1971

Irradiation enhanced decomposition of a nickel-carbon solid solution

Bryce Linn Shriver

Department:

IRRADIATION ENHANCED DECOMPOSITION OF A NICKEL-CARBON SOLID SOLUTION

BY

BRYCE LINN SHRIVER, 1947-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN NUCLEAR ENGINEERING

1971

Approved by

(Advisor)

PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by Acta Metallurgica. Pages iii and 1-19 will be submitted for publication in that journal.

ABSTRACT

This investigation was performed to determine the effects of room temperature neutron irradiation on the distribution of carbon in a nickel--0.3 wt. % carbon alloy. The experiment consisted of comparing the amount of carbon in solid solution and the internal stresses of both unirradiated and irradiated (10^{13} fn-cm^{-2} < Φ_F < 10^{18} fn-cm^{-2}) samples following isochronal anneals between 100°C and 1200°C by using the magnetic disaccommodation technique. The results indicate that the amount of carbon remaining in solid solution decreases with increasing neutron dose. At temperatures below 200°C this is due to the trapping of carbon by mobile irradiation-produced defects. Between 200°C and 600°C the formation of metastable carbides is enhanced by the presence of irradiation-produced defects. No differences are observed in irradiated and unirradiated samples above 600°C.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor Manfred Wuttig for the assistance and guidance which made this investigation possible.

He also wishes to thank the staff at both the University of Missouri-Rolla Reactor and the University of Missouri Research Reactor Facility for their help in irradiating and handling the various samples.

Support by the Atomic Energy Commission by the award of a Special Fellowship in Nuclear Science and Engineering administered by Oak Ridge Associated Universities is also gratefully acknowledged.

This work further benefitted from the support of the National Science Foundation through Grant GK-18460.

TABLE OF CONTENTS

Page

PUBLICATION THESIS OPTION.....ii

ABSTRACT.....iii

ACKNOWLEDGEMENTS.....iv

LIST OF FIGURES.....vi

I. INTRODUCTION.....1

II. EXPERIMENTAL PROCEDURE.....2

A. INTRODUCTION.....2

B. MAGNETIC DISACCOMMODATION TECHNIQUE.....2

C. ELECTRON MICROSCOPY.....3

D. SAMPLE PREPARATION.....3

E. ANNEALING CONDITIONS.....4

III. EXPERIMENTAL RESULTS.....6

IV. DISCUSSION.....7

V. CONCLUSIONS.....10

APPENDIX: THE SOLUBILITY OF CARBON IN NICKEL.....11

BIBLIOGRAPHY.....13

FIGURE CAPTIONS.....15

VITA.....20

LIST OF FIGURES

Figures Page

1. Normalized initial permeability, μ_o', as a function of annealing temperature. $\mu_o' = \mu_o(T)/\mu_o(105°C)$.....16

2. Normalized disaccommodation amplitude, $\Delta\mu'$, as a function of annealing temperature. $\Delta\mu' = \Delta\mu(T)/\Delta\mu(105°C)$.....17

3. Carbon content of nickel as a function of carburization time.....18

4. Normalized initial permeability, μ_o', and normalized disaccommodation amplitude, $\Delta\mu'$, as a function of carburization time.....19

I. INTRODUCTION

It has been shown that neutron irradiation greatly accelerates the rate of decomposition of supersaturated Fe-C alloys.[1-7] This decay of the solid solution was due to both the trapping of carbon at irradiation-produced defects [2-7] and enhanced precipitation due to the nucleation of carbides at defect clusters.[1,2]

This paper reports on a survey type study of irradiation enhanced decomposition in a nickel-0.3 wt. % carbon alloy. The objective of this investigation was to see if this interstitial solid solution is also affected by neutron irradiation and, if so, to characterize the type of interaction responsible for the change.

The nickel-carbon alloy was utilized because its crystal structure is the same as that of austenitic stainless steels which are commonly used in structural components of nuclear reactors. Nickel is also ferromagnetic so that the magnetic disaccommodation technique could be used to obtain information about the internal stresses and the amount of carbon in solid solution.

II. EXPERIMENTAL PROCEDURE

A. INTRODUCTION

This investigation consisted of a series of isochronal anneals between 100°C and 1200°C performed on three samples: an unirradiated sample used as a reference and two samples exposed to fast fluences of 5×10^{13} fn-cm^{-2} and 2×10^{17} fn-cm^{-2} at 40°C. After each thirty minute anneal the amount of carbon in solid solution and the formation of defect clusters or precipitates were checked by using the magnetic disaccommodation technique.

B. MAGNETIC DISACCOMMODATION TECHNIQUE

Magnetic disaccommodation is a useful technique for studying changes in solid solutions since it yields information about both the amount of alloying element in solid solution and its distribution. The value of the magnetic permeability immediately following demagnetization, μ_o, is sensitive to the formation of small precipitates or defect clusters if the stress field caused by them is of the same order as the magnetostrictive stresses.[8] Furthermore, the amplitude of the magnetic disaccommodation, $\Delta\mu$, is proportional to the concentration of the defect causing it.[9] Since the reorientation of dicarbons is believed to be responsible for the disaccommodation in dilute nickel-carbon alloys[10] $\Delta\mu$, is proportional to the square of the amount of carbon in solid solution. Applications of this technique to related problems are discussed elsewhere.[10-13]

Thus, by measuring both $\Delta\mu$ and μ_o after each isochronal anneal, it is possible to detect the redistribution of carbon in nickel and characterize the stresses associated with the change. These measurements were made in an oil bath at 105°C $\pm$ 3°C since this was the temperature which gave the optimum disaccommodation amplitude during the first ten minutes after demagnetization.[10]

C. ELECTRON MICROSOCPY

In order to further characterize the effects of neutron irradiation on this alloy, transmission electron microscopy studies were made on thin foils which had received the same treatment as the magnetic disaccommodation samples. Although the magnetic disaccommodation experiment indicated the formation of both defect clusters and precipitates neither was observed in the thin foils by using a 100 KV electron microscope. This was probably due to the relatively low neutron dose and the low stresses caused by the nickel-carbon precipitates. (Also see Discussion and Appendix.)

D. SAMPLE PREPARATION

The samples were prepared from commercially available nickel wire (1mm diameter) which contained about 20 ppm substitutional impurities; mainly silver and iron. Reactor grade graphite powder was used for the carburization. Each sample consisted of three, five cm long, wires.

The wires were initially recrystallized for 24 hours at 1200°C and in 20 microns of air. They were subsequently carburized by packing in graphite (500 microns of air) and quenching in ice water after 20 minutes at 1200°C. All samples contained about 0.3 wt. % carbon.* The values of the initial permeability and the disaccommodation amplitude indicated nearly equal carbon contents and distributions in all samples.

One of the samples (S-2) was irradiated for three hours at about 40°C in the University of Missouri-Rolla Reactor ($\phi_f \simeq 5 \times 10^9$ fn-cm^{-2}-sec^{-1}**). A second sample (S-3) was irradiated for 100 hours at 40°C in the University of Missouri Research Reactor Facility ($\phi_f \simeq 5 \times 10^{11}$ fn-cm^{-2}-sec^{-1}**).

E. ANNEALING CONDITIONS

Samples S-1 (unirradiated standard) and S-2 ($\Phi_F \simeq 5 \times 10^{13}$ fn-cm^{-2}) were annealed in 25°C steps in either an oil or salt bath at temperatures between 50°C and 500°C. In this range the temperature was controlled within $\pm$ 1°C. At higher temperatures (500°C-1200°C) a wire wound electric tube furnace and 50°C steps were used. The temperature control for this furnace was better than $\pm$ 3%. The samples

* For details see Appendix.

** Approximate fast neutron flux (E>1 MeV) at irradiation position.

were sealed in fused quartz with about 20 microns of air for all anneals above 400°C.

Because of the high radioactivity of sample S-3 ($\Phi_F \simeq 2 \times 10^{17}$ fn-cm^{-2}) it was annealed in the electric tube furnace with a pressure of about 500 microns of air for all temperatures above 225°C. Fifty degree steps were used between 100°C and 600°C and 100°C steps for higher temperatures. Some oxidation of the sample was apparent after annealing above 1000°C.

III. EXPERIMENTAL RESULTS

Neutron irradiation at room temperature and subsequent annealing have a marked effect on the distribution of carbon in nickel as shown by the changes of initial permeability and disaccommodation amplitude as a function of annealing temperature in Figs. 1 and 2. The observed effects may be divided into two groups. The first group consists of quantitative phenomena associated with the normal decomposition of the supersaturated solid solution and the second group is associated with the irradiation induced decomposition that is not seen in the unirradiated case.

The principle features of the variations in μ_o' and $\Delta\mu'$, except those between 100°C and 200°C, are common to all samples and, thus, reflect the formation and dissolution of metastable precipitates. These decomposition processes are quantitatively altered by the presence of the irradiation-produced defects. The apparent disappearance of up to 40% ($\langle C \rangle^2 \propto \Delta\mu' \simeq 0.4$; $\therefore \langle C \rangle \simeq 0.6$) of the carbon solute below 200°C, however, is a qualitatively new phenomenon. No differences are observed in irradiated and unirradiated samples above 600°C.

IV. DISCUSSION

In order to discuss the changes in the Ni-C solid solution it is necessary to know what types of defects are produced by neutron irradiation and how these defects will interact with the interstitial solutes. Since carbon has a low absorption cross section (3.4 mb) the defects formed in the alloy should be basically the same as found in pure nickel irradiated under similar conditions.[14] This was also indicated by the nearly identical drop of μ_o' that was observed during the irradiation of both carbon-free and carbon-doped samples early in this study. A survey of recent literature[15-21] reveals that both vacancy and self-interstitial defects will be formed in nickel during room temperature irradiation. Point defects are produced during irradiation and defect clusters may be formed either during irradiation or upon annealing at temperatures where the respective point defects are mobile. There will be an attractive interaction between the carbon interstitials and irradiation-produced defects[22,23] which may lead to an enhanced decomposition of the solid solution if either the solute or the defects are mobile.

The irradiation-produced quantitative changes in the decomposition of the supersaturated Ni-C alloys at temperatures above 200°C are ultimately the result of solute-defect interactions, which probably result in the enhanced nucleation of carbides, as seen in iron alloys irradiated under similar

conditions.[1,2,24] The present data, however, is insufficient to warrant a detailed discussion of this effect. The difficulties that were encountered in trying to find the cause of these changes were compounded by the apparent similarity of the carbides formed, as indicated by the relatively constant values of μ_o' in the temperature range of 100°C to 450°C. Only the formation of the precipitate at around 550°C is accompanied by a stress field which is large enough to be reflected in the initial permeability data. Ni-C alloys are, therefore, different from Fe-C alloys where the formation of carbides and carbon-defect trapping cause significant changes of μ_o.[7] It may be concluded that the strain energy of the Ni-C alloy is relatively independent of the solute distribution between 100°C and 500°C. This is most likely the main reason for the disagreement on carbide formation in nickel (see Appendix), as well as the failure of the electron microscopy studies mentioned above.

Since both carbon-doped and carbon-free nickel samples showed the same decrease in μ_o' upon irradiation, neither this drop nor the accompaning drop in $\Delta\mu'$ can be related to the formation of nickel carbides. These changes must, instead, be associated with the trapping of carbon at irradiation-produced defects. This trapping cannot occur by the migration of carbon atoms to stationary defects since long range carbon diffusion will not be possible at either the irradiation temperature or the magnetic permeability

measuring temperature.[25] It is more likely that the trapping takes place between stationary carbon atoms and mobile point defects or small defect clusters. The carbon interstitials would then act as preferential sinks for the migrating defects. Self-interstitials and divacancies are two mobile[10-12] defects that may be present in sufficient numbers[22] to account for the amount of trapping observed. The increase in $\Delta\mu$ between 100°C and 200°C indicates the dissociation of the carbon--defect traps.

V. CONCLUSIONS

Room temperature neutron doses of 10^{13} fn-cm^{-2} and 10^{17} fn-cm^{-2} affect the nickel-carbon solid solution in two ways. During irradiation up to 40% of the carbon may be removed from solid solution due to the trapping of carbon by mobile defects; possibly self-interstitials or divacancies. These carbon-defect traps are unstable above 150°C as carbon is returned to solid solution upon annealing between 150°C and 200°C. Above 200°C there is a series of metastable carbides formed in all samples. The formation of these precipitates appears to be enhanced by the presence of the irradiation-produced defects, which may act as additional nucleation sites. The form and type of the defects responsible for this effect is unknown, but they appear to anneal at about 600°C since both irradiated and unirradiated samples have the same values of μ_o and $\Delta\mu$ above that temperature.

APPENDIX: THE SOLUBILITY OF CARBON IN NICKEL

There is some uncertainity about the solubility of carbon in nickel. The values reported for the solubility of carbon, in weight percent, in nickel at 1200°C are: 0.3,[26] 0.35,[27] and 0.52.[28] There is also little agreement on the formation of nickel carbides.[26] The purpose of this Appendix is to indicate some of the reasons for these differences.

Figure 3 shows the increase of carbon content, as determined by the increase in sample weight, in the course of a carburizing treatment at 1200°C. The sample consisted of 99.999% pure nickel and was prepared for carburization by packing in reactor grade graphite powder and sealing in fused quartz under 1000 microns of air.

Figure 4 gives the values of the magnetic disaccommodation amplitude, $\Delta\mu'$, and the initial magnetic permeability, μ_o', as a function of carburization time. Since $\Delta\mu'$ is proportional to the square of the carbon concentration in solid solution,[10] the large drop in $\Delta\mu'$ after annealing for longer than twenty minutes indicates the formation of a precipitate. This is also verified by the simultaneous decrease in μ_o', which is sensitive to the small stress fields associated with precipitates.[8] However, transmission electron microscopy studies revealed no observable precipitate in similar samples, indicating that the precipitates

must be very small and/or cause a low stress field.

These results show that, although the carbon content of the sample increases with increasing carburization time, the amount of carbon that actually goes into solid solution reaches a maximum after a relatively short time. Thus, in the case of Ni-C, excessive carburization times may actually decrease the amount of carbon in solid solution.

Our results indicate that the maximum solubility of carbon in nickel at 1200°C is about 0.3 wt. %. This value agrees with those given by Hansen.[26]

The importance of this observation is that the true solid solubility of carbon in nickel cannot be determined by methods (e.g. combustion or weighing) that do not differentiate between carbon that is in solid solution or present as a precipitate. In order to obtain the actual amount of carbon in solid solution the method used must give this value explicitly. Magnetic disaccommodation and internal friction are two methods that can meet this requirement.

BIBLIOGRAPHY

1. D. Hull and I. Mogford, Phil. Mag. 6, 525 (1961).
2. H. Wagenblast and A. Damask, J. Phys. Chem. Sol. 23, 221 (1962).
3. F. Fujita and A. Damask, Acta Met. 12, 331 (1964).
4. R. Arndt and A. Damask, Acta Met. 12, 341 (1964).
5. H. Wagenblast, F. Fujita and A. Damask, Acta Met. 12, 347 (1964).
6. J. Stanley and W. Brundage, ORNL-3878 UC25, 25 (1965).
7. M. Wuttig, J. Stanley and H. Birnbaum, Phys. Stat. Sol. 27, 701 (1968).
8. M. Kersten, Z. Phys. 44, 1963 (1943).
9. A. Bosman, Thesis, University of Amsterdam, (1960).
10. M. Wuttig and H. Birnbaum, Appl. Phys. Let. 7, 322 (1965).
11. E. Balthesen, K. Isebeck and H. Wenzl, Phys. Stat. Sol. 8, 595 (1965).
12. H. Kronmüller, Vacancies and Interstitials in Metals, Amsterdam: North-Holland Publishing Co. 667 (1970).
13. M. Wuttig and H. Birnbaum, J. Phys. Chem. Sol. 27, 225 (1966).
14. M. Ipohorski and L. Brown, Phil. Mag. 22, 931 (1970).
15. A. Bourret and D. Dautreppe, Phys. Stat. Sol. 29, 283 (1968).
16. B. Mastel and J. Brimhall, J. Nuc. Mat. 28, 115 (1968).
17. J. Brimhall and B. Mastel, J. Nuc. Mat. 33, 186 (1969).
18. J. Brimhall, H. Kissinger and B. Mastel, Pro. Elec. Mic. Soc. 28, 414 (1970).
19. W. Schilling et al, Vacancies and Interstitials in Metals, Amsterdam: North-Holland Publishing Co. 235 (1970).
20. D. Norris, Phil. Mag. 22, 1273 (1970).

21. D. Norris, Phil. Mag. 23, 135 (1971).

22. B. Kelly, Irradiation Damage to Solids, New York: Pergamon Press. (1966).

23. R. Johnson and A. Damask, Acta Met. 12, 443 (1964).

24. J. Stanley, Diffusion in Body-Center Cubic Metals. Metals Park, Ohio: American Society for Metals, 349 (1964).

25. S. Diamond and C. Wert, Tran. Met. Soc. AIME 239, 705 (1967).

26. M. Hansen, Constitution of Binary Alloys. New York: McGraw-Hill, 374 (1968).

27. Metals Handbook. Novelty Ohio: The American Society for Metals, 1183 (1948).

28. W. Dunn, R. McLeooan and W. Oates, Tran. Met. Soc. AIME 242, 2129 (1968).

FIGURE CAPTIONS

Figure 1. Normalized initial permeability, μ_o', as a function of annealing temperature. $\mu_o' = \mu_o(T)/\mu_o$ (105°C).

Figure 2. Normalized disaccommodation amplitude, $\Delta\mu'$, as a function of annealing temperature. $\Delta\mu' = \Delta\mu(T)/\Delta\mu(105°C)$.

Figure 3. Carbon content of nickel as a function of carburization time.

Figure 4. Normalized initial permeability, μ_o', and normalized disaccommodation amplitude, $\Delta\mu'$, as a function of carburization time.

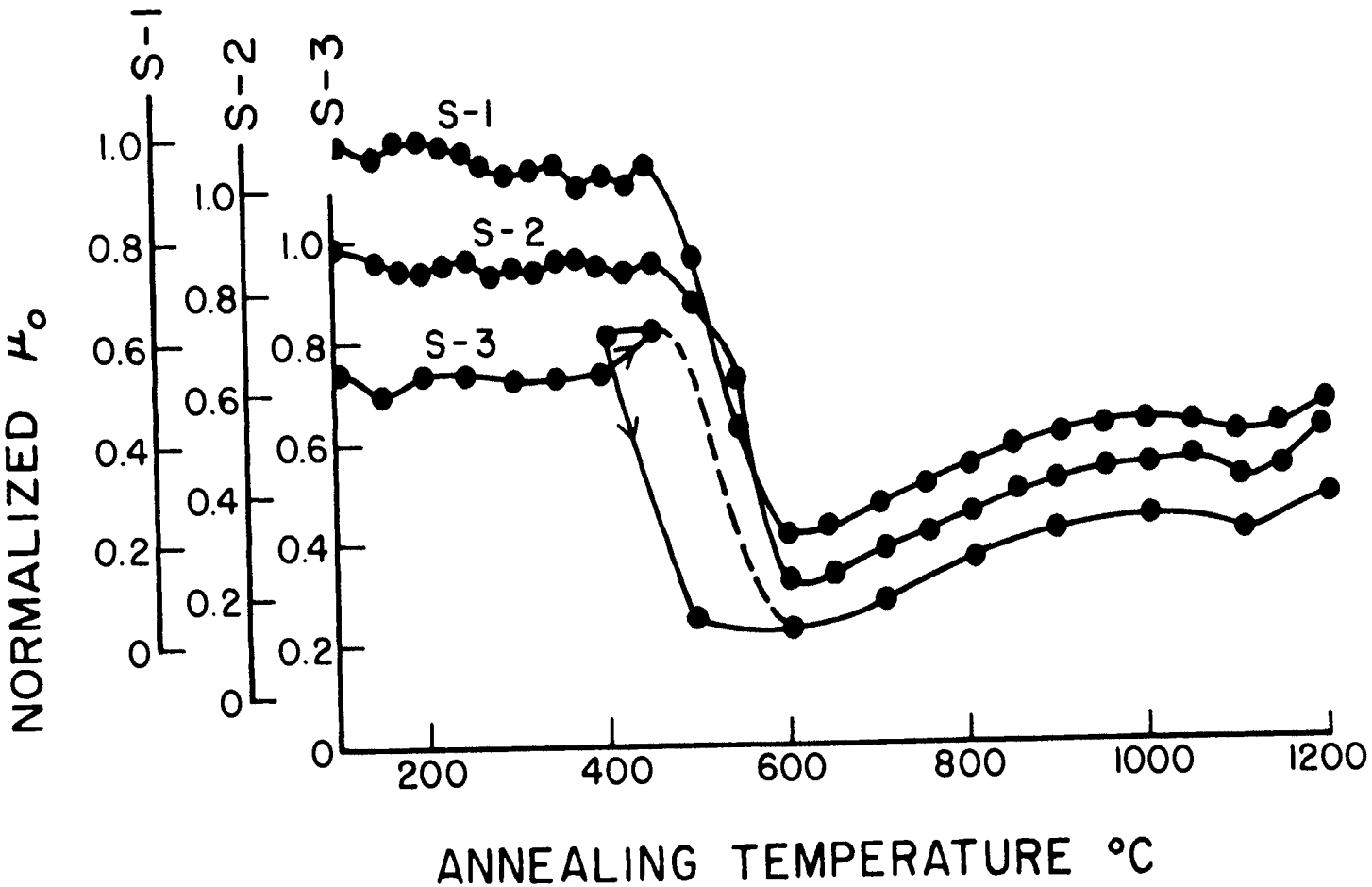
S-1
S-2
S-3
S-1
S-2
S-3
NORMALIZED μ_o
1.0
0.8
0.6
0.4
0.2
0
200
400
600
800
1000
1200
ANNEALING TEMPERATURE °C

FIGURE 1

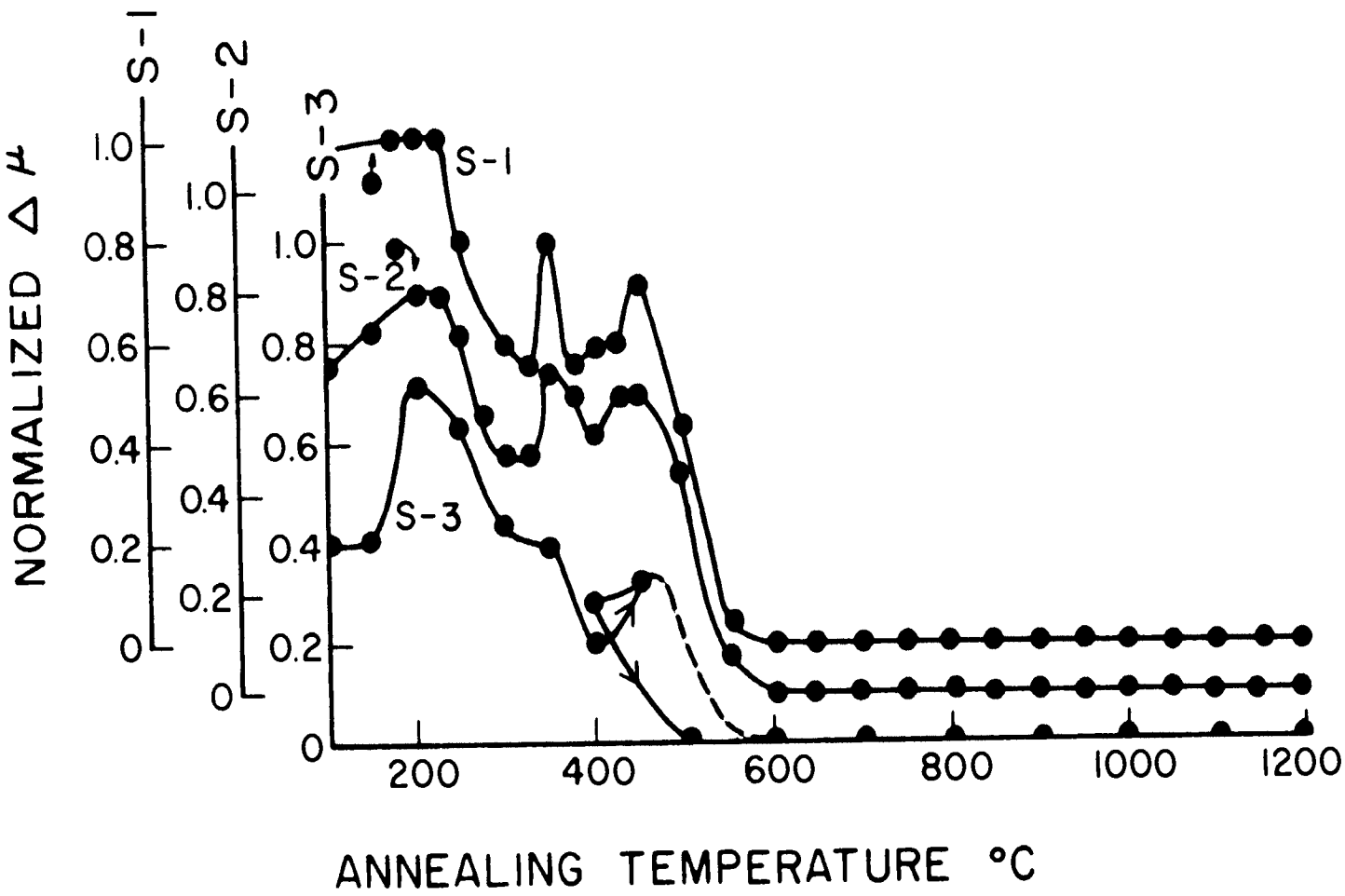
NORMALIZED Δ μ
S-1
S-2
S-3
1.0
0.8
0.6
0.4
0.2
0
200
400
600
800
1000
1200
ANNEALING TEMPERATURE °C

FIGURE 2

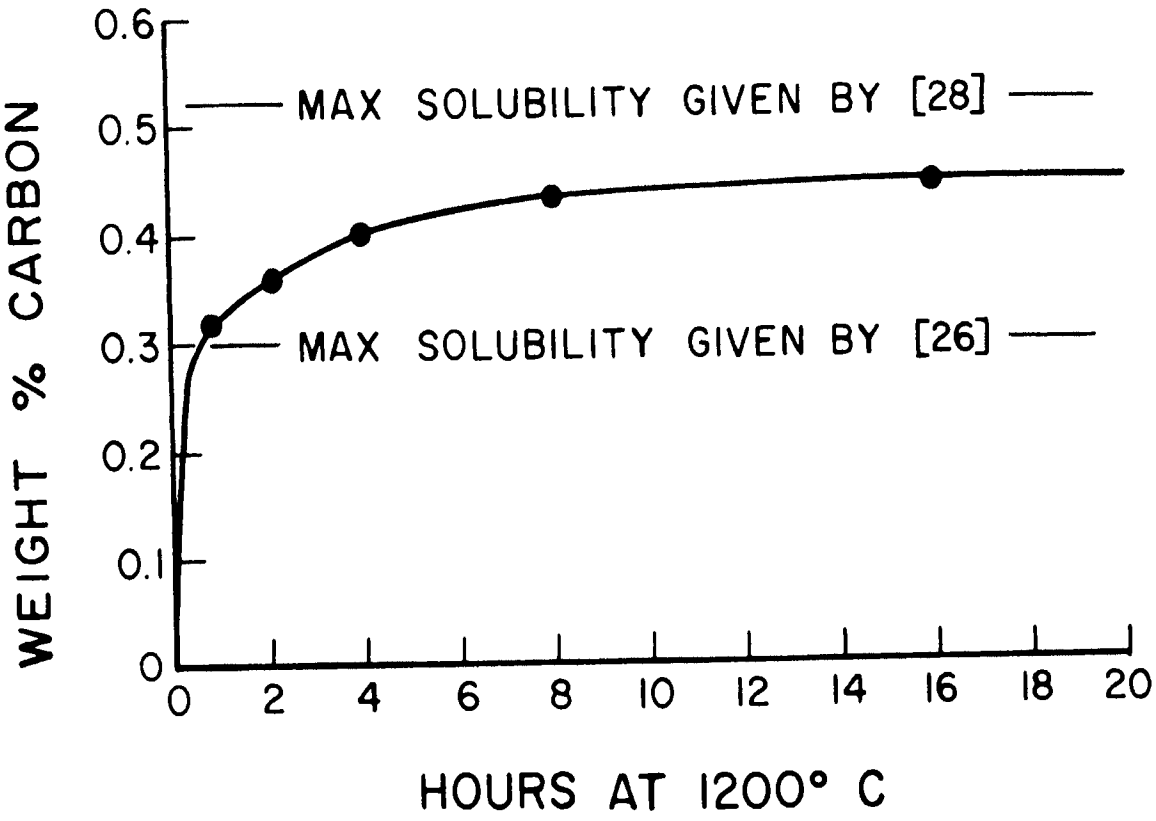
0.6
0.5
0.4
0.3
0.2
0.1
0
MAX SOLUBILITY GIVEN BY [28]
MAX SOLUBILITY GIVEN BY [26]
WEIGHT % CARBON
0
2
4
6
8
10
12
14
16
18
20
HOURS AT 1200° C

FIGURE 3

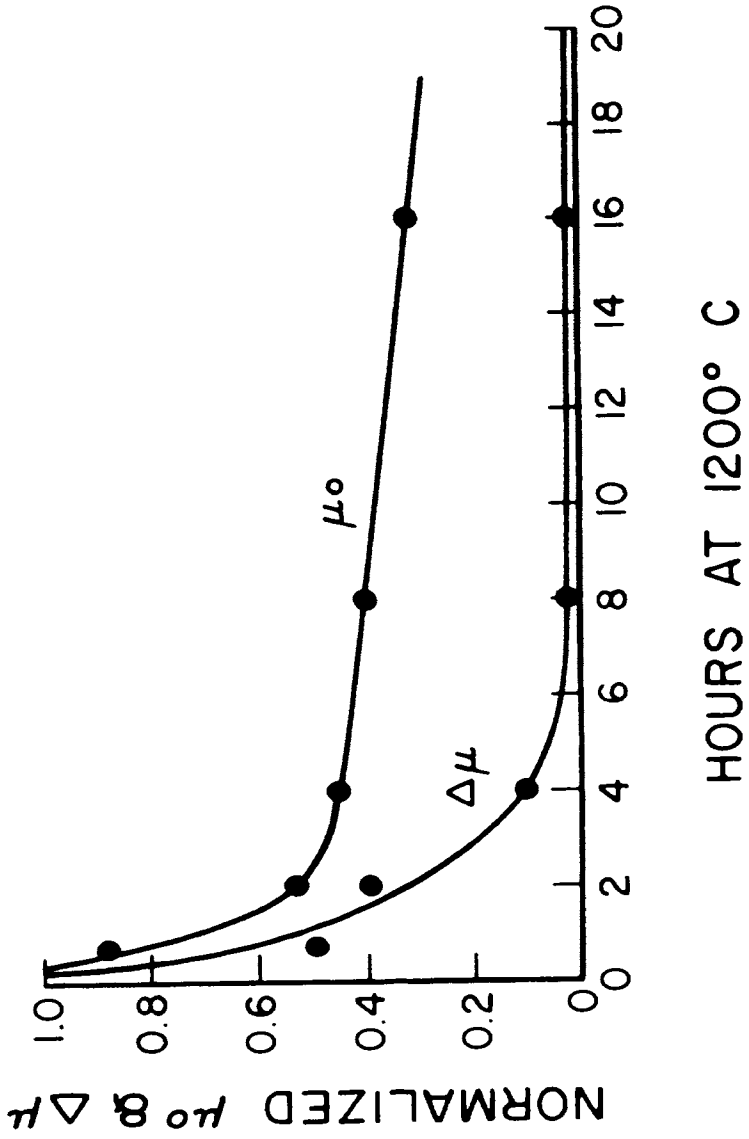
NORMALIZED μo & Δμ
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
20
HOURS AT 1200° C
μo
Δμ

FIGURE 4

VITA

Bryce Linn Shriver was born on December 31, 1947, in Kansas City, Missouri. He received his primary and secondary education in Belton, Missouri, and his college education from the University of Missouri-Rolla, Rolla, Missouri, where he held an Army ROTC Scholarship. He received a Bachelor of Science degree in Metallurgical Engineering (Nuclear Engineering Option) in May 1970.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since June 1970 and has held an Atomic Energy Commission Special Fellowship in Nuclear Science and Engineering.