hastelloy N After a 1-hr Anneal at 1177°C. (a) Photo-micrograph of specimen etched with aqua regia. (b) Autoradiograph of specimen in the as-polished condition, 16-hr exposure. 100x.
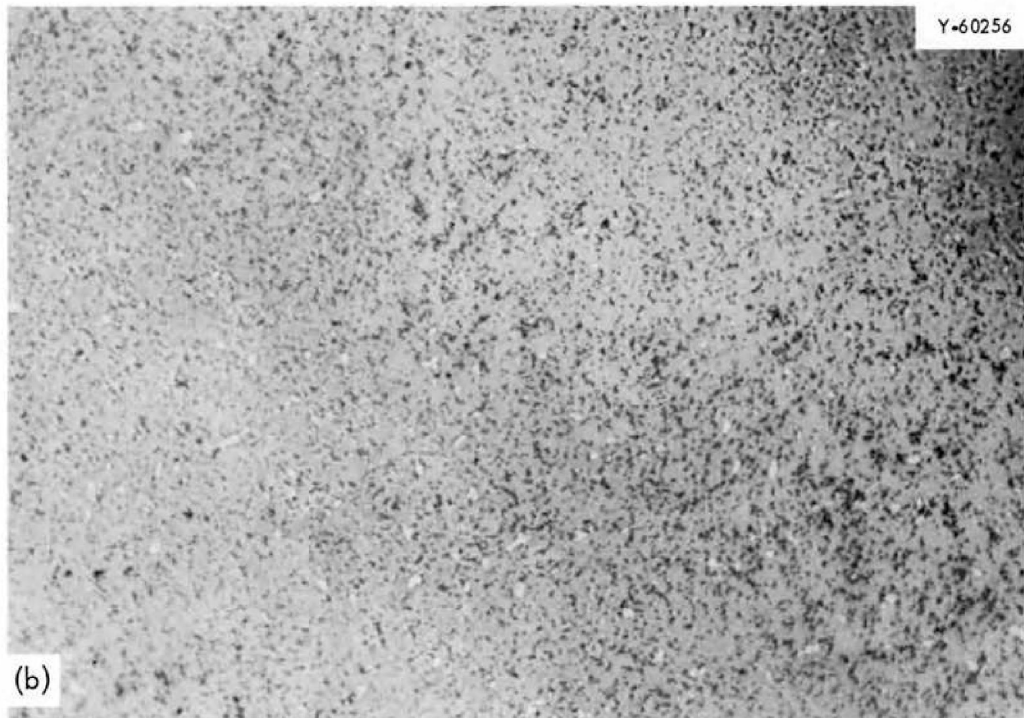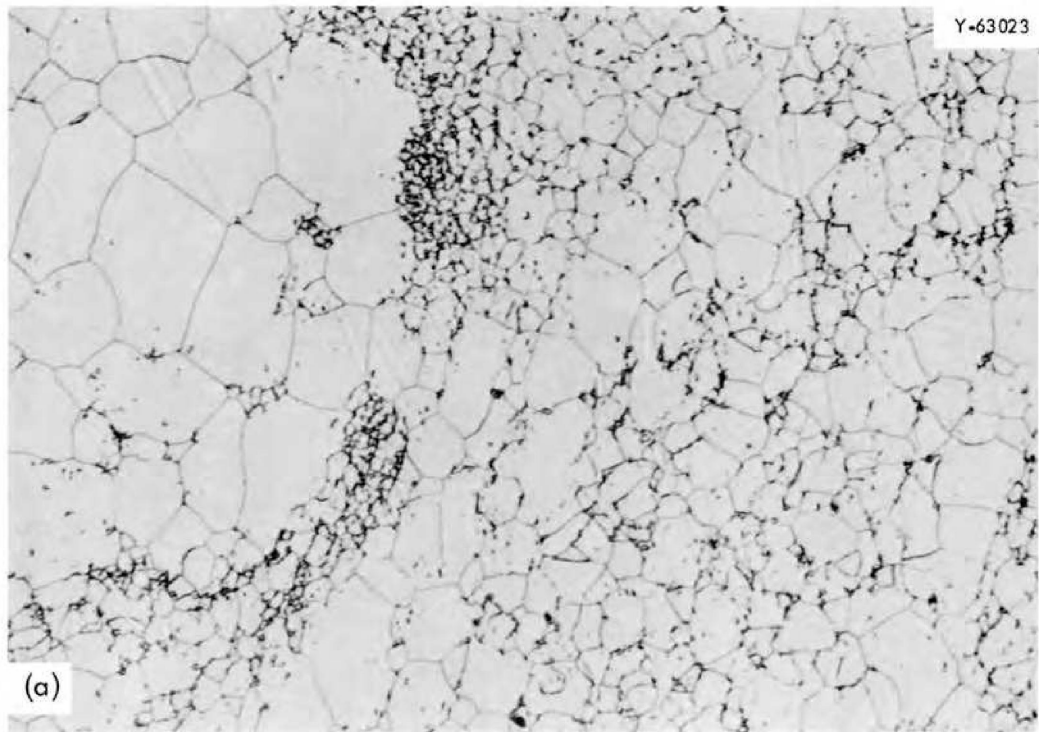
Fig. 3. Hastelloy N After a 1-hr Anneal at 1232°C. (a) Photo-micrograph of specimen etched with aqua regia. 250×. (b) Autoradiograph of specimen in the as-polished condition, 16-hr exposure. 750×.
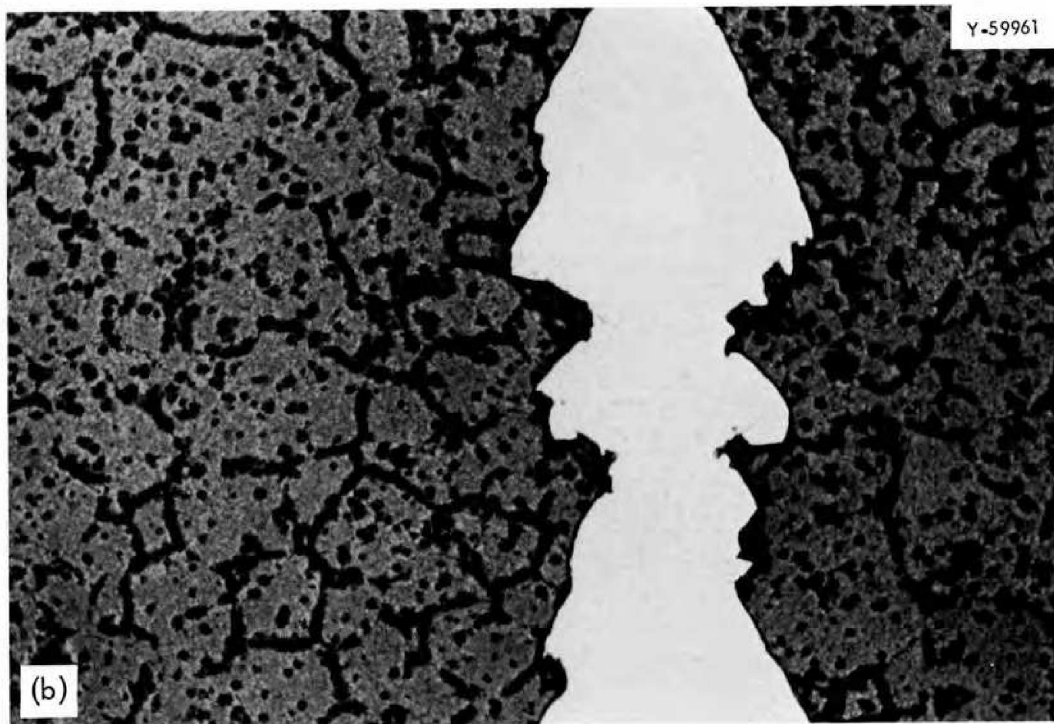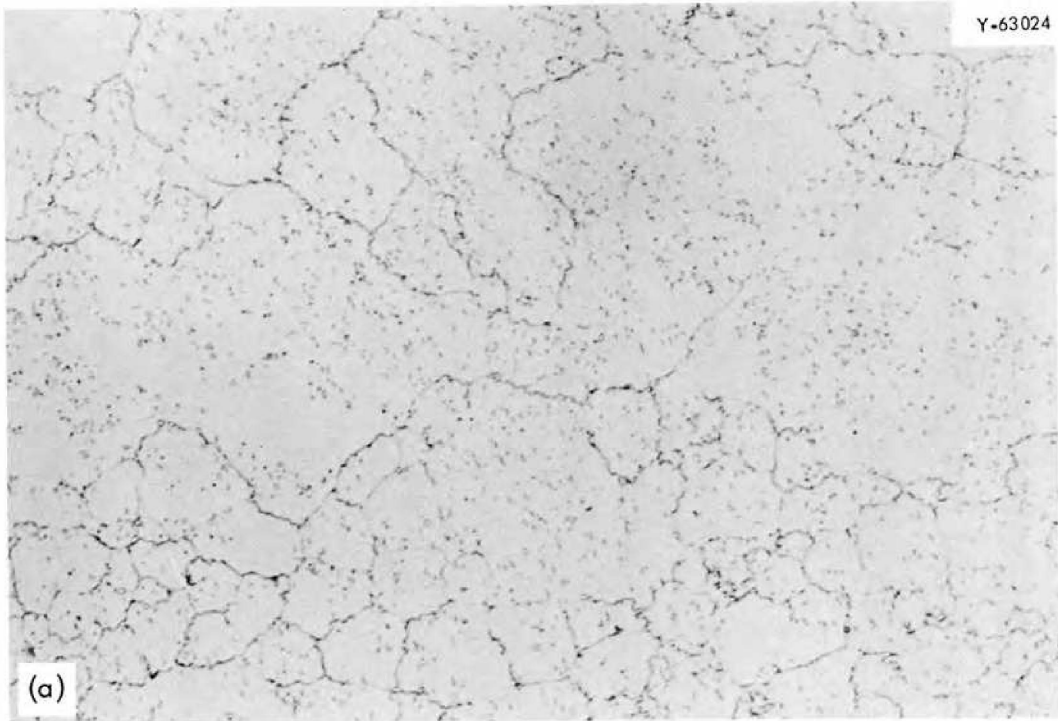
Fig. 4. Hastelloy N After a 1-hr Anneal at 1260°C. (a) Photo-micrograph of specimen etched with aqua regia. (b) Autoradiograph of specimen in the as-polished condition, 48-hr exposure. 250X.
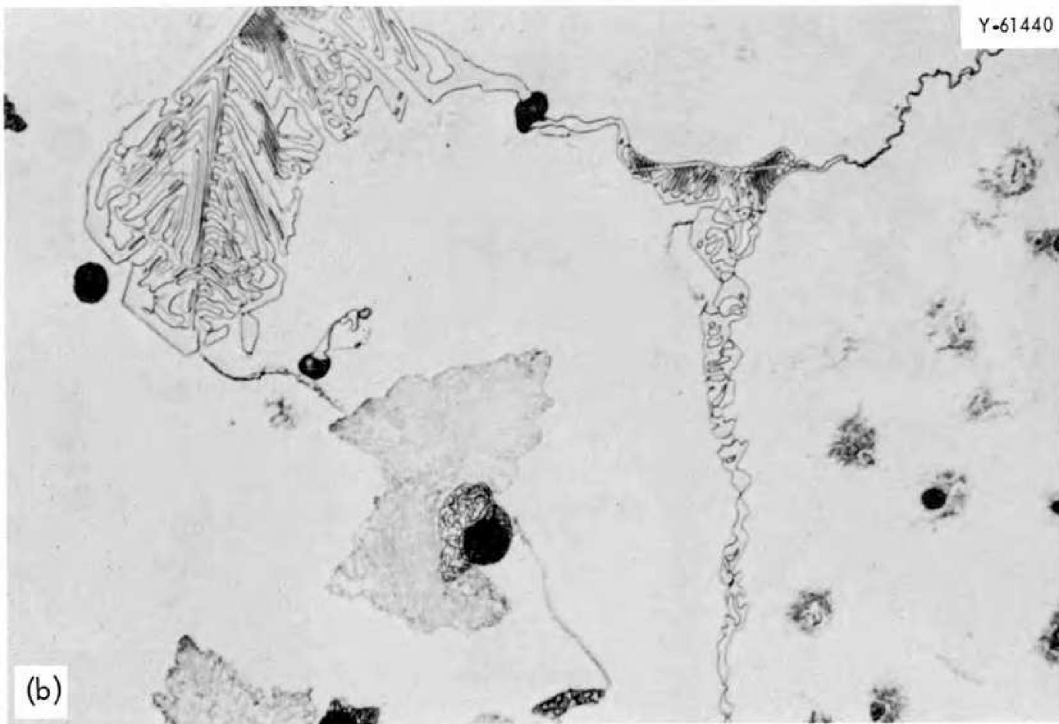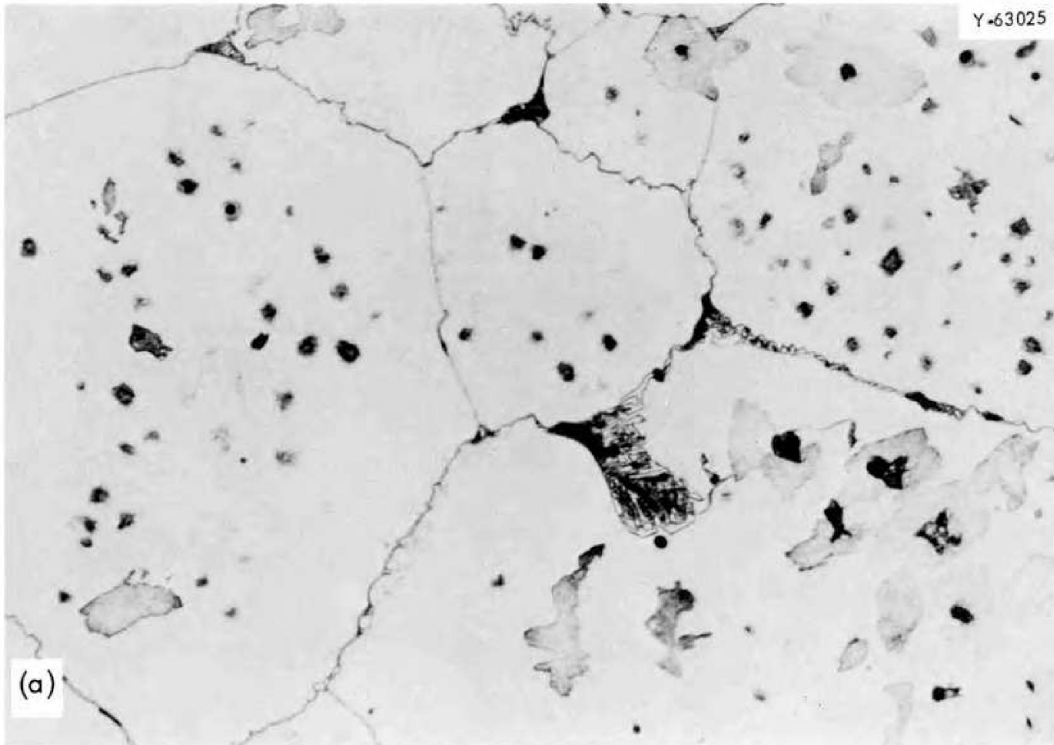
Fig. 5. Hastelloy N After a 1-hr Anneal at 1316°C. Etched with aqua regia. (a) 250×. (b) 1000×.
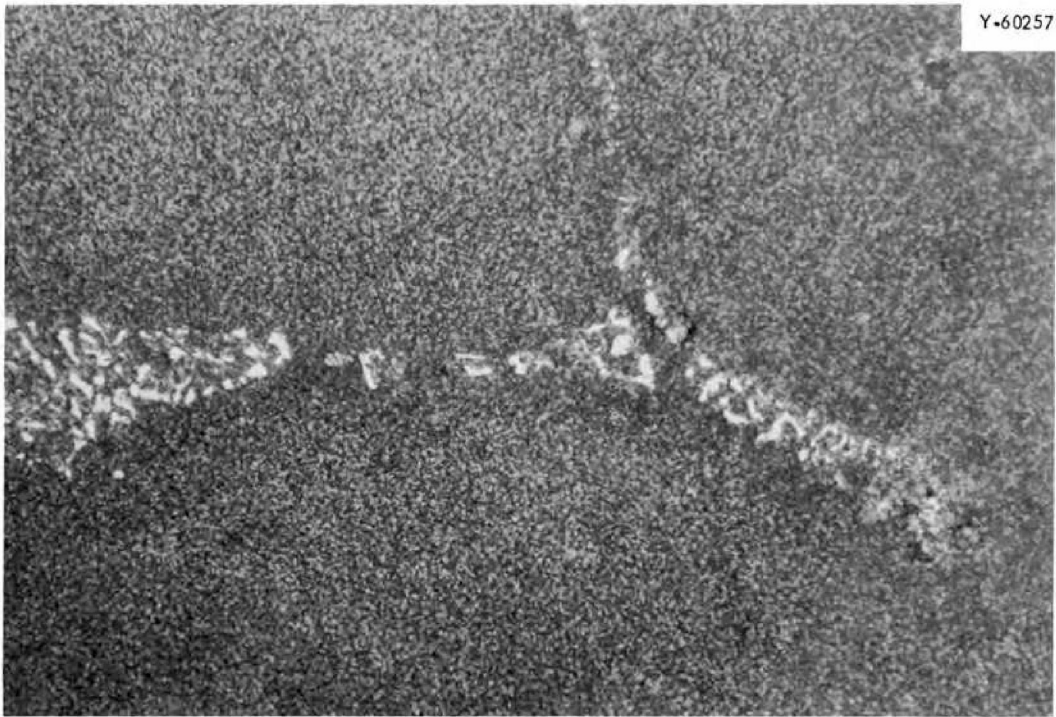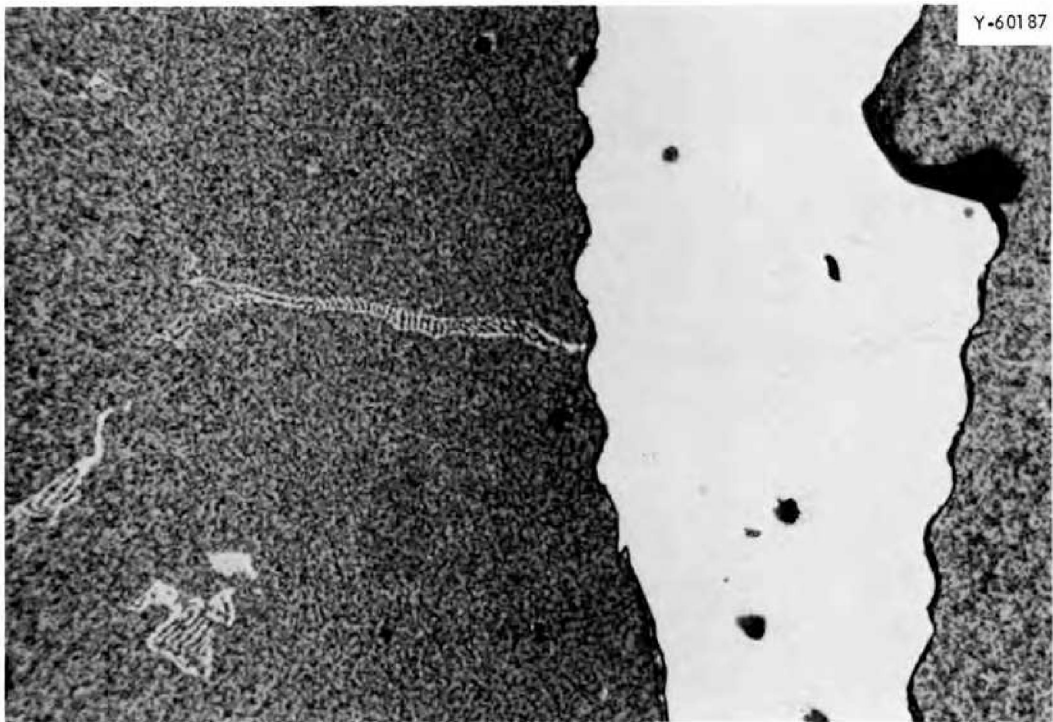
Fig. 6. Autoradiographs of Hastelloy N After a 1-hr Anneal at 1316°C. Exposed in the as-polished condition, 16-hr exposure. 750x.
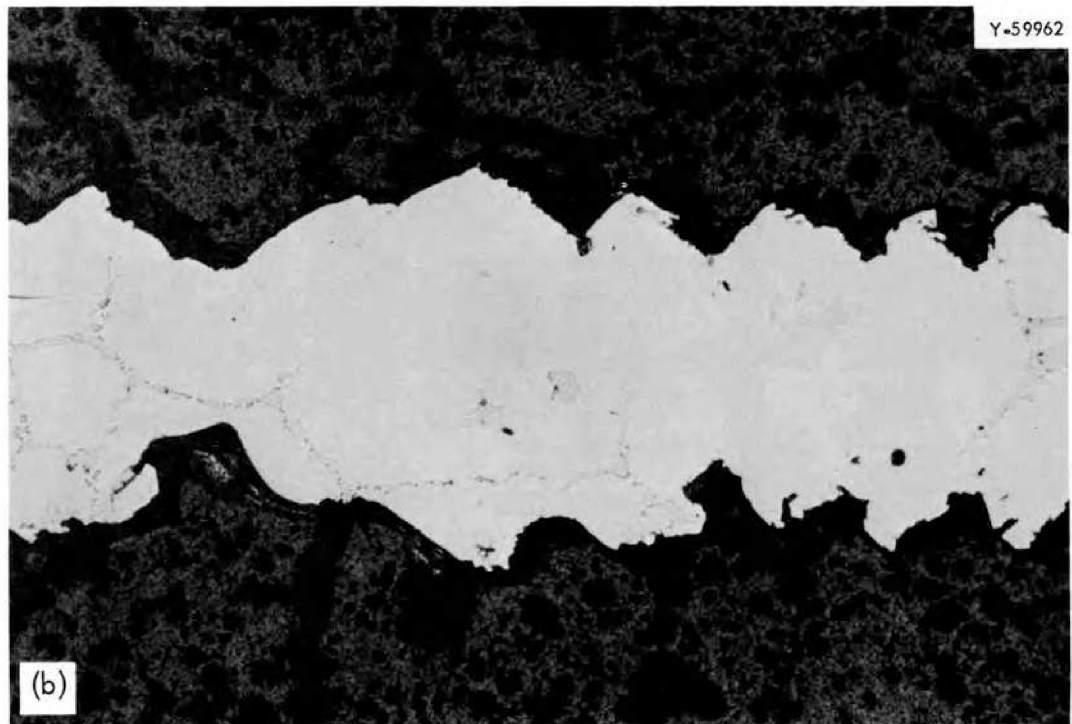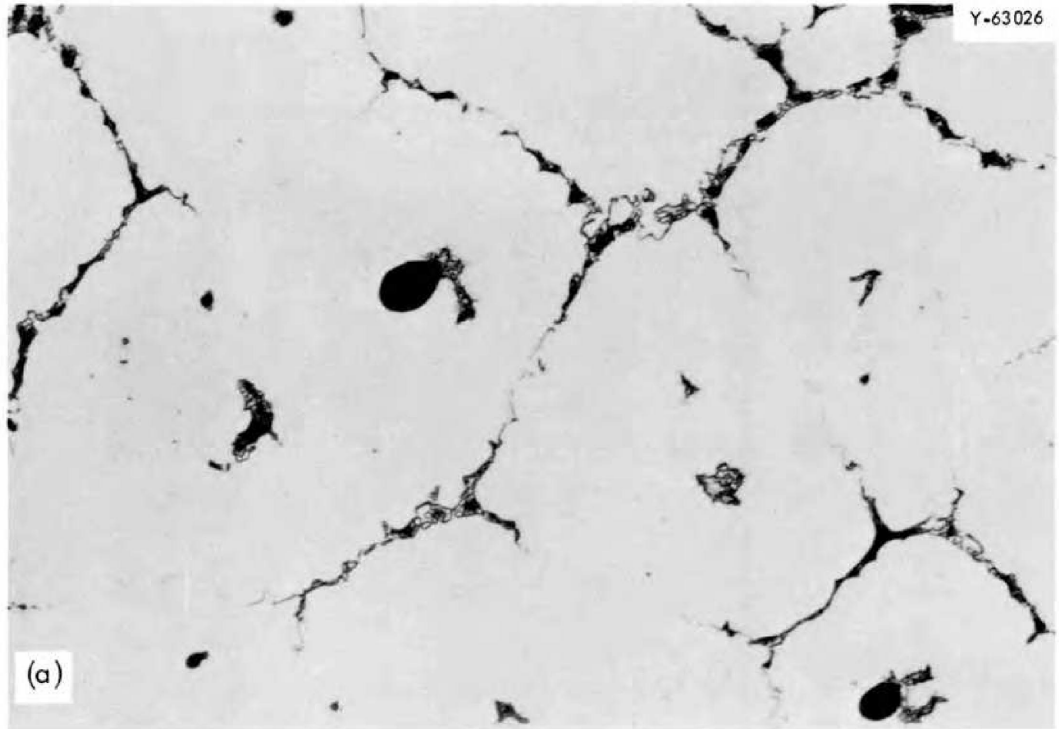
Fig. 7. Hastelloy N after a 1-hr Anneal at 1371°C. (a) Photomicro-graph etched with aqua regia. (b) Autoradiograph made in the as-polished condition, 72-hr exposure. 250x.

Figure 8 shows that the lamellar product in the grain boundary contains a constituent that is low in carbon. The carbon enrichment seems to be adjacent to the grain-boundary product rather than in the grain-boundary phase.

Figure 9 shows the microstructure of the alloy after a 1-hr anneal at 1177°C followed by 100 hr at 649°C. Figure 10a and b show that rather gross segregation of carbon to the grain boundaries occurs as a result of this treatment.

Annealing for 1 hr at 1260°C followed by 24 hr at 871°C produces the microstructure shown in Fig. 11a. The autoradiograph shown in Fig. 11b illustrates the inhomogeneous distribution of carbon in the alloy after this heat treatment.

Two pieces of the alloy were rolled into 1 × 1/2 × 0.040-in. sheets. They were fused together by Heliarc welding without the addition of any filler metal. A transverse section of the weld was prepared for metallographic examination. The base metal has a microstructure similar to that shown in Fig. 1. Figure 12a shows the heat-affected zone and the weld metal. Figure 12b is an autoradiograph of the area shown in Fig. 12a. There does not seem to be any segregation of carbon in the part of the base metal that recrystallized during welding. Near the fusion line, the carbon segregated to the grain boundaries. Figure 13a is a high magnification photograph which shows the carbon segregation near the fusion line. Figure 13b shows that the carbon distribution in the weld metal is quite uniform.

Two variations in experimental techniques with respect to metallographic study of the weld specimen should be mentioned. First, the weld specimen was etched lightly before the liquid emulsion was applied. This was necessary because the carbon segregation was not sufficient to delineate the various regions of the weld. Secondly, the exposure time for the autoradiographs was 300 hr as compared with times of 16 to 72 hr for the other specimens. This resulted from differences in the properties of the NTB Liquid Emulsion. One lot of emulsion was used for the wrought specimens and a second lot was used for the weld. By appropriate cross checks it was found that both lots of emulsion revealed similar details if the exposure times were varied by a factor of about ten.
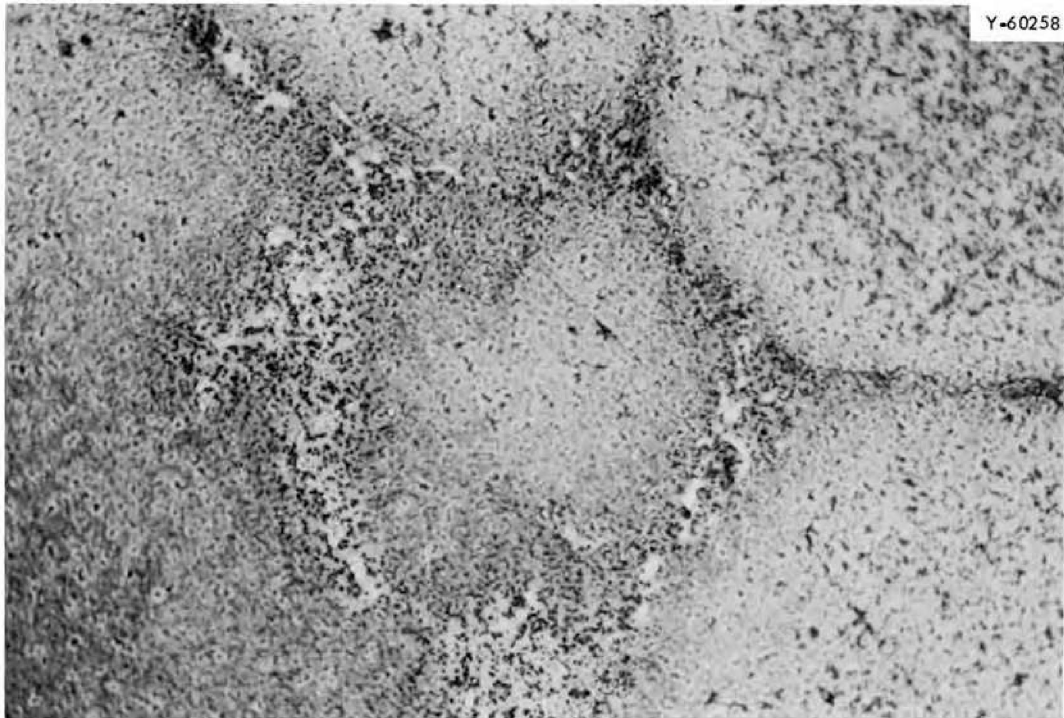
Fig. 8. Autoradiograph of Hastelloy N after a 1-hr Anneal at 1371°C. As-polished condition, 16-hr exposure. 750x.
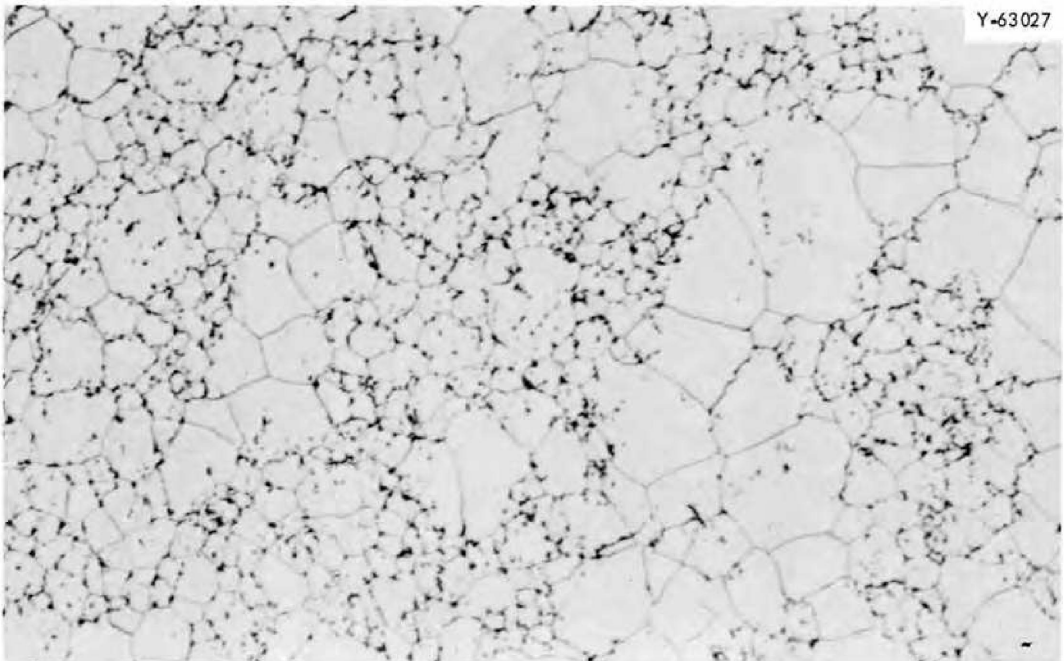
Fig. 9. Hastelloy N after a 1-hr Anneal at 1177°C Followed by 100 hr at 871°C. Etchant: aqua regia.
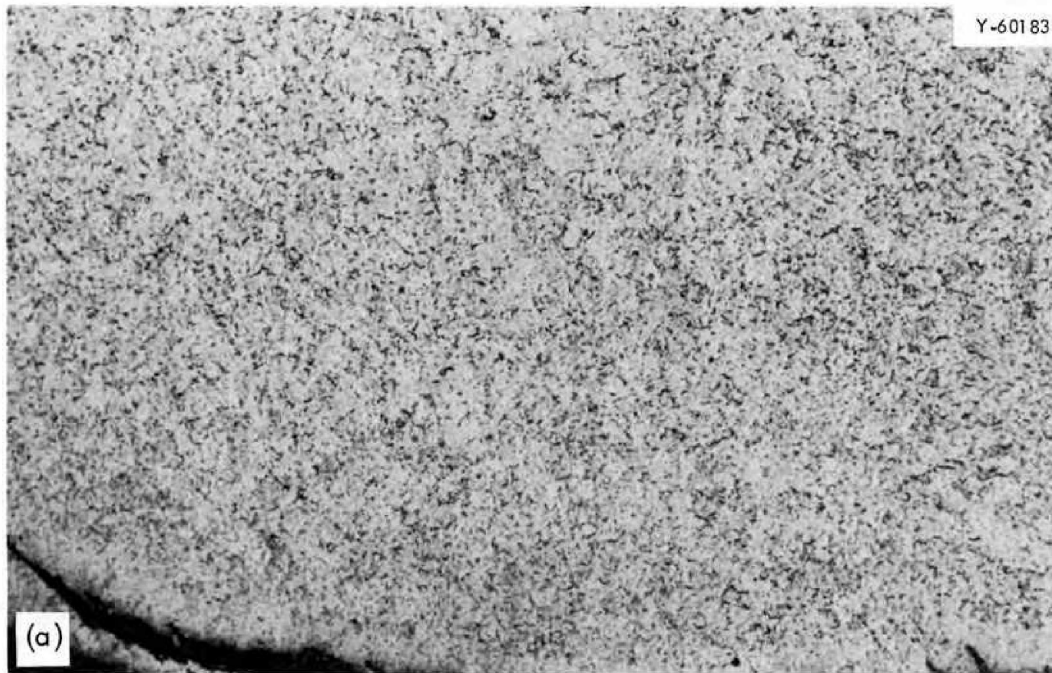
Fig. 10. Autoradiographs of Hastelloy N After a 1-hr Anneal at 1177°C Followed by 100 hr at 649°C. As-polished condition. (a) 16-hr exposure. (b) 72-hr exposure. 250X.
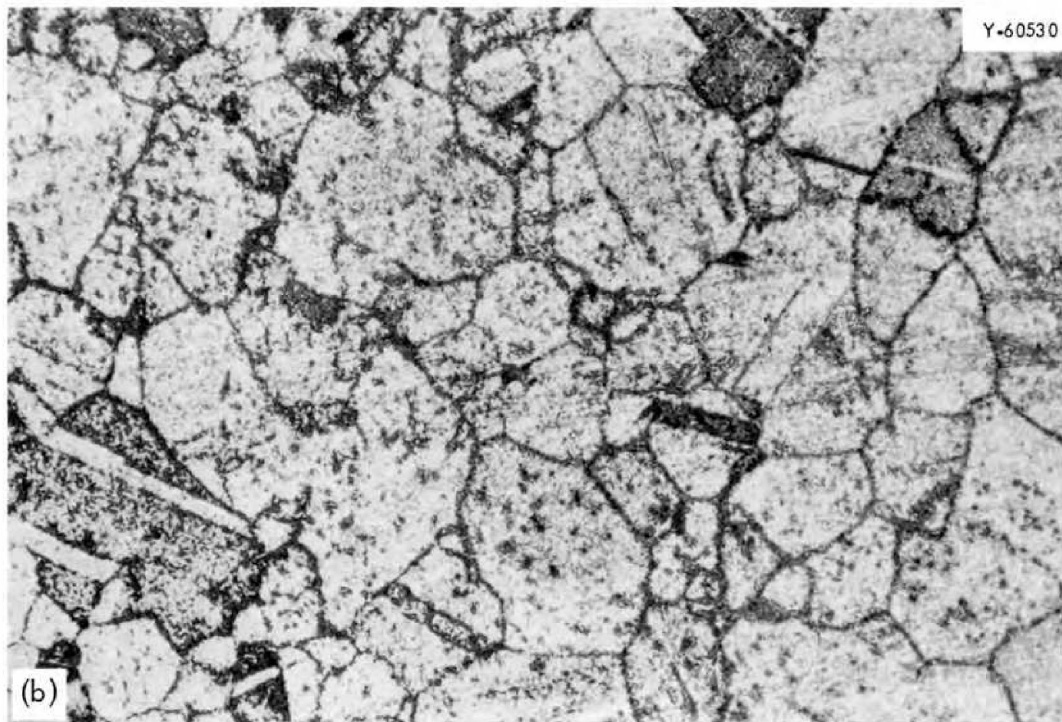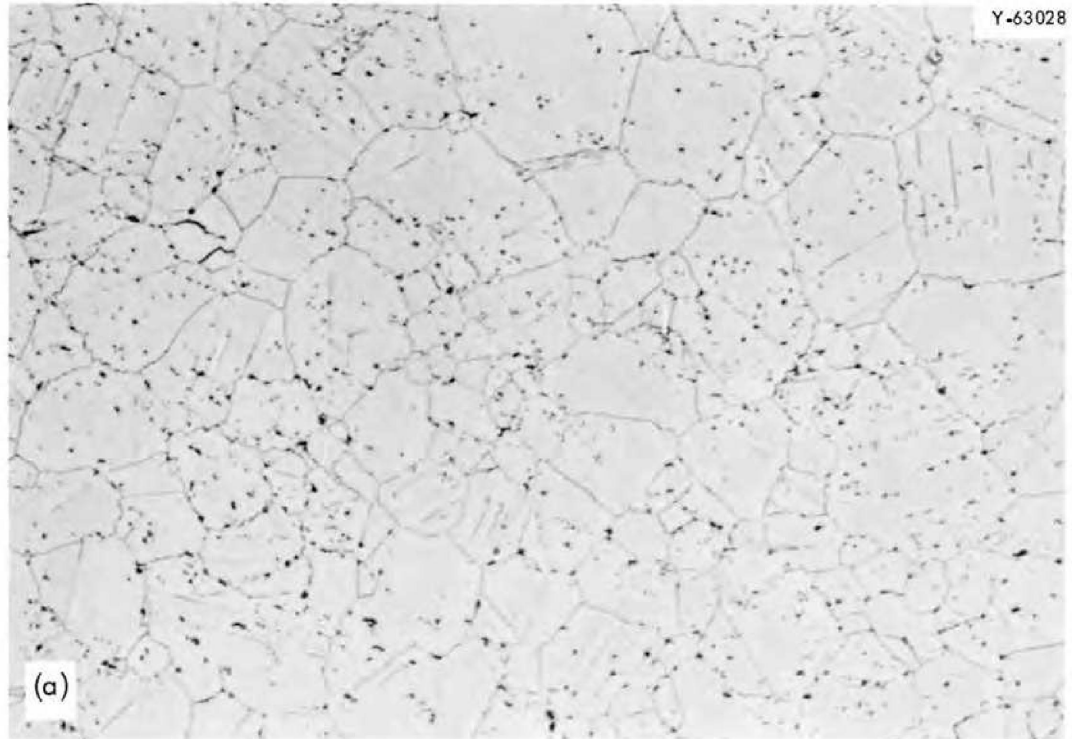
Fig. 11. Hastelloy N After a 1-hr Anneal at 1260°C Followed by 24 hr at 871°C. (a) Photomicrograph of specimen etched with aqua regia. (b) Autoradiograph of specimen in as-polished condition, 72-hr exposure. 250x.

Fig. 12. Weld Metal and Heat-Affected Zone of a Hastelloy N Weld.
(a) Photomicrograph of specimen etched with aqua regia. (b) Autoradio-
graph of specimen after a light etch, 300-hr exposure. 250X.

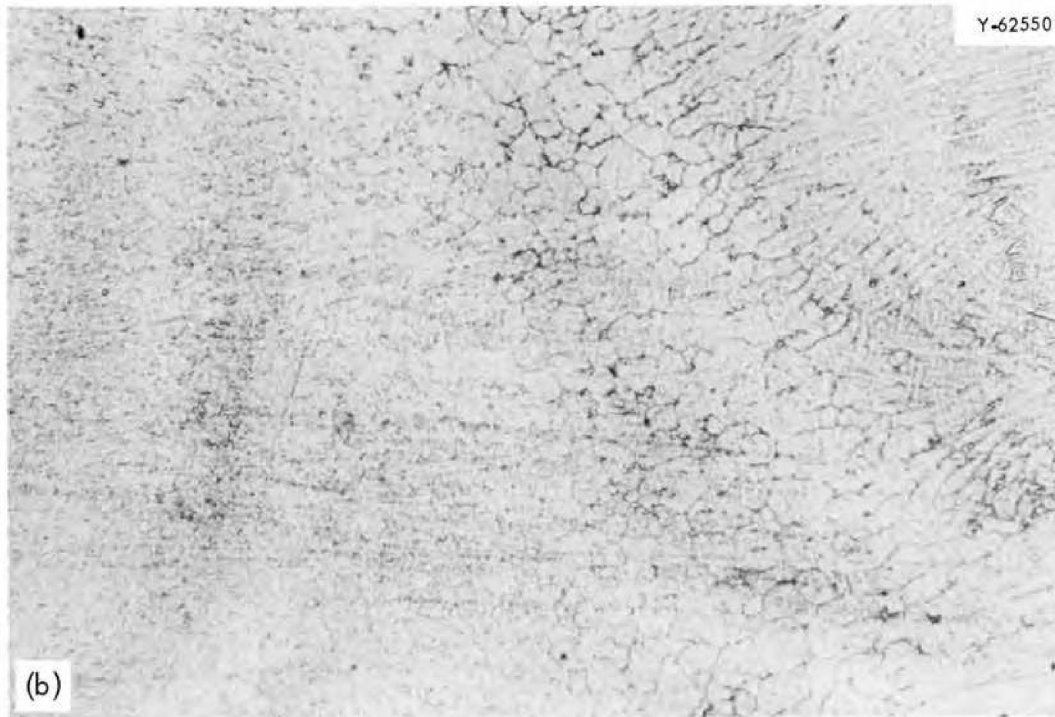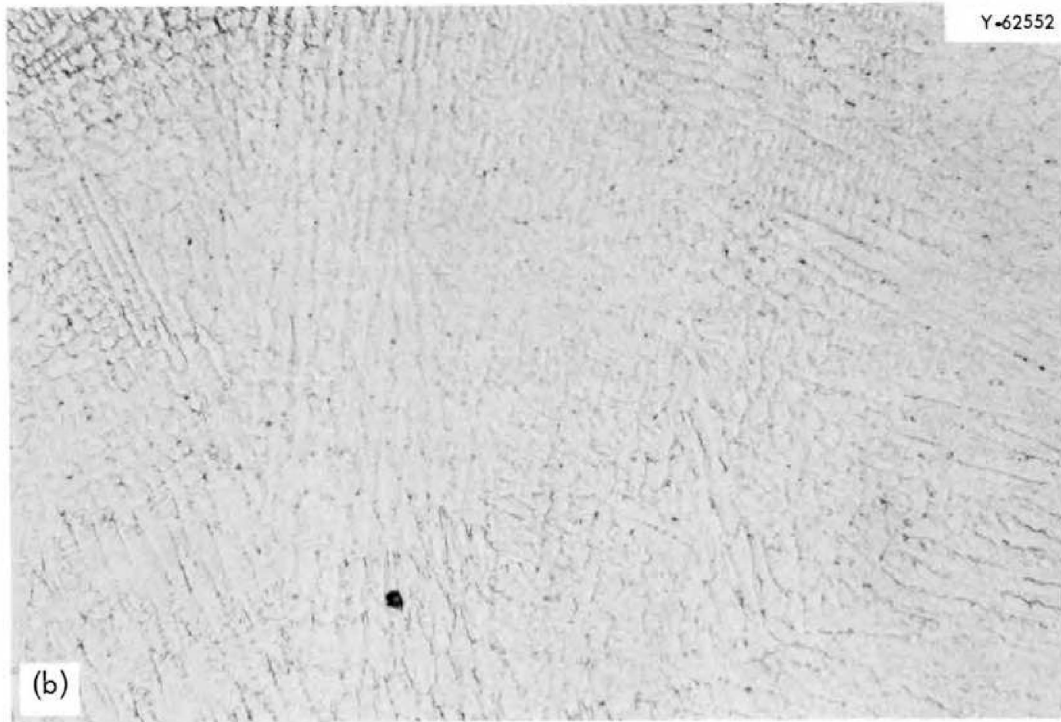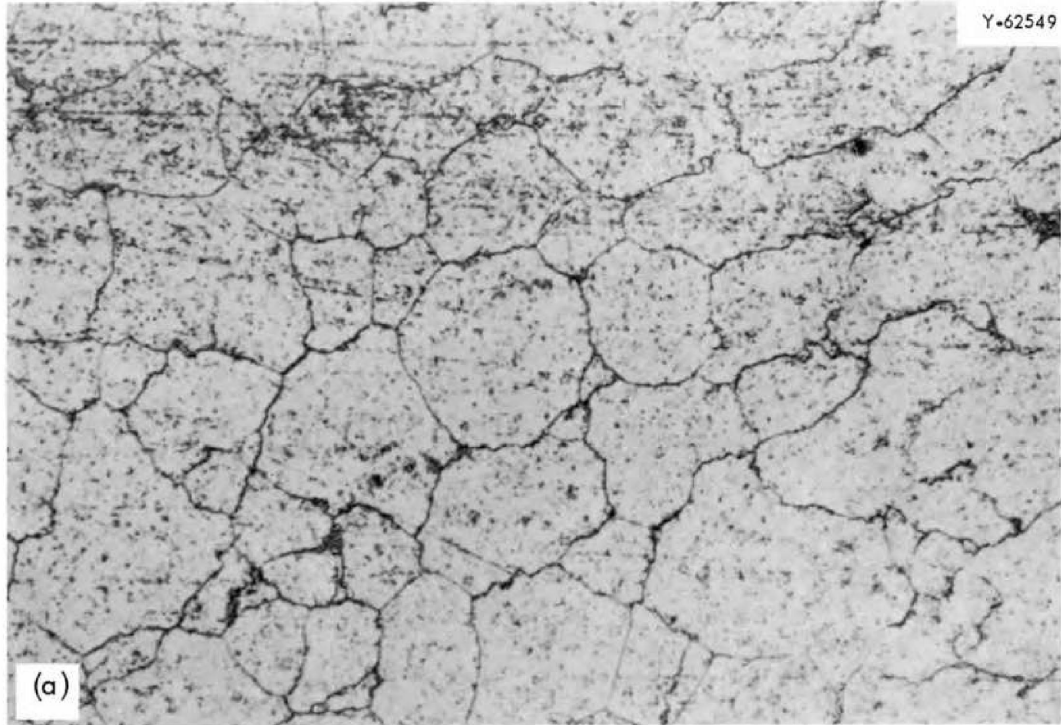Fig. 13. Autoradiographs of Hastelloy N Welds After a Light Etch, 300-hr Exposure. (a) Heat-affected zone. 750x. (b) Weld metal. 250x.

DISCUSSION OF RESULTS

The results which have been presented may be summarized as follows:

1. Neither the coarse precipitate particles which are present as stringers nor the lamellar phase are enriched in carbon. In fact, the coarse precipitate particles and one constituent of the lamellar phase are depleted in carbon with respect to the matrix.

2. The carbon is distributed fairly uniformly at annealing temperatures up to 1260°C.

3. At temperatures above 1260°C the carbon is segregated to the grain boundaries, although the areas adjacent to the grain-boundary precipitate are more enriched than the precipitates themselves.

4. Annealing at 1177°C followed by 100 hr at 649°C and annealing at 1260°C followed by 24 hr at 871°C both produced gross segregation of carbon to the grain boundaries.

5. Welding produced some intergranular carbon segregation in a small region of the heat-affected zone.

The first observation indicates very strongly that Hastelloy N is not basically a solid-solution alloy and that intermetallic phases are present. There are numerous possibilities of compounds which could be formed from the various alloying elements present. However, the observation that the quantity of precipitate in Hastelloy N does not depend on the concentration of minor alloying elements leads one to believe that the second phase in actually a nickel-molybdenum intermetallic. The binary nickel-molybdenum phase diagram[4] shown in Fig. 14 indicates that a binary alloy of 16 wt % Mo and nickel would be single phase up to about 1400°C. However, studies by Lundy on the nickel-rich corner of the nickel-molybdenum-chromium system have shown that the addition of chromium to nickel reduces the solubility of molybdenum in the alloy. This is equivalent to saying that the alpha filed in Fig. 14 is reduced in size and

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[4]*Metals Handbook*, American Society for Metals, Cleveland, 1948, p. 1230.

[5]T. S. Lundy, *A Metallographic and X-Ray Study of Nickel-Base Alloys of 20-25 Per Cent Molybdenum and 3-15 Per Cent Chromium*, M.S. Thesis, The University of Tennessee, 1957.
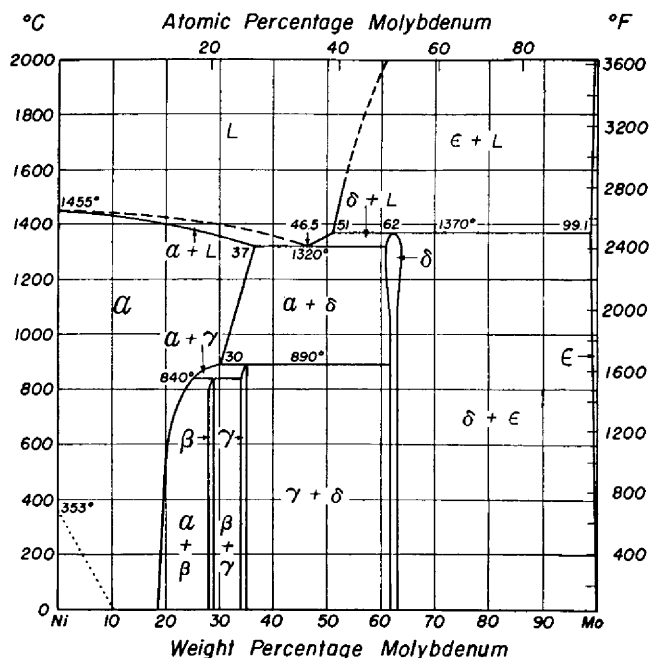
Fig. 14. Nickel-Molybdenum Equilibrium Diagram.

that the alpha and beta fields are moved to the left. Lundy also noted
that the addition of chromium suppressed the formation of beta. Recent
studies by Norman[6] on the nickel-molybdenum-iron system have shown that
iron has very little effect on the solubility of molybdenum in nickel,
but that iron also suppresses beta formation. Both Lundy and Norman
noted that the phase transformations in these alloys are quite sluggish.
In light of these facts, it is hypothesized that the coarse precipitates
that are present in Hastelloy N after fabrication are a modified delta
phase which is formed in the melt as it cools. Reheating for 1 hr at
1260°C or at higher temperatures causes the delta to decompose to form
alpha and gamma (the lamellar phase).

The second, third, and fourth observations which concern carbide
segregation indicate that the ductility of this material is not controlled

[6]W. E. Norman and E. E. Stansbury, An Investigation of Nickel-Rich
Alloys Containing Molybdenum and Iron, The University of Tennessee
(August 1963).

by the carbon distribution. The studies reported previously[7] showed
that the minimum fracture elongation (measured in a tensile test at
871°C) is reduced by a factor of 3 as a result of annealing at 1204°C
as compared with that obtained by annealing at 1177°C. Annealing at
1232°C produced another twofold decrease in elongation. However, the
autoradiographs show no significant carbon segregation until annealing
temperatures of 1260°C were used. Both of the aging treatments that were
used (1 hr at 1177°C followed by 100 hr at 871°C, and 1 hr at 1260°C
followed by 16 hr at 871°C) produced gross carbide segregation. The
material receiving the first heat treatment was found to have about one-
half the ductility of the material given the second treatment. From
Figs. 9, 10, and 11 it is not obvious that any great difference exists in
the degree of carbon segregation.

In view of these results, it is felt that the loss in ductility in
this alloy does not correlate with the grain-boundary segregation of car-
bon. A close examination of the test results[7] obtained on various heats
of Hastelloy N and the compositions of these various heats leads one to
suggest that the troublesome element may be silicon, although no direct
evidence exists for this conclusion.

The carbon segregation that occurred in the weld can be rationalized
in terms of the microstructures that were obtained during 1-hr anneals.
The carbon was segregated to the grain boundaries by 1-hr anneals above
1260°C. For the short time that heat was applied to the weld, higher
temperatures would probably be required to cause carbon segregation. The
weld metal did not show any carbon segregation. Hence the observation
that the carbon was segregated only in a small region in the heat-affected
zone is as expected.

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[7]H. E. McCoy, *Influence of Several Metallurgical Variables on the
Tensile Properties of Hastelloy N*, ORNL-3661 (August 1964).

SUMMARY AND CONCLUSIONS

It has been observed by autoradiographic studies on a heat of
Hastelloy N containing carbon-14 that (1) the large precipitates in this
alloy are not enriched in carbon, and (2) the loss in ductility cannot
be associated with the segregation of carbon. It is hypothesized that
the major precipitates in this alloy are nickel-molybdenum intermetallic
compounds which form as a result of the solubility of molybdenum in
nickel being reduced by the presence of chromium in the alloy. The loss
in ductility in this alloy as a result of annealing at elevated tempera-
tures is probably associated with a minor alloying element other than
carbon. It is hypothesized that silicon is this troublesome element.

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