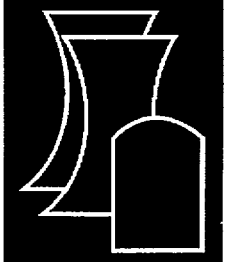
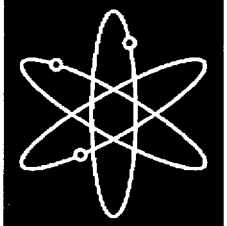
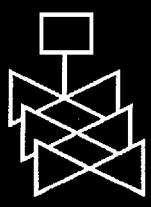
NUREG/CR-6629
ORNL/TM-13768







Atom Probe Tomography Characterization of the Solute Distributions in a Neutron-Irradiated and Annealed Pressure Vessel Steel Weld

Oak Ridge National Laboratory

U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001

AVAILABILITY OF REFERENCE MATERIALS IN NRC PUBLICATIONS

NRC Reference Material

As of November 1999, you may electronically access NUREG-series publications and other NRC records at NRC's Public Electronic Reading Room at www.nrc.gov/NRC/ADAMS/index.html.
Publicly released records include, to name a few, NUREG-series publications; *Federal Register* notices; applicant, licensee, and vendor documents and correspondence; NRC correspondence and internal memoranda; bulletins and information notices; inspection and investigative reports; licensee event reports; and Commission papers and their attachments.

NRC publications in the NUREG series, NRC regulations, and *Title 10, Energy*, in the Code of *Federal Regulations* may also be purchased from one of these two sources.

1. The Superintendent of Documents
   U.S. Government Printing Office
   P. O. Box 37082
   Washington, DC 20402–9328
   www.access.gpo.gov/su_docs
   202–512–1800
2. The National Technical Information Service
   Springfield, VA 22161–0002
   www.ntis.gov
   1–800–533–6847 or, locally, 703–805–6000

A single copy of each NRC draft report for comment is available free, to the extent of supply, upon written request as follows:

Address: Office of the Chief Information Officer,
Reproduction and Distribution
Services Section
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001
E-mail: DISTRIBUTION@nrc.gov
Facsimile: 301–415–2289

Some publications in the NUREG series that are posted at NRC's Web site address www.nrc.gov/NRC/NUREGS/indexnum.html are updated periodically and may differ from the last printed version. Although references to material found on a Web site bear the date the material was accessed, the material available on the date cited may subsequently be removed from the site.

Non-NRC Reference Material

Documents available from public and special technical libraries include all open literature items, such as books, journal articles, and transactions, *Federal Register* notices, Federal and State legislation, and congressional reports. Such documents as theses, dissertations, foreign reports and translations, and non-NRC conference proceedings may be purchased from their sponsoring organization.

Copies of industry codes and standards used in a substantive manner in the NRC regulatory process are maintained at—

The NRC Technical Library
Two White Flint North
11545 Rockville Pike
Rockville, MD 20852–2738

These standards are available in the library for reference use by the public. Codes and standards are usually copyrighted and may be purchased from the originating organization or, if they are American National Standards, from—

American National Standards Institute
11 West 42nd Street
New York, NY 10036–8002
www.ansi.org
212–642–4900

The NUREG series comprises (1) technical and administrative reports and books prepared by the staff (NUREG–XXXX) or agency contractors (NUREG/CR–XXXX), (2) proceedings of conferences (NUREG/CP–XXXX), (3) reports resulting from international agreements (NUREG/IA–XXXX), (4) brochures (NUREG/BR–XXXX), and (5) compilations of legal decisions and orders of the Commission and Atomic and Safety Licensing Boards and of Directors' decisions under Section 2.206 of NRC's regulations (NUREG–0750).

NUREG/CR-6629
ORNL/TM-13768

Atom Probe Tomography Characterization of the Solute Distributions in a Neutron-Irradiated and Annealed Pressure Vessel Steel Weld

Manuscript Completed: July 1999
Date Published: November 2000

Prepared by
M. K. Miller, K. F. Russell,
R. E. Stoller, P. Pareige*

Oak Ridge National Laboratory
Managed by Lockheed Martin Energy Research Co.
Oak Ridge, TN 37831-6151

*Groupe de Métallurgie Physique, UMR-6634 CNRS
Faculté des Sciences de l'Université de Rouen
76821 Mont Saint AIGNAN, France

C. J. Fairbanks, NRC Project Manager

Prepared for
Division of Engineering Technology
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001
NRC Job Code W6953

NUREG/CR-6629 has been reproduced from the best available copy.

ABSTRACT

A combined atom probe tomography and atom probe field ion microscopy study has been performed on a submerged arc weld irradiated to high fluence in the Heavy-Section Steel Irradiation (HSSI) fifth irradiation series (Weld 73W). The composition of this weld is Fe – 0.27 at. % Cu, 1.58% Mn, 0.57% Ni, 0.34% Mo, 0.27% Cr, 0.58% Si, 0.003% V, 0.45% C, 0.009% P, and 0.009% S. The material was examined after five conditions: after a typical stress relief treatment of 40 h at 607°C, after neutron irradiation to a fluence of 2×10^{23} n m^{-2} (E > 1 MeV), and after irradiation and isothermal anneals of 0.5, 1, and 168 h at 454°C. This report describes the matrix composition and the size, composition, and number density of the ultrafine copper-enriched precipitates that formed under neutron irradiation and the change in these parameters with post-irradiation annealing treatments.

CONTENTS

ABSTRACT iii

LIST OF FIGURES vii

LIST OF TABLES ix

ACKNOWLEDGMENTS xi

FOREWORD xiii

INTRODUCTION 1

EXPERIMENT 1

RESULTS AND DISCUSSION 2

CONCLUSIONS 12

REFERENCES 13

LIST OF FIGURES

Figure		Page
1	Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2}	4
2	Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C	4
3	Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 1 h at 454°C	5
4	Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 168 h at 454°C	5
5	Atom maps of the phosphorus and copper distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C. A small phosphorus-enriched region is evident	6
6	Concentration correlation of the copper-enriched precipitates in weld 73 after (a) neutron irradiation to a fluence of 2×10^{23} n m^{-2}, (b) anneal for 0.5 h, (c) anneal for 1 h, and (d) anneal for 168 h at 454°C	10
7	Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2}	11
8	Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C	11
9	Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 1 h at 454°C	12
10	Radial concentration distribution of a copper-enriched precipitate in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 168 h at 454°C	12

LIST OF TABLES

Table		Page
1	Bulk chemical composition of the submerged arc weld (weld 73W)	1
2	Matrix compositions of the submerged arc weld (weld 73W) for the five different heat treatments in atomic percent	2
3	Number of copper atoms detected in the precipitates and their estimated radii based on the number of copper atoms in the submerged arc weld (weld 73W) for the different heat treatments	6
4	The radii of gyrations of the precipitates in the submerged arc weld (weld 73W) for the different heat treatments. The order of the data is the same as in Table 3	8
5	Selected volume precipitate compositions in the submerged arc weld (weld 73W) for the different heat treatments. Concentrations are quoted in atomic percent and are listed in order of decreasing number of copper atoms for each material	9

ACKNOWLEDGMENTS

The authors would like to thank Dr. M. A. Sokolov of Oak Ridge National Laboratory and Dr. J. M. Hyde of AEA Technologies for helpful discussions. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation and by the Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, under inter-agency agreement DOE 1886-N695-3W with the U.S. Department of Energy. This research was conducted utilizing the Shared Research Equipment (SHaRE) User Program facilities at Oak Ridge National Laboratory.

FOREWORD

The work reported here was performed at the Oak Ridge National Laboratory (ORNL) under the Heavy-Section Steel Irradiation (HSSI) Program, T. M. Rosseel, Program Manager. The program is sponsored by the Office of Nuclear Regulatory Research of the U.S. Nuclear Regulatory Commission (NRC). The technical monitor for the NRC is C. J. Fairbanks.

This report is designated HSSI Report 24. Reports in this series are listed below:

1. F. M. Haggag, W. R. Corwin, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Irradiation Effects on Strength and Toughness of Three-Wire Series-Arc Stainless Steel Weld Overlay Cladding*, USNRC Report NUREG/CR-5511 (ORNL/TM-11439), February 1990.

2. L. F. Miller, C. A. Baldwin, F. W. Stallman, and F. B. K. Kam, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Neutron Exposure Parameters for the Metallurgical Test Specimens in the Sixth Heavy-Section Steel Irradiation Series*, USNRC Report NUREG/CR-5409 (ORNL/TM-11267), March 1990.

3. S. K. Iskander, W. R. Corwin, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Results of Crack-Arrest Tests on Two Irradiated High-Copper Welds*, USNRC Report NUREG/CR-5584 (ORNL/TM-11575), December 1990.

4. R. K. Nanstad and R. G. Berggren, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Irradiation Effects on Charpy Impact and Tensile Properties of Low Upper-Shelf Welds, HSSI Series 2 and 3*, USNRC Report NUREG/CR-5696 (ORNL/TM-11804), August 1991.

5. R. E. Stoller, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Modeling the Influence of Irradiation Temperature and Displacement Rate on Radiation-Induced Hardening in Ferritic Steels,* USNRC Report NUREG/CR-5859 (ORNL/TM-12073), August 1992.

6. R. K. Nanstad, D. E. McCabe, and R. L. Swain, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Chemical Composition RT_{NDT} Determinations for Midland Weld WF-70*, USNRC Report NUREG/CR-5914 (ORNL-6740), December 1992.

7. R. K. Nanstad, F. M. Haggag, D. E. McCabe, S. K. Iskander, K. O. Bowman, and B. H. Menke, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Irradiation Effects on Fracture Toughness of Two High-Copper Submerged-Arc Welds,* USNRC Report NUREG/CR-5913 (ORNL/TM-12156/V1), October 1992.

8. S. K. Iskander, W. R. Corwin, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Crack-Arrest Tests on Two Irradiated High-Copper Welds*, USNRC Report NUREG/CR-6139 (ORNL/TM-12513), March 1994.

9. R. E. Stoller, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *A Comparison of the Relative Importance of Copper Precipitates and Point Defects in Reactor Pressure Vessel Embrittlement,* USNRC Report NUREG/CR-6231 (ORNL/TM-6811), December 1994.

10. D. E. McCabe, R. K. Nanstad, S. K. Iskander, and R. L. Swain, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Unirradiated Material Properties of Midland Weld WF-70,* USNRC Report NUREG/CR-6249 (ORNL/TM-12777), October 1994.

11. P. M. Rice and R. E. Stoller, Lockheed Martin Energy Systems, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Microstructural Characterization of Selected AEA/UCSB Model FeCuMn Alloys,* USNRC Report NUREG/CR-6332 (ORNL/TM-12980), June 1996.

12. J. H. Giovanola and J. E. Crocker, SRI International, *Fracture Toughness Testing with Cracked Round Bars: Feasibility Study*, USNRC Report NUREG/CR-6342 (ORNL/SUB/94-DHK60), to be published.

13. F. M. Haggag and R. K. Nanstad, Lockheed Martin Energy Systems, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Effects of Thermal Aging and Neutron Irradiation on the Mechanical Properties of Three-Wire Stainless Steel Weld Overlay Cladding,* USNRC Report NUREG/CR-6363 (ORNL/TM-13047), May 1997.

14. M. A. Sokolov and D. J. Alexander, Lockheed Martin Energy Systems, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *An Improved Correlation Procedure for Subsize and Full-Size Charpy Impact Specimen Data,* USNRC Report NUREG/CR-6379 (ORNL/TM-13088), March 1997.

15. S. K. Iskander and R. E. Stoller, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Results of Charpy V-Notch Impact Testing of Structural Steel Specimens Irradiated at ~30 °C to 1 x 10^6 neutrons/cm^2 in a Commercial Reactor Cavity*, USNRC Report NUREG/CR-6399 (ORNL-6886), April 1997.

16. S. K. Iskander, P. P. Milella, and A. Pini, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Results of Crack-Arrest Tests on Irradiated A 503 Class 3 Steel,* USNRC Report NUREG/CR-6447 (ORNL-6894), February 1998.

17. P. Pareige, K. F. Russell, R. E. Stoller, and M. K. Miller, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Influence of Long-Term Thermal Aging on the Microstructural Evolution of Nuclear Reactor Pressure Vessel Materials: An Atom Probe Study,* USNRC Report NUREG/CR-6537(ORNL-13406), March 1998.

18. I. Remec, C. A. Baldwin, and F. B. K. Kam, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Neutron Exposure Parameters for Capsule 10.05 in the Heavy-Section Steel Irradiation Program Tenth Irradiation Series,* USNRC Report NUREG/CR-6600 (ORNL/TM-13548), October 1998.

19. I. Remec, C. A. Baldwin, and F. B. K. Kam, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Neutron Exposure Parameters for the Dosimetry Capsule in the Heavy-Section Steel Irradiation Program Tenth Irradiation Series*, USNRC Report NUREG/CR-6601 (ORNL/TM-13549), October 1998.

20. D. E. McCabe, R. K. Nanstad, S. K. Iskander, D. W. Heatherly, and R. L. Swain, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Evaluation of WF-70 Weld Metal from the Midland Unit 1 Reactor Vessel—Final Report*, USNRC Report NUREG/CR-5736 (ORNL/TM-13748), to be published.

21. Mikhail A. Sokolov and Randy K. Nanstad, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Comparison of Irradiation-Induced Shifts of K_{Jc} and Charpy Impact Toughness for Reactor Pressure Vessel Steels*, USNRC Report NUREG/CR-6609 (ORNL/TM-13755), to be published.

22. S. K. Iskander, C. A. Baldwin, D. W. Heatherly, D. E. McCabe, I. Remec, and R. L. Swain, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Detailed Results of Testing Unirradiated and Irradiated Crack-Arrest Toughness Specimens from the Low Upper-Shelf Energy, High Copper Weld, WF-70*, USNRC Report NUREG/CR-6621 (ORNL/TM-13764), to be published.

23. D. J. Alexander, K. B. Alexander, M. K. Miller, and R. K. Nanstad, Lockheed Martin Energy Research Corporation, Oak Ridge Natl. Lab., Oak Ridge, Tenn., *The Effect of Aging at 343 °C on the Microstructure and Mechanical Properties of Type 308 Stainless Steel Welds*, USNRC Report NUREG/CR-6628 (ORNL/TM-13767), to be published.

24. This report.

The HSSI Program includes both follow-on and the direct continuation of work that was performed under the Heavy-Section Steel Technology (HSST) Program. Previous HSST reports related to irradiation effects in pressure vessel materials and those containing unirradiated properties of materials used in HSSI and HSST irradiation programs are tabulated below as a convenience to the reader.

C. E. Childress, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Fabrication History of the First Two 12-in.-Thick A-533 Grade B, Class 1 Steel Plates of the Heavy-Section Steel Technology Program*, ORNL-4313, February 1969.

T. R. Mager and F. O. Thomas, Westinghouse Electric Corporation, PWR Systems Division, Pittsburgh, Pa., *Evaluation by Linear Elastic Fracture Mechanics of Radiation Damage to Pressure Vessel Steels*, WCAP-7328 (Rev.), October 1969.

P. N. Randall, TRW Systems Group, Redondo Beach, Calif., *Gross Strain Measure of Fracture Toughness of Steels*, HSSTP-TR-3, Nov. 1, 1969.

L. W. Loechel, Martin Marietta Corporation, Denver, Colo., *The Effect of Testing Variables on the Transition Temperature in Steel*, MCR-69-189, Nov. 20, 1969.

W. O. Shabbits, W. H. Pryle, and E. T. Wessel, Westinghouse Electric Corporation, PWR Systems Division, Pittsburgh, Pa., *Heavy-Section Fracture Toughness Properties of A533 Grade B Class 1 Steel Plate and Submerged Arc Weldment*, WCAP-7414, December 1969.

C. E. Childress, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Fabrication History of the Third and Fourth ASTM A-533 Steel Plates of the Heavy-Section Steel Technology Program*, ORNL-4313-2, February 1970.

P. B. Crosley and E. J. Ripling, Materials Research Laboratory, Inc., Glenwood, Ill., *Crack Arrest Fracture Toughness of A533 Grade B Class 1 Pressure Vessel Steel*, HSSTP-TR-8, March 1970.

F. J. Loss, Naval Research Laboratory, Washington, D.C., *Dynamic Tear Test Investigations of the Fracture Toughness of Thick-Section Steel*, NRL-7056, May 14, 1970.

T. R. Mager, Westinghouse Electric Corporation, PWR Systems Division, Pittsburgh, Pa., *Post-Irradiation Testing of 2T Compact Tension Specimens*, WCAP-7561, August 1970.

F. J. Witt and R. G. Berggren, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Size Effects and Energy Disposition in Impact Specimen Testing of ASTM A533 Grade B Steel*, ORNL/TM-3030, August 1970.

D. A. Canonico, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Transition Temperature Considerations for Thick-Wall Nuclear Pressure Vessels,* ORNL/TM-3114, October 1970.

T. R. Mager, Westinghouse Electric Corporation, PWR Systems Division, Pittsburgh, Pa., *Fracture Toughness Characterization Study of A533, Grade B, Class 1 Steel*, WCAP-7578, October 1970.

W. O. Shabbits, Westinghouse Electric Corporation, PWR Systems Division, Pittsburgh, Pa., *Dynamic Fracture Toughness Properties of Heavy-Section A533 Grade B Class 1 Steel Plate*, WCAP-7623, December 1970.

C. E. Childress, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Fabrication Procedures and Acceptance Data for ASTM A-533 Welds and a 10-in.-Thick ASTM A-543 Plate of the Heavy Section Steel Technology Program*, ORNL-TM-4313-3, January 1971.

D. A. Canonico and R. G. Berggren, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Tensile and Impact Properties of Thick-Section Plate and Weldments,* ORNL/TM-3211, January 1971.

C. W. Hunter and J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *Fracture and Tensile Behavior of Neutron-Irradiated A533-B Pressure Vessel Steel*, HEDL-TME-71-76, Feb. 6, 1971.

C. E. Childress, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Manual for ASTM A533 Grade B Class 1 Steel (HSST Plate 03) Provided to the International Atomic Energy Agency*, ORNL/TM-3193, March 1971.

P. N. Randall, TRW Systems Group, Redondo Beach, Calif., *Gross Strain Crack Tolerance of A533-B Steel*, HSSTP-TR-14, May 1, 1971.

C. L. Segaser, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Feasibility Study, Irradiation of Heavy-Section Steel Specimens in the South Test Facility of the Oak Ridge Research Reactor*, ORNL/TM-3234, May 1971.

H. T. Corten and R. H. Sailors, University of Illinois, Urbana, Ill., *Relationship Between Material Fracture Toughness Using Fracture Mechanics and Transition Temperature Tests*, T&AM Report 346, Aug. 1, 1971.

L. A. James and J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *Heavy Section Steel Technology Program Technical Report No. 21, The Effect of Temperature and Neutron Irradiation Upon the Fatigue-Crack Propagation Behavior of ASTM A533 Grade B, Class 1 Steel*, HEDL-TME 72-132, September 1972.

P. B. Crosley and E. J. Ripling, Materials Research Laboratory, Inc., Glenwood, Ill., *Crack Arrest in an Increasing K-Field*, HSSTP-TR-27, January 1973.

W. J. Stelzman and R. G. Berggren, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Radiation Strengthening and Embrittlement in Heavy-Section Steel Plates and Welds*, ORNL-4871, June 1973.

J. M. Steichen and J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *High Strain Rate Tensile Properties of Irradiated ASTM A533 Grade B Class 1 Pressure Vessel Steel*, HEDL-TME 73-74, July 1973.

J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *The Irradiation and Temperature Dependence of Tensile and Fracture Properties of ASTM A533, Grade B, Class 1 Steel Plate and Weldment*, HEDL-TME 73-75, August 1973.

J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *Some Comments Related to the Effect of Rate on the Fracture Toughness of Irradiated ASTM A553-B Steel Based on Yield Strength Behavior*, HEDL-SA 797, December 1974.

J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *The Irradiated Fracture Toughness of ASTM A533, Grade B, Class 1 Steel Measured with a Four-Inch-Thick Compact Tension Specimen*, HEDL-TME 75-10, January 1975.

J. G. Merkle, G. D. Whitman, and R. H. Bryan, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *An Evaluation of the HSST Program Intermediate Pressure Vessel Tests in Terms of Light-Water-Reactor Pressure Vessel Safety*, ORNL/TM-5090, November 1975.

J. A. Davidson, L. J. Ceschini, R. P. Shogan, and G. V. Rao, Westinghouse Electric Corporation, Pittsburgh, Pa., *The Irradiated Dynamic Fracture Toughness of ASTM A533, Grade B, Class 1 Steel Plate and Submerged Arc Weldment*, WCAP-8775, October 1976.

J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *Tensile Properties of Irradiated and Unirradiated Welds of A533 Steel Plate and A508 Forgings*, NUREG/CR-1158 (ORNL/SUB-79/50917/2), July 1979.

J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *The Ductile Fracture Toughness of Heavy-Section Steel Plate*, NUREG/CR-0859, September 1979.

K. W. Carlson and J. A. Williams, Hanford Eng. Dev. Lab., Richland, Wash., *The Effect of Crack Length and Side Grooves on the Ductile Fracture Toughness Properties of ASTM A533 Steel*, NUREG/CR-1171 (ORNL/SUB-79/50917/3), October 1979.

G. A. Clarke, Westinghouse Electric Corp., Pittsburgh, Pa., *An Evaluation of the Unloading Compliance Procedure for J-Integral Testing in the Hot Cell, Final Report*, NUREG/CR-1070 (ORNL/SUB-7394/1), October 1979.

P. B. Crosley and E. J. Ripling, Materials Research Laboratory, Inc., Glenwood, Ill., *Development of a Standard Test for Measuring K_{Ia} with a Modified Compact Specimen*, NUREG/CR-2294 (ORNL/SUB-81/7755/1), August 1981.

H. A. Domian, Babcock and Wilcox Company, Alliance, Ohio, *Vessel V-8 Repair and Preparation of Low Upper-Shelf Weldment*, NUREG/CR-2676 (ORNL/SUB/81-85813/1), June 1982.

R. D. Cheverton, S. K. Iskander, and D. G. Ball, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *PWR Pressure Vessel Integrity During Overcooling Accidents: A Parametric Analysis*, NUREG/CR-2895 (ORNL/TM-7931), February 1983.

J. G. Merkle, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *An Examination of the Size Effects and Data Scatter Observed in Small Specimen Cleavage Fracture Toughness Testing*, NUREG/CR-3672 (ORNL/TM-9088), April 1984.

W. R. Corwin, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Assessment of Radiation Effects Relating to Reactor Pressure Vessel Cladding*, NUREG/CR-3671 (ORNL-6047), July 1984.

W. R. Corwin, R. G. Berggren, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Charpy Toughness and Tensile Properties of a Neutron Irradiated Stainless Steel Submerged-Arc Weld Cladding Overlay*, NUREG/CR-3927 (ORNL/TM-9709), September 1984.

J. J. McGowan, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Tensile Properties of Irradiated Nuclear Grade Pressure Vessel Plate and Welds for the Fourth HSST Irradiation Series*, NUREG/CR-3978 (ORNL/TM-9516), January 1985.

J. J. McGowan, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Tensile Properties of Irradiated Nuclear Grade Pressure Vessel Welds for the Third HSST Irradiation Series*, NUREG/CR-4086 (ORNL/TM-9477), March 1985.

W. R. Corwin, G. C. Robinson, R. K. Nanstad, J. G. Merkle, R. G. Berggren, G. M. Goodwin, R. L. Swain, and T. D. Owings, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Effects of Stainless Steel Weld Overlay Cladding on the Structural Integrity of Flawed Steel Plates in Bending, Series 1*, NUREG/CR-4015 (ORNL/TM-9390), April 1985.

W. J. Stelzman, R. G. Berggren, and T. N. Jones, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *ORNL Characterization of Heavy-Section Steel Technology Program Plates 01, 02, and 03*, NUREG/CR-4092 (ORNL/TM-9491), April 1985.

G. D. Whitman, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Historical Summary of the Heavy-Section Steel Technology Program and Some Related Activities in Light-Water Reactor Pressure Vessel Safety Research*, NUREG/CR-4489 (ORNL-6259), March 1986.

R. H. Bryan, B. R. Bass, S. E. Bolt, J. W. Bryson, J. G. Merkle, R. K. Nanstad, and G. C. Robinson, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Test of 6-in.-Thick Pressure Vessels. Series 3: Intermediate Test Vessel V-8A — Tearing Behavior of Low Upper-Shelf Material*, NUREG-CR-4760 (ORNL-6187), May 1987.

D. B. Barker, R. Chona, W. L. Fourney, and G. R. Irwin, University of Maryland, College Park, Md., *A Report on the Round Robin Program Conducted to Evaluate the Proposed ASTM Standard Test Method for Determining the Plane Strain Crack Arrest Fracture Toughness, K_{Ia}, of Ferritic Materials*, NUREG/CR-4966 (ORNL/SUB/79-7778/4), January 1988.

L. F. Miller, C. A. Baldwin, F. W. Stallman, and F. B. K. Kam, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Neutron Exposure Parameters for the Metallurgical Test Specimens in the Fifth Heavy-Section Steel Technology Irradiation Series Capsules*, NUREG/CR-5019 (ORNL/TM-10582), March 1988.

J. J. McGowan, R. K. Nanstad, and K. R. Thoms, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Characterization of Irradiated Current-Practice Welds and A533 Grade B Class 1 Plate for Nuclear Pressure Vessel Service*, NUREG/CR-4880 (ORNL-6484/V1 and V2), July 1988.

R. D. Cheverton, W. E. Pennell, G. C. Robinson, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Impact of Radiation Embrittlement on Integrity of Pressure Vessel Supports for Two PWR Plants,* NUREG/CR-5320 (ORNL/TM-10966), February 1989.

J. G. Merkle, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *An Overview of the Low-Upper-Shelf Toughness Safety Margin Issue*, NUREG/CR-5552 (ORNL/TM-11314), August 1990.

R. D. Cheverton, T. L. Dickson, J. G. Merkle, and R. K. Nanstad, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., *Review of Reactor Pressure Vessel Evaluation Report for Yankee Rowe Nuclear Power Station (YAEC No. 1735)*, NUREG/CR-5799 (ORNL/TM-11982), March 1992.

INTRODUCTION

The embrittlement of pressure vessel steels during service in a nuclear reactor is clearly evident from the change in mechanical properties. These changes are manifested in an upward shift in the ductile-to-brittle transition temperature and a loss in fracture toughness. These changes have been correlated with the composition of the pressure vessel steel, in particular with the levels of copper, nickel, manganese, and phosphorus, and also with the magnitude of the fluence of the irradiation.

Previous atom probe field ion microscopy investigations of neutron-irradiated pressure vessel steels have clearly established that there are several different types of microstructural features present in these materials. The atom probe field ion microscope has indicated that the most prevalent change in the microstructure during neutron irradiation is the evolution of ultrafine (~2 nm) copper-enriched regions and phosphorus-enriched regions. Other microstructural changes that have been characterized include solute segregation to and precipitation at dislocations and grain and lath boundaries. The contributions of the techniques of atom probe field ion microscopy and atom probe tomography to the understanding of the microstructure of neutron-irradiated pressure vessel steels and related alloys have been reviewed recently [1].

This report presents the results of an atom probe tomography study of the effects of high-fluence neutron irradiation and subsequent short- and long-term post-irradiation annealing treatments of a high-copper submerged arc weld. The technique of atom probe tomography is an extension to atom probe field ion microscopy that enables the x, y, and z coordinates and the elemental identities of the atoms within a small volume to be determined with atomic resolution [2–4]. The analysis volume typically contains between 500,000 and 1,000,000 atoms and originates from a volume in the specimen that is ~10 to ~15 nm square by ~100 to ~250 nm long. These data may then be reconstructed in a computer so that the distribution of all the elements present in the material may be visualized. In addition, material and microstructural parameters such as the size, shape, and number density of ultrafine precipitates and the compositions of precipitates and the surrounding matrix may be estimated.

EXPERIMENT

This atom probe tomography and atom probe field ion microscopy study was performed on a submerged arc weld from the HSSI fifth irradiation series (Weld 73W). The chemical composition of this high copper (0.27 at. % Cu) weld is given in Table 1 [5]. The material was examined after five conditions: after a typical stress relief treatment of 40 h at 607°C, after neutron irradiation to a high fluence of 2×10^{23} n m^{-2} (E > 1 MeV), and after irradiation

Table 1. Bulk chemical composition of the submerged arc weld (weld 73W)

Element	Atomic percent	Weight percent
Cu	0.27	0.25
Mn	1.58	1.56
Ni	0.57	0.60
Mo	0.34	0.58
Si	0.89	0.45
Cr	0.27	0.25
C	0.45	0.098
P	0.009	0.005
S	0.009	0.005
Fe	Balance	Balance

and isothermal anneals of 0.5, 1, and 168 h at 454°C. Blanks (0.25 × 0.25 × 10 mm) for atom probe specimens were cut from Charpy bar specimens with the use of a slow-speed diamond saw. The electropolishing methods used to prepare needle-shaped field ion specimens from these bulk samples have been described previously [6].

The material was characterized in both energy-compensated atom probe field ion microscopes (ECAP) [7,8] and an energy-compensated optical position-sensitive atom probe (ECOPoSAP) [4]. The former type of instrument was used primarily for characterization of the composition of the matrix and for general field ion microscopy of the microstructure. This instrument features high mass resolution. The latter three-dimensional ECOPoSAP instrument was used primarily to provide information on the size, morphology, number density, and composition of the copper-enriched regions formed during irradiation, since the number of atoms collected from each specimen was significantly higher. In both instruments, the conditions used for composition determinations were a specimen temperature of 50K, a pulse fraction of 20% of the standing voltage, and a pulse repetition rate of 1500 Hz. Field ion images were recorded with a specimen temperature of 50K and with the use of neon as the image gas.

RESULTS AND DISCUSSION

The results of the matrix composition determinations for all the materials are summarized in Table 2. It should be noted that these determinations do not include any contributions from the copper-enriched regions and are strictly the copper levels in solid solution in the matrix. As in previous investigations of pressure vessel steels [1], the copper level in the matrix was found to decrease during neutron irradiation, and a small additional decrease in the copper level was observed after post-irradiation annealing. These results are in agreement with previous studies of a surveillance weld and a weld from the Midland reactor [9,10].

Table 2. Matrix compositions of the submerged arc weld (weld 73W) for the five different heat treatments in atomic percent

Element	Stress relieved	Irradiated 2×10^{23} n m^{-2} (E > 1 MeV)	Irradiated + annealed for 0.5 h at 454°C	Irradiated + annealed for 1 h at 454°C	Irradiated + annealed for 168 h at 454°C
Cu	0.12	0.055	0.052	0.049	0.039
Mn	0.94	0.78	1.00	0.82	0.89
Ni	0.51	0.53	0.70	0.57	0.89
Mo	0.15	0.30	0.17	0.19	0.12
Si	0.75	0.62	0.61	0.51	0.66
Cr	0.14	0.20	0.16	0.18	0.15
C	0.01	0.027	0.023	0.01	0.01
P	0.011	0.024	0.003	—	—
Fe	Balance	Balance	Balance	Balance	Balance

— = not detected.

A series of three-dimensional atom maps of the copper, nickel, and manganese atom distributions are shown in Figs. 1–4 for the different materials. In this type of representation, each sphere is the location of an individual atom in the volume [4]. It is evident from the local increase in the density of copper atoms that ultrafine copper-enriched regions are present in all neutron-irradiation and post-irradiation annealed materials. It is also evident from the comparison between the copper, nickel, manganese, and silicon atom maps that the copper-enriched regions are also enriched in nickel, manganese, and silicon. The size and shape of each copper-enriched region may be obtained from these atom maps. The copper-enriched regions were found to be roughly spherical, but the surface of the enriched region was extremely irregular on an atomic scale. The irregular surface has previously been described as a ramified structure [6]. These observations are in agreement with previous atom probe characterizations of neutron-irradiated pressure vessel steels [1].

In addition to the copper-enriched precipitates, phosphorus-enriched regions were also observed. An example of a phosphorus-enriched region in the material that was neutron-irradiated and annealed for 0.5 h at 454°C is shown in Fig. 5. No copper was associated with this phosphorus-enriched region. The number density of these features was at least an order of magnitude lower than that of the copper-enriched regions.

This type of high spatial resolution analysis also enables estimation of the number of atoms associated with each copper-enriched region. Since the spatial coordinates of all the copper atoms are known, the copper atoms that are associated with each copper-enriched precipitate can be determined by locating the copper atoms that were within 0.7 nm of other copper atoms. The value of 0.7 nm was selected from the visual examination of extent of the copper-enriched regions and the absence of the copper concentration in the atom maps. The results for the different materials are summarized in Table 3. It is evident that there is a large variation in the number of copper atoms associated with each precipitate. The minimum size of the precipitate may be estimated from the number of copper atoms by assuming that the copper atoms are arranged within a spherical envelope on a body-centered cubic lattice with the same lattice parameter as iron (or any lattice with the equivalent atomic volume). These results are included in Table 3. It should be noted that these results slightly underestimate the true minimum size, as they are not corrected for the detection efficiency of the mass spectrometer. This correction increases the minimum radius of the precipitate by approximately 12%.

In addition, the center and the radius of gyration of each copper-enriched region can be calculated from the positions of the copper atoms. The center of mass $(\bar{x}, \bar{y}, \bar{z})$ of a feature, such as a precipitate, is given by

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i m_i}{\sum_{i=1}^{n} m_i}, \quad \bar{y} = \frac{\sum_{i=1}^{n} y_i m_i}{\sum_{i=1}^{n} m_i}, \quad \text{and} \quad \bar{z} = \frac{\sum_{i=1}^{n} z_i m_i}{\sum_{i=1}^{n} m_i} \tag{1}$$

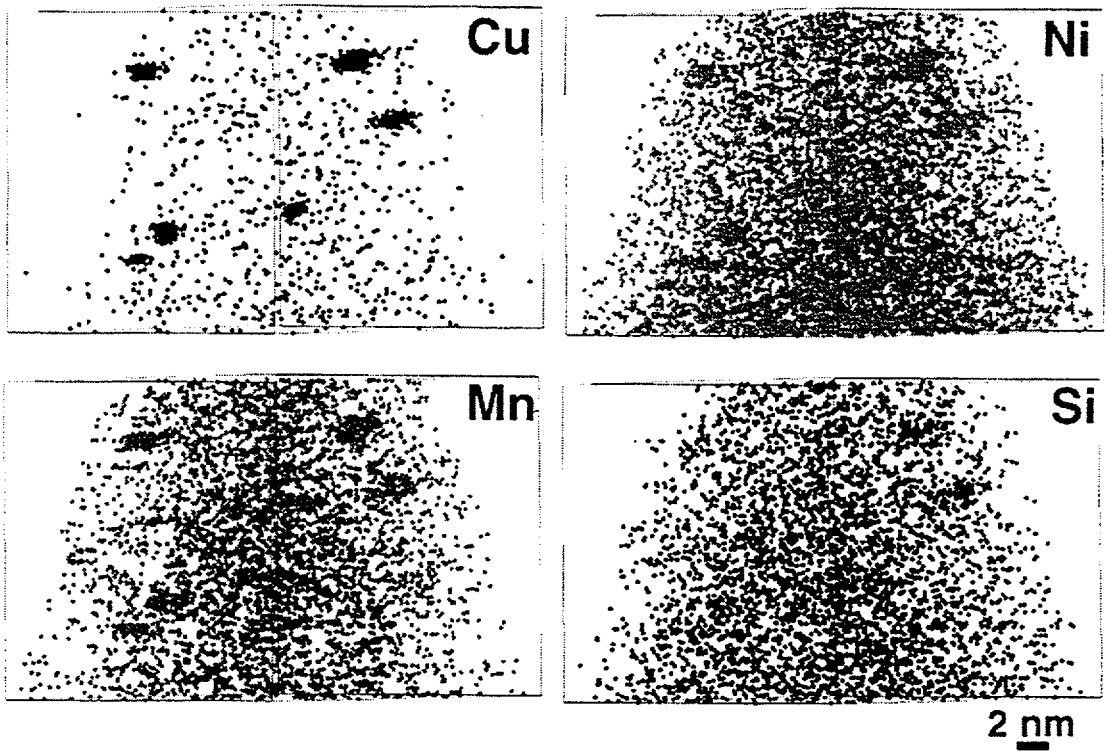


Figure 1. Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2}.

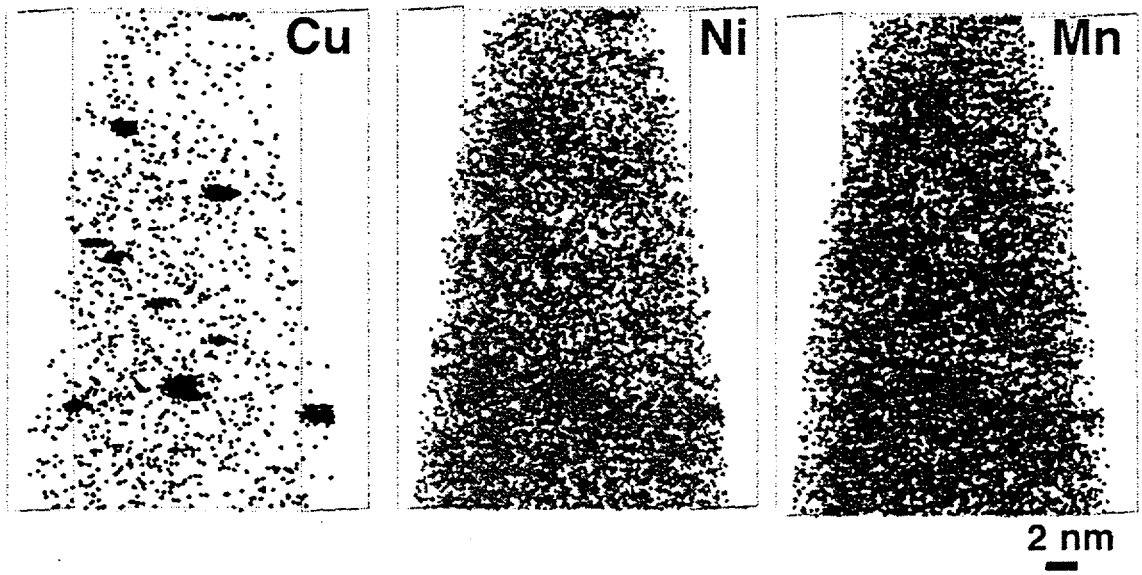


Figure 2. Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C.

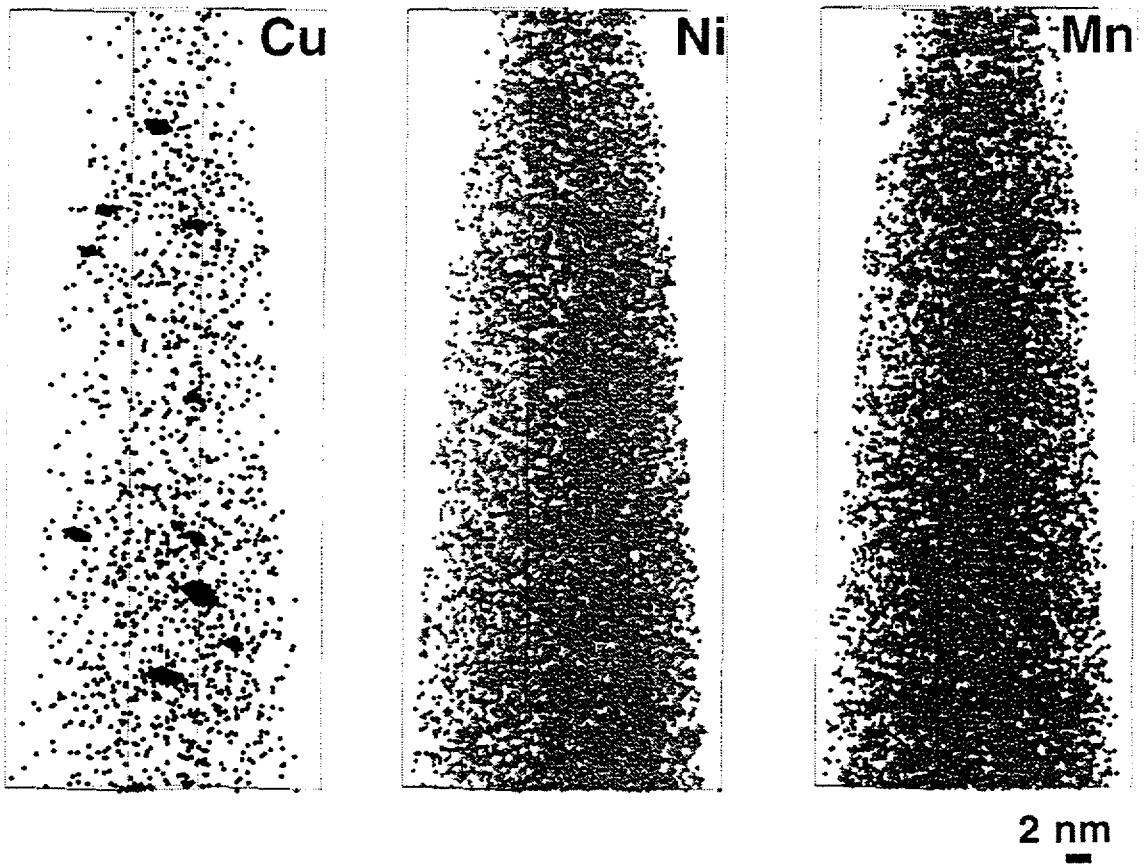


Figure 3. Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 1 h at 454°C.

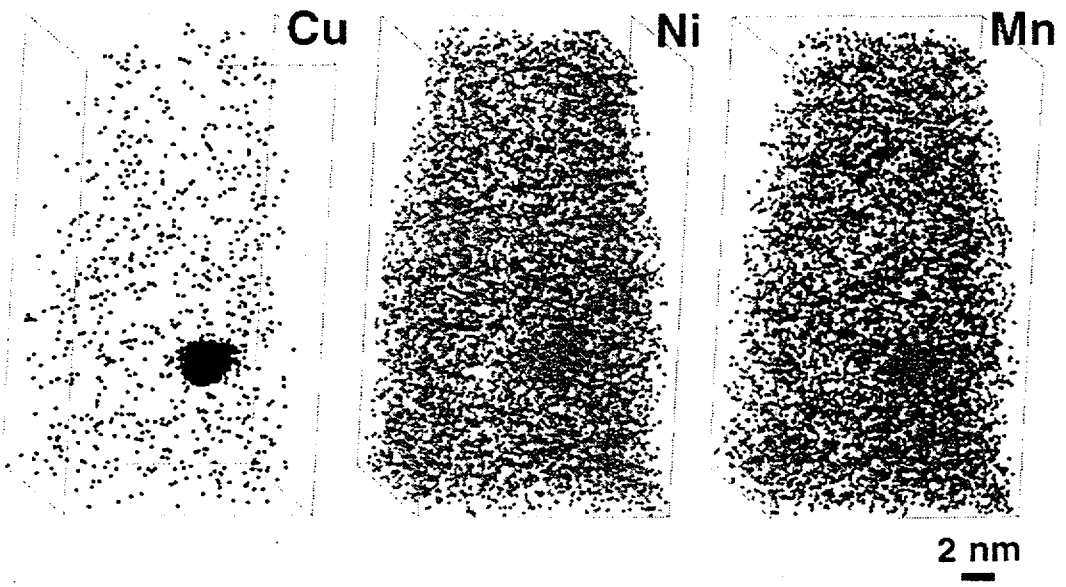


Figure 4. Atom maps of the solute distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 168 h at 454°C.

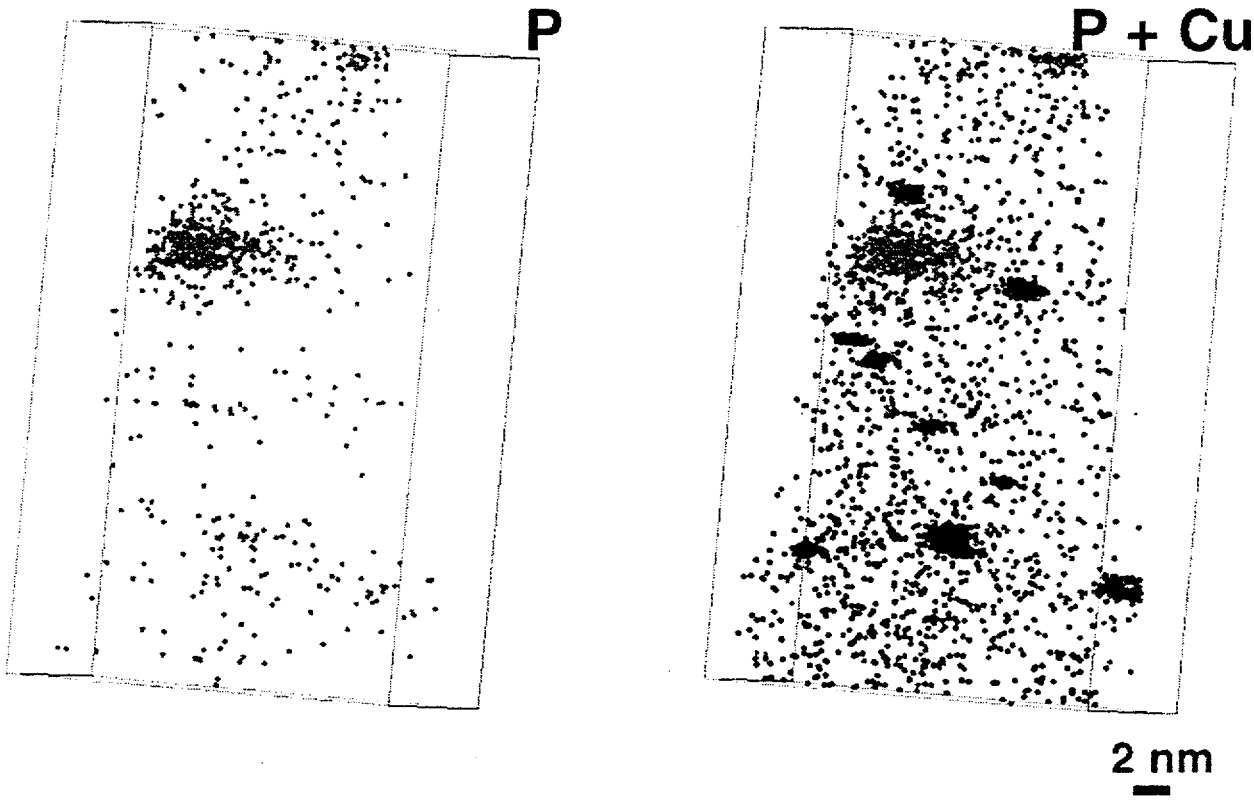


Figure 5. **Atom maps of the phosphorus and copper distribution in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C. A small phosphorus-enriched region is evident.**

Table 3. Number of copper atoms detected in the precipitates and their estimated radii based on the number of copper atoms in the submerged arc weld (weld 73W) for the different heat treatments

Copper-enriched precipitate	Irradiated 2×10^{23} n m^{-2} (E > 1 MeV)		Irradiated + annealed 0.5 h at 454°C		Irradiated + annealed 1 h at 454°C		Irradiated + annealed 168 h at 454°C	
	Ions	r, nm	Ions	r, nm	Ion	r, nm	Ions	r, nm
1	241	0.88	653	1.23	307	0.96	>2287	1.87
2	135	0.73	170	0.79	247	0.89	445	1.08
3	<123	0.71	135	0.73	173	0.79	>35	0.46
4	115	0.69	>122	0.71	163	0.77		
5	84	0.62	75	0.60	122	0.70		
6	43	0.50	75	0.60	120	0.70		
7	36	0.43	60	0.56	115	0.69		
8			34	0.46	89	0.63		
9			>33	0.45	67	0.58		

> Denotes that precipitate was clipped by the analysis volume.

where x_i, y_i, and z_i are the spatial coordinates of each atom; m_i is the mass of each one; and n is the number of atoms in the feature. If all atoms are the same species (i.e., the same mass), this reduces to [11]

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}, \quad \bar{y} = \frac{\sum_{i=1}^{n} y_i}{n}, \quad \text{and} \quad \bar{z} = \frac{\sum_{i=1}^{n} z_i}{n} \tag{2}$$

The radius of gyration is a measurement of how far from the origin (i.e., the center of mass of the precipitate at $\bar{x}$, $\bar{y}$, $\bar{z}$) the entire mass, m_o, might be concentrated and still give the same moment of inertia, I_x. It is given for the one-dimensional case by

$$I_x = \sqrt{\frac{I_x}{m_o}} = \sqrt{\frac{\sum_{i=1}^{n} m_i (x_i - \bar{x})^2}{\sum_{i=1}^{n} m_i}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}} \tag{3}$$

where x_i, y_i, and z_i are the spatial coordinates of each atom; m_i is the mass of each one, and n is the number of atoms in the feature. Similarly the radius of gyration, I_g, for the three-dimensional case is given by

$$I_g = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2 + (y_i - \bar{y})^2 + (z_i - \bar{z})^2}{n}} \tag{4}$$

These estimates assume that the copper distribution defines the extent of the copper-enriched region. These values are summarized for some of the largest copper-enriched precipitates in each treatment in Table 4. A small increase in the radius of gyration was observed with annealing time at 454°C. However, the magnitude of the increase was not statistically significant because of the small number of precipitates encountered and the large variations in their sizes. The variation in the radius of gyration measurements was less than expected from the number of copper atoms in each precipitate. This small variation, coupled with the ramified nature of the precipitates, suggests that the precipitates are far from an equilibrium state during neutron irradiation and the early stages of annealing. It should be noted that these radii of gyration measurements do not take into account the differences in the local magnification between the matrix and the copper-enriched precipitates [10] and are therefore an underestimate of the true size (see below).

Table 4. The radii of gyrations of the precipitates in the submerged arc weld (weld 73W) for the different heat treatments

The order of the data is the same as in Table 3

Copper-enriched precipitate	Irradiated 2×10^{23} n m^{-2} (E > 1 MeV) l_g, nm	Irradiated + annealed 0.5 h at 454°C l_g, nm	Irradiated + annealed 1 h at 454°C l_g, nm	Irradiated + annealed 168 h at 454°C l_g, nm
1	1.00 [1.81]	1.00 [2.06]	1.08 [1.39]	1.47 [2.92]
2	0.96 [1.47]	1.00 [1.47]	0.95 [1.70]	1.79
3	(0.70) [1.28]	1.17 [1.62]	1.10 [1.42]	(0.98)
4	0.78 [1.29]	(0.76) [0.99]	0.97 {1.21]	
5	0.77 [1.26]	0.85 [1.11]	0.88 [1.12]	
6	1.09 [1.47]	0.88 [1.25]	0.92 [1.19]	
7	0.64 [0.80]	0.88 [1.08]	0.88 [1.34]	
8		0.95	0.99 [1.33]	
9		(0.81)	0.98 [1.22]	

( ) Denotes severely clipped precipitate.

[ ] Denotes corrected for local magnification.

The number density of the copper-enriched regions was also estimated from the number of copper-enriched regions in the volume analyzed. The number of particles was taken as either the number of particles whose centers were inside the analyzed volume or the number of particles in the volume that did not intersect the top, left or rear surfaces of the volume. The volume, V, was estimated from the total number of atoms in the volume, N, which was corrected for the detection efficiency of the mass spectrometer, ξ, and the number of atoms per unit volume of the body-centered cubic iron crystal structure (lattice parameter, a_0 = 0.288 nm with 2 atoms per unit cell; that is, $V = N a_0^3/2\xi$. The number densities were estimated to be ~6.4×10^{23} m^{-3} for the neutron-irradiated material and ~6.2, ~6.1, and ~0.5×10^{23} m^{-3} for the materials annealed for 0.5, 1, and 168 h, respectively. As expected because of the coarsening of the copper-enriched regions, the number density decreased slowly over the first hour of annealing and by more than an order of magnitude after 168 h.

The compositional variations of the copper-enriched precipitates were investigated by several different methods. In the first method, the numbers of different types of atoms within a small spherical volume were determined for each copper-enriched region. This measurement yields the average composition of the core of the copper-enriched region. The position of the analysis volume was adjusted to yield the highest local copper concentration within each copper-enriched region. The solute concentration results are summarized in Table 5 for the different treatments. In all cases, the iron, manganese, nickel, and silicon concentrations in the copper-enriched regions were found to be significant. A significant variation in the composition of the individual precipitates was observed. The measured copper levels were significantly different from the equilibrium concentration of the ε-Cu phase of ~95% Cu. The correlation between the copper concentration and the concentration of the other solute elements (i.e., iron, manganese, nickel, and silicon) is shown in Fig. 6. All results indicated that high copper levels were correlated with low iron levels. The correlation with the other elements is less defined.

Table 5. Selected volume precipitate compositions in the submerged arc weld (weld 73W) for the different heat treatments

Concentrations are quoted in atomic percent and are listed in order of decreasing number of copper atoms for each material

	% Fe	% Cu	% Ni	% Mn	% Si
Irradiated 2×10^{23} n m^{-2} (E > 1 MeV)	45.1 63.4 45.1 52.9 78.5 61.2 54.3	35.9 24.8 36.8 36.1 12.7 25.4 32.8	4.9 3.0 6.3 4.2 1.3 4.5 5.2	10.6 5.9 9.0 3.4 2.5 6.0 5.2	2.8 1.0 2.1 2.5 3.8 1.5 2.6
Irradiated + annealed 0.5 h at 454°C	36.1 59.6 58.5 49.6 72.9 69.8 64.8 72.3 77.8 32.4	48.1 35.1 36.6 28.5 22.0 24.7 26.1 21.5 19.4 24.3	7.1 4.3 2.4 7.3 1.7 1.4 3.4 1.5 2.8 16.2	4.4 1.1 2.4 9.8 — 2.7 2.3 3.1 — 18.9	1.1 — — 0.8 1.7 1.4 3.4 1.5 — 2.7
Irradiated + annealed 1 h at 454°C	50.0 56.6 57.7 55.7 64.6 68.3 68.6 73.2	41.1 38.6 38.8 36.1 27.1 29.3 24.6 17.1	2.4 — 1.2 4.1 3.1 1.2 3.3 2.4	3.0 4.8 2.4 2.5 5.2 1.2 3.3 4.9	2.4 — — 1.64 — — — 1.22
Irradiated + annealed 168 h at 454°C	42.9 55.0 48.7	51.0 30.0 39.0	2.76 — 3.77	2.40 15.0 8.49	0.4 — —

Fourteen concentrations not detected.

The difference in the numbers of atoms in these copper-enriched regions was also compared with the number of atoms in similar volumes in the matrix so that the differences in local magnification between the precipitate and matrix regions could be estimated. Variations between ~1.5 and ~4 times the number of atoms in the copper-enriched precipitate and the matrix were measured, and the local magnification was generally higher in precipitates with higher copper contents. These local magnification measurements indicate that the radius-of-gyration results should be increased by from 1.2 to 2 times. The increase in these values due to local magnification differences is in agreement with previous measurements obtained from field ion images on similar thermally aged iron-copper alloys [13]. The corrected values of the radius-of-gyration measurements are included in Table 4. As expected, the

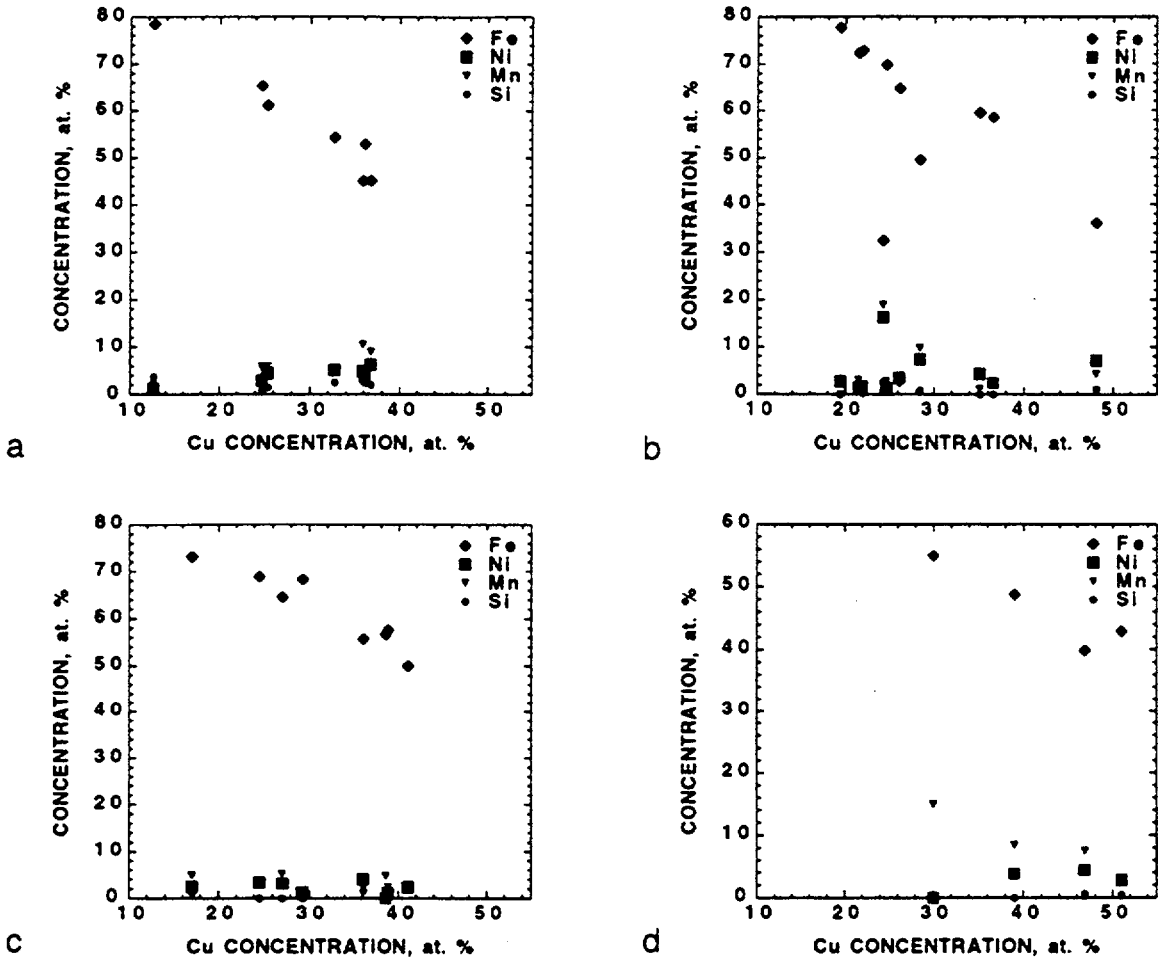
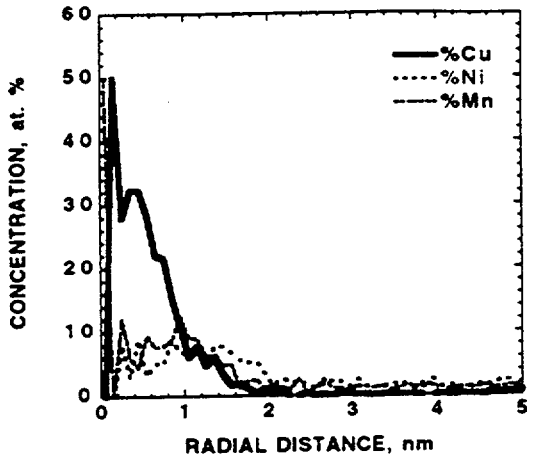
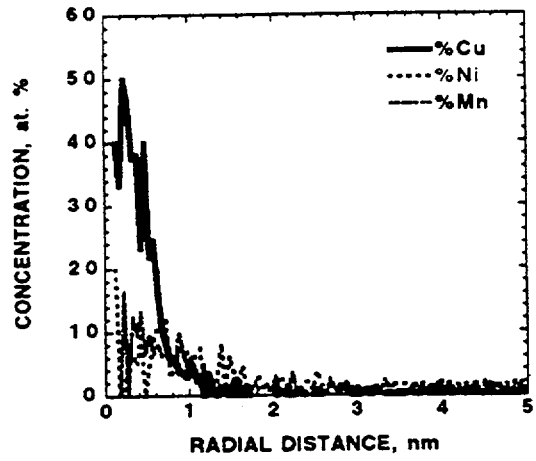


Figure 6. Concentration correlation of the copper-enriched precipitates in weld 73 after (a) neutron irradiation to a fluence of 2×10^{23} n m^{-2}, (b) anneal for 0.5 h, (c) anneal for 1 h, and (d) anneal for 168 h at 454°C.

radius-of-gyration measurements are slightly larger than the estimate based on the number of copper atoms because there are other solutes within the precipitate.

In the second method, the radial concentration profile from the center of the copper-enriched region into the matrix was determined. The center of the copper-enriched region was determined from the distribution of the copper atoms in each copper-enriched region, as described previously. Then the concentrations of the different types of solute atoms that were within spherical shells of equal thickness were determined as a function of distance from the center of the copper-enriched regions. Examples of the results for the different treatments are shown in Figs. 7–10. It should be noted that the ramified or diffuse nature of the copper-enriched regions and small non-uniformities in the shape of each region will influence the sharpness of the interface in these radial composition profiles. The enrichments of copper, manganese, nickel, and silicon and the depletion in iron in the copper-enriched regions are





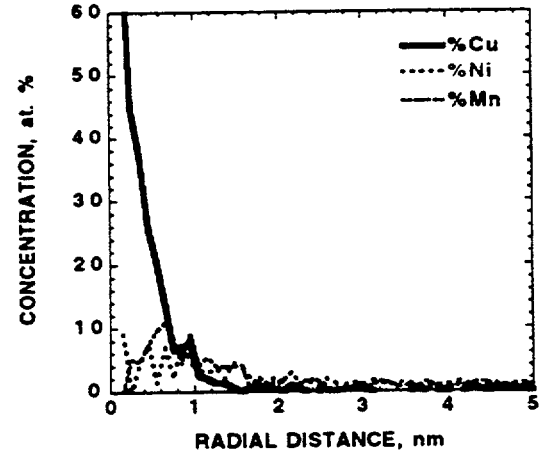
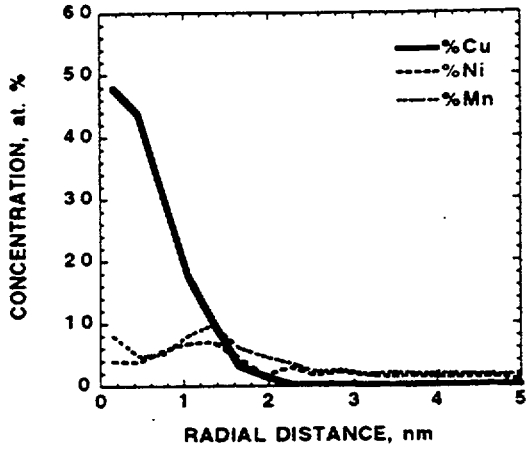
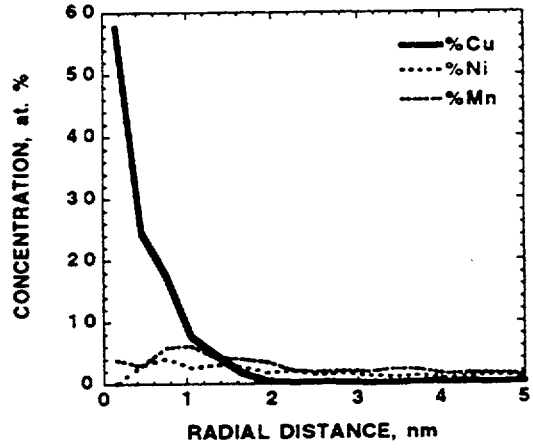


Figure 7. Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2}.





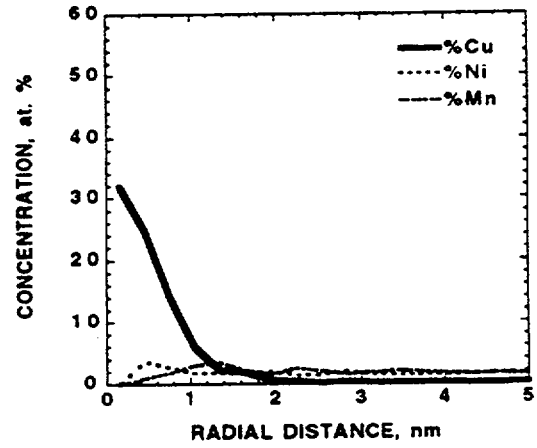


Figure 8. Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 0.5 h at 454°C.

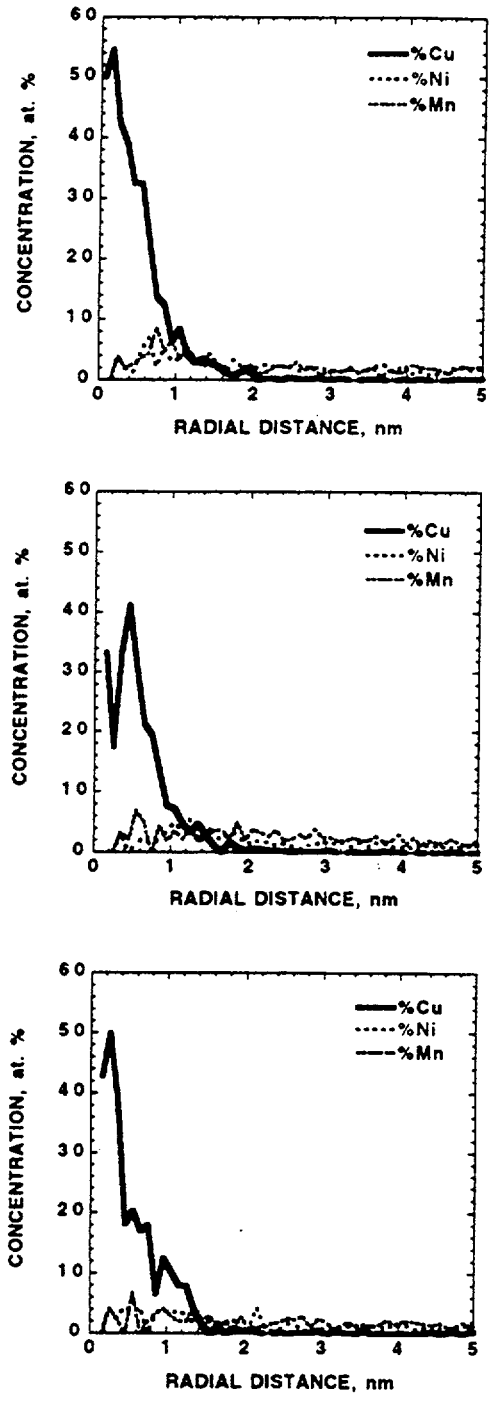


Figure 9. Radial concentration distributions of three copper-enriched precipitates in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 1 h at 454°C.

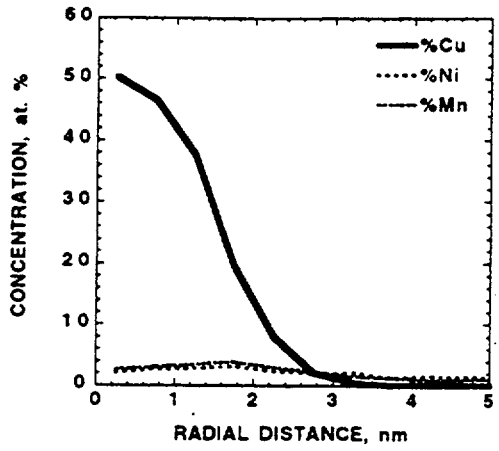


Figure 10. Radial concentration distribution of a copper-enriched precipitate in weld 73 after neutron irradiation to a fluence of 2×10^{23} n m^{-2} and anneal for 168 h at 454°C.

clearly evident. It was also evident that there were some solute enrichments at the precipitate matrix interface. Linear composition profiles through the center of the copper-enriched regions also indicated that the solute enrichments were not always uniformly distributed.

CONCLUSIONS

The size and composition of the copper-enriched precipitates that form during neutron irradiation to a high fluence have been determined by atom probe tomography and atom probe field ion microscopy. As expected, the size was found to increase and the number density of these precipitates to decrease during isothermal annealing at 454°C. Significant levels of iron, nickel, manganese, and silicon were found in the core of the copper-enriched precipitates. Enrichments of nickel and manganese were observed at the precipitate-matrix interface. The distribution of the solute enrichment was not always uniform within the copper-enriched region.

REFERENCES

1. M. K. Miller, P. Pareige, and M. G. Burke, "Understanding Pressure Vessel Steels: An Atom Probe Perspective," *Materials Characterization*, 1999.

2. M. K. Miller, A. Cerezo, M. G. Hetherington, and G. D. W. Smith, *Atom Probe Field Ion Microscopy*, Oxford University Press, Oxford, England, 1996.

3. M. K. Miller and G. D. W. Smith, *Atom Probe Microanalysis, Principles and Applications to Materials Problems*, Material Research Society, Pittsburgh, 1989.

4. M. K. Miller, "Three-Dimensional Atom Probes," *J. Microscopy*, **192**, 1–16 (1997).

5. R. K. Nanstad, F. M. Haggag, D. E. McCabe, S. K. Islander, K. O. Bowman, and B. H. Menke, *Irradiation Effects on Fracture Toughness Of Two High-Copper Submerged Arc Welds*, HSSI Series 5, USNRC Report NUREG/CR-5913, ORNL/TM-12156/V1.

6. M. K. Miller, M. G. Hetherington, and M. G. Burke, "Atom Probe Field-Ion Microscopy: A Technique for Microstructural Characterization of Irradiated Materials on the Atomic Scale," *Metall. Trans.*, 20A, 2651–2261 (1989).

7. M. K. Miller, "The ORNL Atom Probe," *J. de Physique*, 47-C2, 493–498 (1986).

8. J. M. Sarrau, F. Danoix, B. Deconihout, M. Bouet, A. Menand, and D. Blavette, "The Rouen Energy-compensated Atom Probe," *Appl. Surf. Sci.* 76/77, 367–373 (1994).

9. P. Pareige, R. E. Stoller, K. F. Russell, and M. K. Miller, "Atom Probe Characterization of the Microstructure of Nuclear Pressure Surveillance Materials after Neutron Irradiation and after Annealing Treatments," *J. Nucl. Mater.*, **249**, 165–174 (1997).

10. M. K. Miller and K. F. Russell, "Atom Probe Characterization of Copper Solubility in the Midland Weld after Neutron Irradiation and Thermal Annealing," *J. Nucl. Mater.* **250**, 223–228 (1997).

11. P. Pareige, *Etude a La Sonde Atomique de L'Evolution Microstructurale Sous Irradiation D'Alliages Ferritiques FeCu et D'Aciers de Cuve de Reacteurs Nucleaires*, Ph.D. Thesis, University of Rouen, Rouen, France, 1994.

12. M. K. Miller and M. G. Hetherington, "Local Magnification Effects in the Atom Probe," *Surf. Sci.* **246**, 442–449 (1991).

13. P. Auger, P. Pareige, M. Akamatsu, and J. C. Van Duysen, "Microstructural Characterization of Atom Clusters in Irradiated Pressure Vessel Steels and Model Alloys," *J. Nucl. Mater.* **211**, 194–201 (1994).

NRC FORM 335 (2-89) NRCM 1102, 3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER (Assigned by NRC, Add Vol., Supp., Rev., and Addendum Numbers, if any.)

NUREG/CR-6629
ORNL/TM-13768

2. TITLE AND SUBTITLE

Atom Probe Tomography Characterization of the Solute Distributions in a Neutron-Irradiated and Annealed Pressure Vessel Steel Weld

3. DATE REPORT PUBLISHED

MONTH: November YEAR: 2000

4. FIN OR GRANT NUMBER

W6953

5. AUTHOR(S)

M. K. Miller, P. Pareige, K. F. Russell, and R. E. Stoller

6. TYPE OF REPORT

Technical

7. PERIOD COVERED *(Inclusive Dates)*

8. PERFORMING ORGANIZATION - NAME AND ADDRESS *(If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)*

Oak Ridge National Laboratory
Oak Ridge, TN 37831-6285

9. SPONSORING ORGANIZATION - NAME AND ADDRESS *(If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)*

Division of Engineering Technology
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

10. SUPPLEMENTARY NOTES

C. J. Fairbanks, NRC Project Manager

11. ABSTRACT *(200 words or less)*

A combined atom probe tomography and atom probe field ion microscopy study has been performed on a submerged arc weld irradiated to high fluence in the Heavy-Section Steel Irradiation (HSSI) fifth irradiation series (Weld 73W). The composition of this weld is Fe - 0.27 at. % Cu, 1.58% Mn, 0.57% Ni, 0.34% Mo, 0.27% Cr, 0.58% Si, 0.003% V, 0.45% C, 0.009% P, and 0.009% S. The material was examined after five conditions: after a typical stress relief treatment of 40 h at 607 °C, after neutron irradiation to a fluence of 2×10^{23} n m^{-2} (E > 1 MeV), and after irradiation and isothermal anneals of 0.5, 1, and 168 h at 454 °C. This report describes the matrix composition and the size, composition, and number density of the ultrafine copper-enriched precipitates that formed under neutron irradiation and the change in these parameters with post-irradiation annealing treatments.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

Pressure vessel steels
Atom probe tomography
Thermal annealing
Copper
Embrittlement
Irradiated materials
Weldments

13. AVAILABILITY STATEMENT

Unlimited

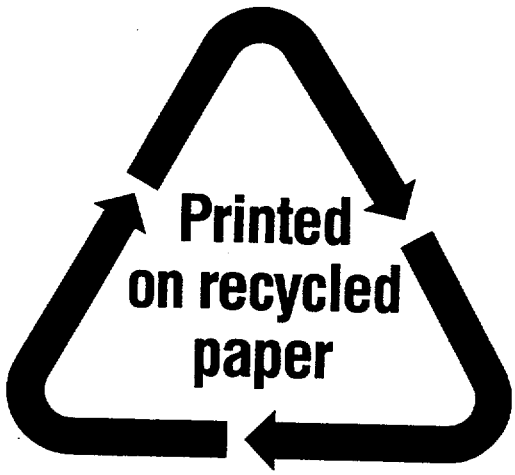
14. SECURITY CLASSIFICATION

(This Page) Unclassified

(This Report) Unclassified

15. NUMBER OF PAGES

16. PRICE



Federal Recycling Program

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001