
Influence of Long-Term Thermal Aging on the Microstructural Evolution of Nuclear Reactor Pressure Vessel Materials

An Atom Probe Study

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Abstract

Atom probe field ion microscopy (APFIM) investigations of the microstructure of unaged (as-fabricated) and long-term thermally aged (~100,000 h at 280°C) surveillance materials from commercial reactor pressure vessel steels were performed. This combination of materials and conditions permitted the investigation of potential thermal-aging effects. This microstructural study focused on the quantification of the compositions of the matrix and carbides. The APFIM results indicate that there was no significant microstructural evolution after a long-term thermal exposure in weld, plate, or forging materials. The matrix depletion of copper that was observed in weld materials was consistent with the copper concentration in the matrix after the stress-relief heat treatment. The compositions of cementite carbides aged for 100,000 h were compared with the Thermocalc™ prediction. The APFIM comparisons of materials under these conditions are consistent with the measured change in mechanical properties such as the Charpy transition temperature.

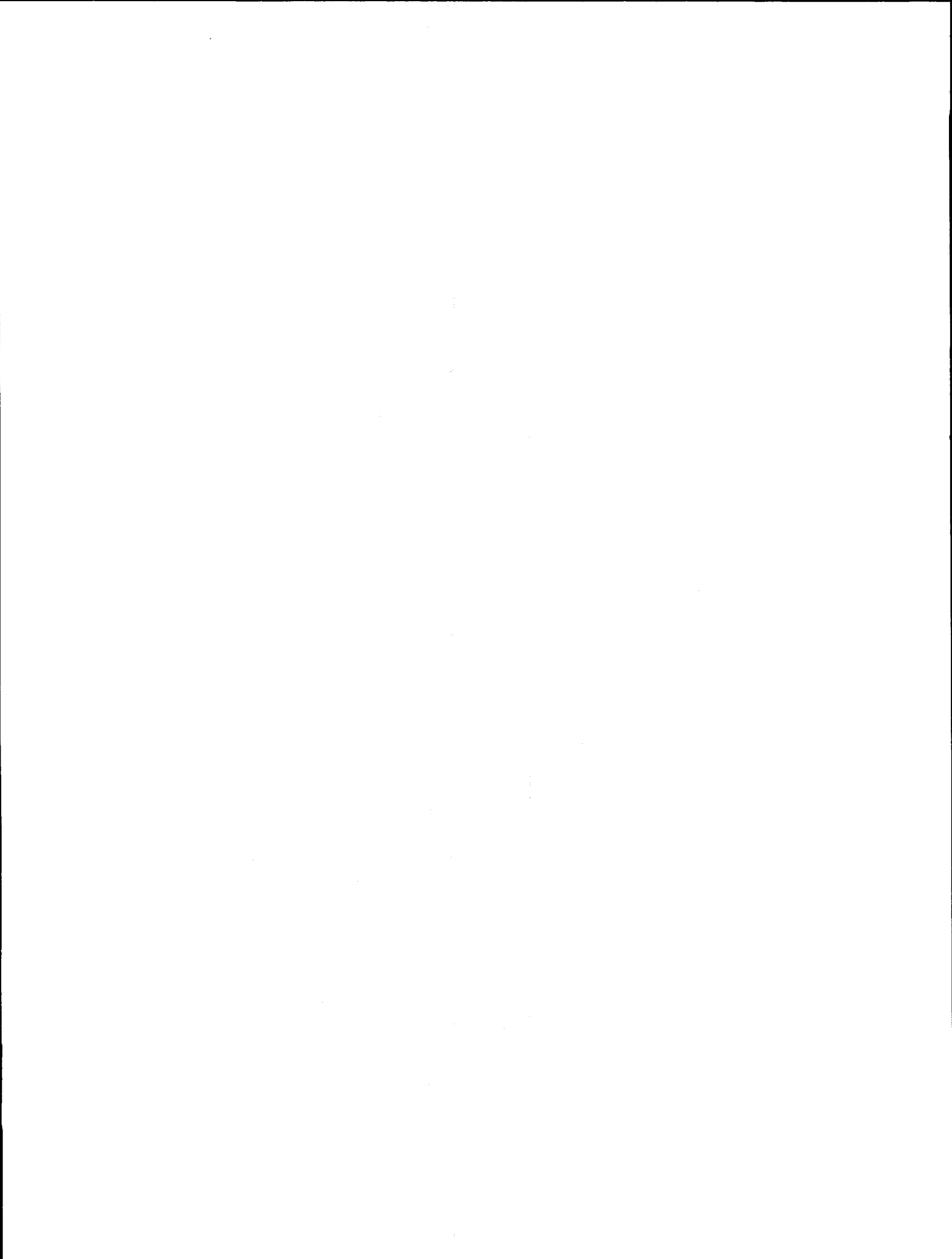
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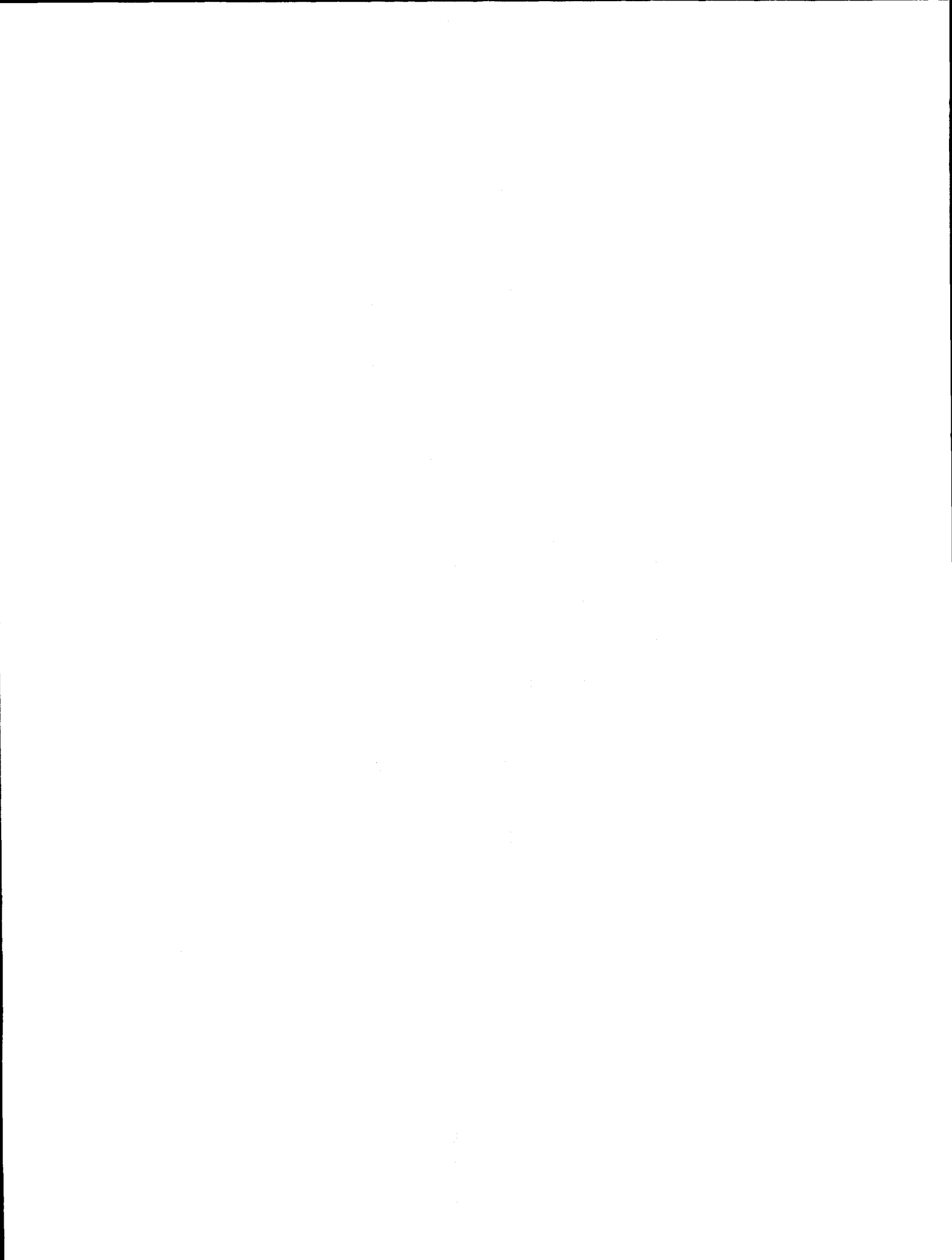
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Foreword

The work reported here was performed at the Oak Ridge National Laboratory (ORNL) under the Heavy-Section Steel Irradiation (HSSI) Program, W. R. Corwin, 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 M. G. Vassilaros.

This report is designated HSSI Report 17. 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/CR5859 (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), to be published.
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 $\sim 30^{\circ}\text{C}$ to 1×10^6 neutrons/cm² in a Commercial Reactor Cavity*, USNRC Report NUREG/CR-6399 (ORNL-6886), April 1997.
16. S. K. Iskander, P. O. 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), to be published.
17. 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.

Influence of Long-Term Thermal Aging on the Microstructural Evolution of Nuclear Reactor Pressure Vessel Materials: An Atom Probe Study*

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Introduction

Surveillance programs for nuclear reactor vessels were primarily designed to monitor the radiation-induced changes occurring in the mechanical properties of the pressure vessel materials. Nowadays, a large set of data is available on the mechanical properties and also the microstructural evolution of irradiated materials. The embrittlement of vessel steels and weldments is known to be related to the presence of residual elements such as copper and phosphorus. Recent microstructural investigations have conclusively shown that the presence of these elements leads to the radiation-enhanced or radiation-induced formation of ultrafine copper-enriched clusters associated with nickel, manganese, silicon, phosphorous, and iron.¹⁻¹⁰ However, this evolution of the microstructure has been observed in materials that have been neutron-irradiated for several years at temperatures near 290°C. It is therefore possible that some of the degradation in mechanical properties may be a result of the long-term thermal-aging component.

Some previous research has indicated the potential for thermal degradation of the mechanical properties of materials used in the construction of nuclear power systems when they are operated at relatively high temperatures (>371°C).¹¹ However, degradation in properties as a result of long-term exposure at lower temperatures (~300°C) is still an open question.¹²

Among the studies on pressure vessel steels, Pense¹³ detected no shift in the ductile-to-brittle transition temperature (DBTT) of an A302 Mn-Mo plate steel after a relatively short aging time of 500 h at 370°C. After the same aging time, an A203 Mn-Ni steel exhibited shifts in the transition temperature in excess of 40°C. Thermal-aging data are also available for a SA-302B steel for periods of 9,726 h and 26,114 h at 307°C; these data were reported from the surveillance program of the Big Rock Point Reactor (BRP).^{14,15} These data indicated little effect of thermal aging on the Charpy impact results of both the SA-302, Grade B modified steel (which is equivalent to the current SA-533, Grade B1 steel) base metal and weld metal. Also, one capsule from the Oconee Unit 1 pressurized water reactor (PWR) aged at 304°C for 15,800 h showed no significant shift in DBTT for the same materials as described above.¹⁶ Recent results¹⁷ concerning materials removed from Oconee Unit 3, aged for 103,000 h at 280°C, and from Arkansas Unit 1, aged for 93,000 h at 280°C, have shown that thermal aging had only a minor effect on the impact properties of both SA-302B base and weld metal. Both modest increases and decreases in the DBTT and the energy on the upper shelf were observed; however, the overall changes resulting from thermal aging were of such small magnitude as to be considered insignificant. Because the evaluation of the Charpy impact properties was inconclusive, the authors of Ref. 17 recommended that additional investigation should be performed to determine whether thermal aging was having an impact on these materials. They suggested that tensile and fracture toughness testing should be performed and that microstructural characterization of the materials was needed.

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The main objective of the work presented in this paper was to use the technique of atom probe field ion microscopy (APFIM)^{18,19} to characterize the microstructure and the composition of low-temperature (~300°C), long-term (~100,000 h) thermally aged plate, forging, and weld materials from the Babcock and Wilcox (B&W) Master Integrated Reactor Vessel Surveillance Program in order to investigate the potential thermal-aging effects. It is important to determine whether there are any changes in the composition of the matrix and whether any ultrafine precipitates had formed due to the thermal component of the service environment only. If such changes were observed they would provide an early indication of the potential for thermal embrittlements at the longer times (~300,000 h) associated with the vessel lifetime.

Also, the embrittlement of pressure vessel steels and weldments during neutron irradiation is known to be related to the presence of residual elements, especially copper and phosphorus. Thus, it is of prime interest to have accurate estimates of the levels of these impurities in the materials prior to irradiation. These parameters are key factors in the prediction of the embrittlement of a pressure vessel during neutron irradiation, and they can only be measured by an ultrafine scale microstructural technique such as APFIM. Thus unaged specimens have been investigated with the atom probe in addition to characterizing the thermally aged materials.

Materials Description

Five structural steels were selected for the examination of long-term thermal-aging effects. Both Oconee Unit 3 and Arkansas Unit 1 reactors have thermal-aging boxes containing pieces of surveillance materials. The material removed from the thermal-aging boxes included forging, plate, and two weld metals. The base and weld metals are representative of the materials used to fabricate the beltline shell course regions of the Oconee Unit 3 and Arkansas Unit 1 reactor pressure vessels. In addition, the boxes contained ASTM correlation monitor plate material. The base metal materials were SA-533, Grade B, Class 1 plate steel and SA-508, Class 2 forging steel. The two weld metals were typical Mn-Mo-Ni weld wire, Linde 80 flux submerged-arc welds. The chemical compositions of the five materials are reported in Table 1.

The specimen-aging capsules were located in boxes used for irradiation on the service structure support of the reactor vessel heads. The boxes were located under the head insulation to help maintain the aging temperature and within the flow of the entering coolant, which helped maintain the capsules at the same temperature as the reactor vessel wall. As a result of the location of these boxes, the surveillance material was exposed to an actual neutron fluence of less than $1 \times 10^{14} \text{ n.m}^{-2}$, or essentially zero insofar as material damage is concerned. The exact exposure time for each set of materials was difficult to determine because of the time allowance for reactor heat-up, cool-down, and hot standby. The aging times given in Table 2 for these materials reflect a 10% increase of the actual effective full-power times when the surveillance material was removed.

The materials have also been characterized in the unaged condition to have a full characterization of the microchemistry of materials prior to irradiation and to be able to determine the effects of exposure to temperature alone. The heat-treatment and stress-relief histories of these materials are given in Table 2.

Experimental

The APFIM technique is particularly well suited to the characterization of these pressure vessel steels because of its near-atomic resolution and its ability to chemically analyze features on the near-atomic

Table 1. Chemical composition (bulk chemistry) of Babcox and Wilcox
Owners Group surveillance materials

Identification	%	Cu	Ni	Mn	Si	P	C	S	Mo	Cr
Plate A	wt %	0.15	0.52	1.32	0.2	0.01	0.21	0.016	0.57	0.19
	at. %	0.13	0.49	1.33	0.39	0.018	0.97	0.028	0.33	0.20
Plate B	wt %	0.17	0.64	1.39	0.21	0.013	0.23	0.013	0.50	—
	at. %	0.15	0.60	1.40	0.41	0.023	1.06	0.022	0.29	—
Forging	wt %	0.02	0.76	0.72	0.21	0.014	0.24	0.012	0.62	0.34
	at. %	0.017	0.72	0.72	0.41	0.025	1.11	0.021	0.36	0.36
Weld A	wt %	0.28	0.59	1.49	0.51	0.016	0.09	0.016	0.39	0.06
	at. %	0.24	0.56	1.5	1.01	0.03	0.42	0.03	0.23	0.06
Weld B	wt %	0.30	0.58	1.63	0.61	0.017	0.08	0.012	0.39	0.10
	at. %	0.26	0.55	1.64	1.20	0.03	0.37	0.021	0.22	0.10

Table 2. Thermal history of as-received (reference) and long-term
thermally aged commercial alloys

Material type	Heat number	Heat treatment ^a (as-received)	Thermal aging condition
Plate A	C5114-1	Austenitized 899–927°C for 1 h/in., WQ Tempered 649°C for 1 h/in., AC Stress-relieved 593–621°C for 29 h, FC	93,000 h Arkansas Unit-1 280°C
Plate B HSST 02	A1195-1	Austenitized 829–913°C for 4 h, WQ Tempered 649–677°C for 4 h, FC Stress-relieved 593–621°C for 40 h, FC	93,000 h, Arkansas Unit-1 280°C
Forging	ANK-191	Austenitized 854–877°C for 4 h, WQ Tempered 666–688°C for 10 h, WQ Stress-relieved 593–621°C for 30 h, FC	103,000 h, Oconee Unit-3 282°C
Weld A	WF-193	Stress-relieved 593–621°C for 29 h, FC	93,000 h Arkansas Unit-1 280°C
Weld B	WF-209-1	Stress-relieved 593–621°C for 30 h, FC	103,000 h Oconee Unit-3 282°C

^a(WQ = water quench, AC = air cool, FC = furnace cool).

scale.^{18,19} The microstructural characterizations were performed in the ORNL energy-compensated IPFIM.²⁰

The experimental conditions required to obtain accurate APFIM data are well known for these ferritic steels. In particular, it is necessary to cool down the specimen to a temperature of 50 K to avoid a systematic error on the copper-level measurement. Field ion specimens were electropolished using standard procedures¹⁸ from blanks that were cut from Charpy specimens. All compositions reported in this work are quoted in atomic percent.

Results

A parallel set of experiments has been undertaken with unaged and thermally aged materials. The results concerning the chemical compositions of the ferritic matrix are summarized in Table 3. Concentration uncertainties (2σ) result from counting statistics, as given by the standard deviation $\sigma = [X(1 - X)/N]^{1/2}$, where X is the measured concentration of an element and N is the number of atoms collected in each analysis.¹⁹ It must be noted that these reactor pressure vessel steels can exhibit significant compositional variation from one specimen to another, particularly because only a small volume of material ($\approx 3 \times 10^{-25} \text{ m}^3$) is sampled from any given specimen. The values in Table 3 are an average of several experiments in which N is typically $\sim 60,000$ atoms.

Because copper repartitioning is a major contributing factor in the embrittlement of pressure vessel steels, particular attention has been paid to this element. The composition variation was particularly evident in the measurement of the copper level in the plates A and B. Severe fluctuations in the copper content from one specimen to another were observed, varying from 0.02 to 0.14 at. % Cu. However, the average copper solute concentration determined in the ferritic matrix is consistent with the nominal level for the two plates and the forging materials. On the other hand, a depletion of copper was observed in the matrix of the weld A and weld B metals for both unaged and thermally aged samples. This depletion cannot be due to the spatial fluctuation mentioned above because only 70% of the nominal level was detected.

A coarser microstructural characterization with the techniques of optical metallography and analytical transmission electron microscopy has been performed on the weld A material.²¹ Results from the literature show that the weld metal contains mixed equiaxed and dendritic grains. The steel contains predominantly mixtures of acicular ferrite and ferrite-carbide aggregate totaling about 97% of the microstructure of the material. This alloy shows the presence of large, randomly distributed, spherical inclusions containing primarily Mn and Si. The average measured composition of these Mn-containing precipitates indicates the presence of 0.2 at. % Cu in the precipitates. The microstructure also exhibits rounded elongated precipitates, identified as M_3C carbides, which are located primarily on grain boundaries with only occasional carbides within the grains. The average composition of these carbides indicates the presence of 0.6 at. % Cu in the precipitates. Small M_2C -type carbides were also found, again mostly on grain boundaries, randomly distributed, but generally associated with other precipitates. The average composition indicates the presence of 0.4 at. % Cu in these carbides. However, the low level of copper encountered in these different features cannot fully account for the measured copper depletion from the nominal ~ 0.25 to ~ 0.17 at. % Cu measured in the matrix.

The stress relief heat treatment for the weld A and weld B materials was performed at a temperature between 593 and 621 °C. The predicted solubility limit of copper in the iron-copper binary system ranges between 0.17 and 0.24 at. % for these two temperatures. The detected value of 0.17 at. % can be explained by the solubility limit of copper in the ferritic solid solution at the stress-relief treatment. This suggests the formation of other copper-rich precipitates during the stress-relief heat treatment, or

Table 3. Chemical compositions (at. %) of the ferritic matrix determined by APFIM in unaged (UnA) and long-term thermally aged (Th-A) materials^a

	Plate A		Plate B		Forging		Weld A		Weld B	
	UnA	Th-A	UnA	Th-A	UnA	Th-A	UnA	Th-A	UnA	Th-A
Cu	0.11 ± 0.05	0.09 ± 0.03	0.09 ± 0.05	0.07 ± 0.03	0.03 ± 0.01	0.03 ± 0.02	0.14 ± 0.03	0.15 ± 0.05	0.16 ± 0.03	0.17 ± 0.02
Ni	0.64 ± 0.13	0.74 ± 0.10	0.74 ± 0.15	0.50 ± 0.11	0.72 ± 0.07	0.63 ± 0.10	0.45 ± 0.06	0.45 ± 0.09	0.42 ± 0.05	0.43 ± 0.05
Mn	0.95 ± 0.15	1.30 ± 0.13	0.64 ± 0.14	1.05 ± 0.17	0.48 ± 0.06	0.53 ± 0.09	1.20 ± 0.10	0.90 ± 0.12	1.24 ± 0.09	1.22 ± 0.09
Si	0.41 ± 0.10	0.62 ± 0.09	0.44 ± 0.12	0.43 ± 0.10	0.50 ± 0.06	0.44 ± 0.08	1.05 ± 0.10	0.80 ± 0.12	1.73 ± 0.10	1.49 ± 0.09
P	0.02 ± 0.02	0.003 ± 0.003	0.01 ± 0.01	0.007 ± 0.007	0.02 ± 0.01	0.003 ± 0.003	0.03 ± 0.03	0.02 ± 0.02	0.05 ± 0.02	0.07 ± 0.02
C	— —	0.006 ± 0.006	0.02 ± 0.02	— —	0.004 ± 0.004	— —	0.005 ± 0.005	— —	0.008 ± 0.008	0.03 ± 0.01
Mo	0.11 ± 0.05	0.17 ± 0.04	0.12 ± 0.06	0.15 ± 0.06	0.12 ± 0.03	0.08 ± 0.03	0.18 ± 0.04	0.14 ± 0.05	0.20 ± 0.04	0.23 ± 0.04
Cr	0.11 ± 0.05	0.06 ± 0.02	0.04 ± 0.04	0.08 ± 0.05	0.15 ± 0.03	0.20 ± 0.05	0.03 ± 0.03	0.03 ± 0.01	0.07 ± 0.02	0.06 ± 0.02

^aAll compositions are the average of several experiments ($\pm 2\sigma$).

also during the furnace cooling period (at a cooling rate of $\sim 8^\circ\text{C/h}$ to $\sim 310^\circ\text{C}$), even though they have not been detected in this investigation. However, coarse copper-enriched precipitates have been detected at grain boundaries of A533B steels by APFIM.⁷

The Si and Ni contents of the matrix are, within the standard deviation, in good agreement with the nominal composition of the alloy. The depletion of carbon and molybdenum in the materials suggests the presence of a high volume fraction of carbides, particularly in plates A and B and the forging materials. This high volume fraction of carbides in these materials may also explain the observed phosphorus matrix depletion. Indeed, phosphorus is often encountered at ferrite-carbide interfaces. In all materials, the detected level of manganese is always slightly lower than the nominal concentration. This depletion is due to its presence in cementite carbides, as shown below.

Analyses were performed on both the carbides and the matrix to characterize the structure of these unaged and long-term thermally aged materials. The more common features encountered in the atom probe analyses of these steels are M_3C cementite carbides and molybdenum-containing carbides.

Molybdenum-containing carbides were frequently observed in both unaged and thermally aged specimens. The small carbides have a disc, needle, or spherical shape, whereas the larger precipitates are generally spherical, as shown in Figures 1 and 2. The sizes of the observed carbides were determined to be between 5 to 20 nm. The core composition of these particles is given in Table 4. The large uncertainties for these features are due to the small numbers of ions collected from such small precipitates. The Mo:C ratio, in both the unaged and thermally aged materials, is close to that of Mo_2C .



Figure 1. Field ion micrograph of disk-shaped molybdenum carbides in the weld B surveillance material.

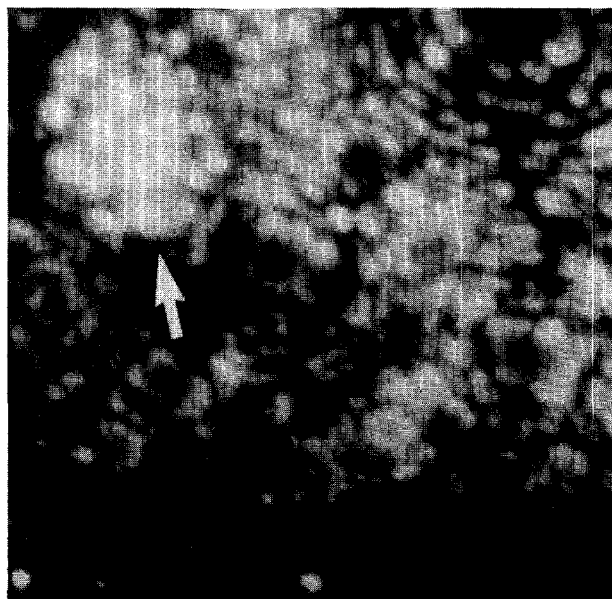


Figure 2. Field ion micrograph of spherical molybdenum carbides in the weld B surveillance material.

Table 4. Composition of intragranular molybdenum-rich carbides in unaged or long-term thermally aged materials

Element	% at	2 σ
Mo	63.6	16.7
Cr	3.0	3.0
C	33.4	16.4

atoms during the atom probe analysis of the core of the dislocation is shown in Figure 4. Each line represents the number of atoms detected per two atomic planes of materials field evaporated from the specimen. This figure clearly indicates that Mo, P, and C are detected in the vicinity of the dislocation. The concentrations of these elements decrease significantly in regions far removed from the dislocation.

In addition, molybdenum atoms were also detected in the vicinity of dislocations, sometimes associated with carbon and phosphorus, as evident in Figures 3 and 4. A field ion image of a dislocation having a Burgers vector component normal to the specimen surface is shown in Figure 3. The presence of a dislocation converts the usual pattern of concentric rings at a crystallographic pole into a spiral at its point of emergence on the specimen surface.²² Bright spots, characteristic of molybdenum atoms, that decorate the dislocation can be observed near its point of emergence. The sequence of evaporation of the

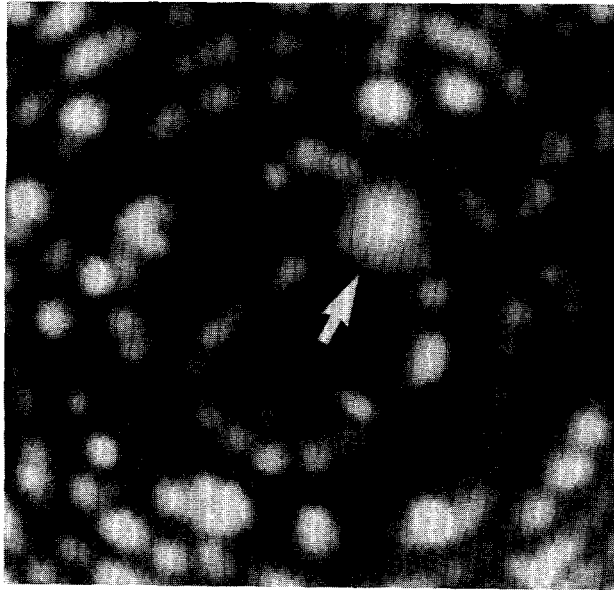


Figure 3. Field ion micrograph of a decorated dislocation in the unaged forging material. Bright and diffuse spots are molybdenum or phosphorus.

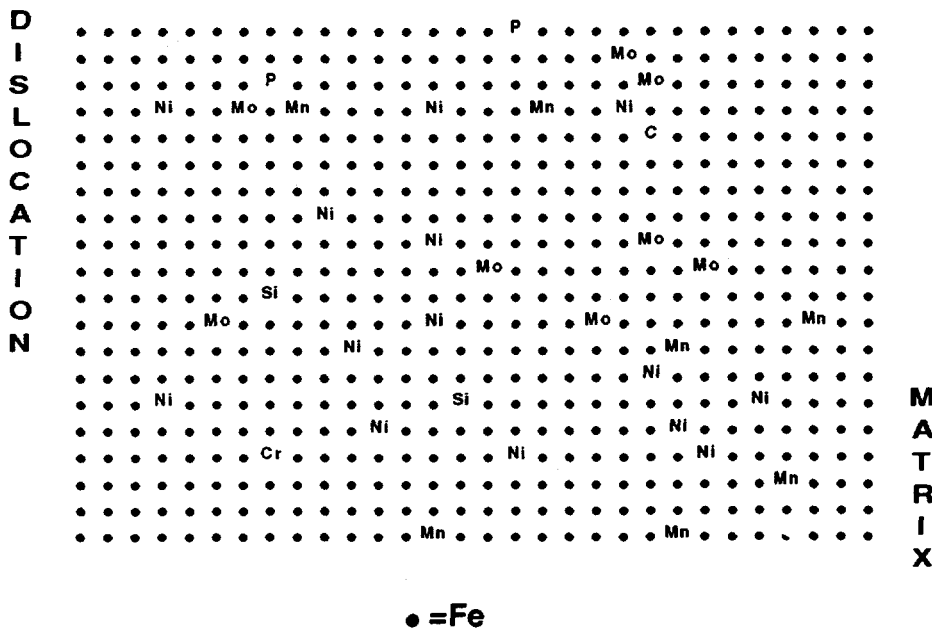


Figure 4. Sequence of arrival of ions at the detector from the analyzed dislocation (see Figure 3). Note the Mo, C, and P enrichments in the core of the dislocation. Each line represents the removal of approximately two atomic planes of material from the specimen.

In addition to the Mo_2C carbides and the cores of decorated dislocations, molybdenum is also observed at the grain boundaries. A field ion image of a grain boundary observed in the long-term thermally aged weld B material is shown in Figure 5. This micrograph clearly indicates that the grain boundary is decorated with a 1- to 2-nm-thick layer of molybdenum carbide precipitates. This type of decoration has been observed in various Russian and Western steels and is a common feature of molybdenum-containing pressure vessel steels.^{7,8,23}

Another common feature encountered in these materials is the presence of M_3C cementite carbides. A field ion micrograph of a cementite-ferrite interface observed in the thermally aged Plate B material is shown in Figure 6. The ferrite can be easily recognized by the presence of crystallographic poles (i.e., families of concentric rings), which are not evident in the darkly imaging cementite phase. A brightly imaging molybdenum carbide precipitate is also evident at the interface. A composition profile starting in this molybdenum carbide and emerging immediately into a cementite

precipitate located at the interface is shown in Figure 7. It is evident from this composition profile that there is a large Fe and Mn content in the cementite but little solubility of the Fe, Cr, or Mn alloying elements in the Mo_2C precipitate. Analyses were performed in unaged and thermally aged specimens to determine whether there was an effect of the ~10 years thermal-aging treatment on the evolution of the composition of cementite. Analyses were successful in the Plate A for the unaged specimen and in the Plate B for the thermally aged one. The chemical compositions and stress-relief heat treatment of these two materials are so similar that they can be compared. In addition, the atom probe results were compared with

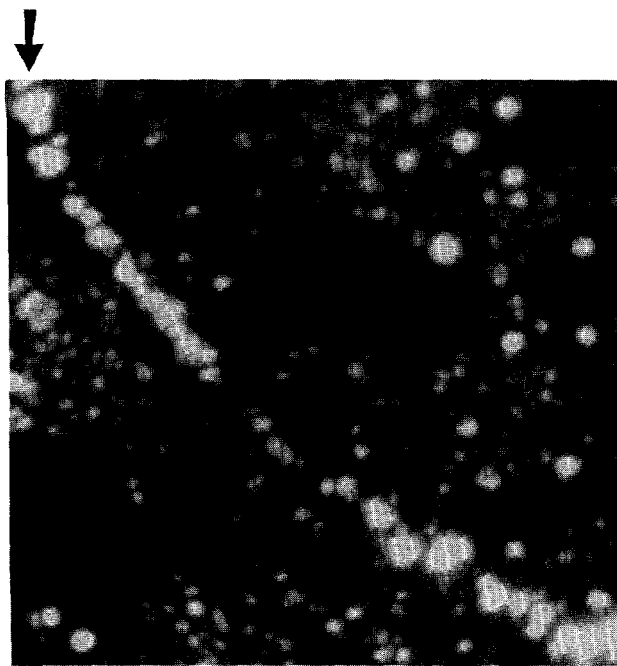


Figure 5. Decorated grain boundary in the weld B long-term thermally aged surveillance material. Bright spots are ultrafine Mo_2C carbides.

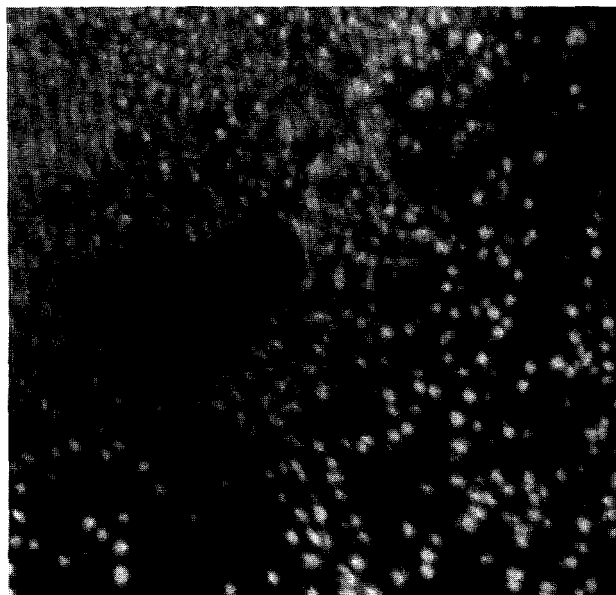


Figure 6. Darkly imaging cementite and brightly imaging ferrite in long-term thermally aged plate B material. Bright region at the interface is Mo_2C carbide (see Figure 7).

thermodynamic predictions.²⁴ ThermocalcTM calculations were performed at two temperatures (620 and 593°C) within the stress-relief heat treatment and also at 300°C, the temperature at which specimens were thermally aged (93,000 h in the case of the Plate B). The results are summarized in Table 5.

The atom probe results revealed, in both unaged and thermally aged materials, carbides with classic M_3C stoichiometry, where M stands for Fe and Mn (in majority), Mo, Cr, and Ni (in minority) and also Cu and V (as traces, 0.02 at. %). These results are similar to those observed in previous analyses of the Chooz A pressure vessel steel⁹ and weld metal.²¹ In addition, the experimental compositions are in good agreement with the ThermocalcTM predictions for materials aged at 593 to 620°C. In all cases, the compositions are comparable to the predicted values at ~600°C. This agreement indicates that long-term thermal aging has no significant impact on the evolution of the microchemistry of cementite carbides.

These initial APFIM microstructural examinations performed on unaged and long-term, low-temperature, thermally aged materials show no significant evolution of the structure of the material. No phase transformation has been observed for this low-temperature heat treatment. Unaged materials and materials thermally aged for approximately 10 years have a similar ferritic matrix chemistry and carbide compositions. These results are consistent with the observed mechanical properties of these materials.¹⁷ A general review of the data on thermally aged material indicates virtually no significant change in the impact data. Only small variations in the Charpy V-notch impact properties were observed for all materials after exposure at the thermal-aging temperature. Small

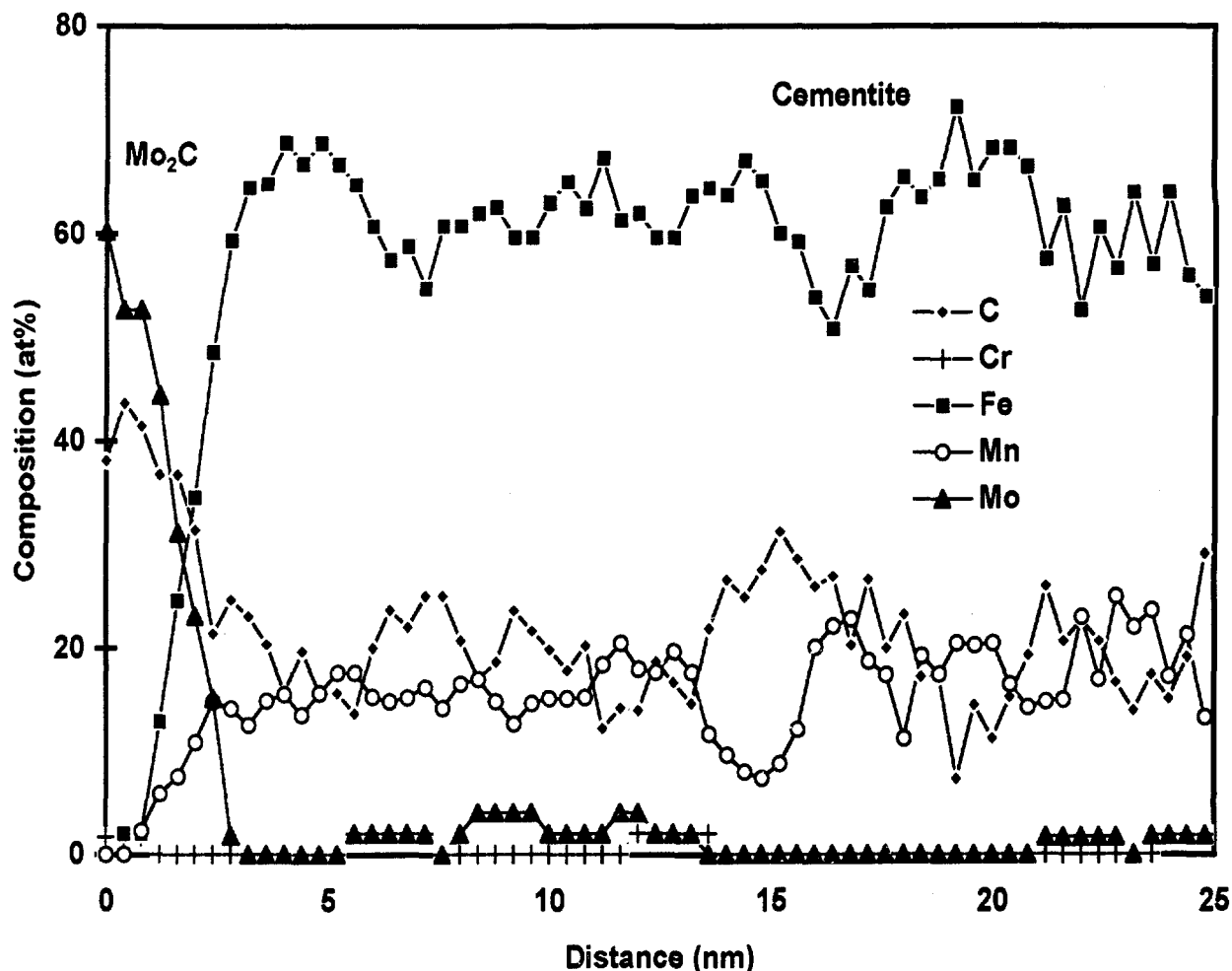


Figure 7. Composition profile through a molybdenum carbide and cementite in long-term thermally aged plate B surveillance material.

increases ($\sim 1^{\circ}\text{C}$) in transition temperature were observed for the forging metal and weld B surveillance materials aged at 103,000 h, and their upper-shelf energies demonstrated small decreases (3 to 11 J). The Charpy V-notch results for plate A and weld metal A aged for 93,000 h revealed differences in that the 41-J transition temperatures for both materials decreased slightly.

Also, and especially for the weld materials, the copper remains in solid solution with a concentration following the solubility of copper in iron for unaged specimens. A metastable solid solution is observed for thermally aged specimens. This confirms that the thermal mobility of copper in iron at 300°C is effectively zero.

Conclusion

Microstructural characterization of long-term ($\sim 100,000$ h) thermally aged (300°C) and unaged surveillance materials obtained from the B&W Owners Group was performed. Two welds, two plates, and one forging material were investigated. The comparison between the thermally aged materials and unaged materials permitted, for the first time, the investigation of a potential thermal-aging effect. Although a general review of the thermal-aging data indicates that there may be some propensity toward embrittlement in sensitive materials,^{11,12} the materials examined in this study did not exhibit any

Table 5. Atom probe analyses of the cementite carbides. Comparison of the atom probe results with the Thermocalc™ predictions

	Fe	C	Mn	Mo	Cr	Ni
Plate A Unaged Stress-relieved 593–621°C for 29 h, FC						
Thermocalc prediction (620°C)	59.1	25.0	11.1	1.5	3.1	0.1
Thermocalc prediction (593°C)	57.5	25.0	12.5	1.6	3.3	0.1
Atom probe experiment (593–620°C)	64 ± 0.8	25.6 ± 0.7	8.7 ± 0.5	1.2 ± 0.2	0.5 ± 0.1	–
Thermocalc prediction (300°C)	36.5	25.0	29.9	3.4	5.0	0.1
Plate B Long-term thermally aged Stress-relieved 593–621°C for 40 h, FC 93,000 h at 280°C						
Thermocalc prediction (620°C)	61.8	25.0	11.6	1.5	–	0.1
Thermocalc prediction (593°C)	60.4	25.0	12.9	1.5	–	0.1
Thermocalc prediction (300°C)	42.1	25.0	29.3	3.35	–	0.2
Atom probe experiment 93,000 h @ 280°C	61.1 ± 0.1	25.4 ± 0.9	11.9 ± 0.7	0.9 ± 0.2	–	0.2 ± 0.1

significant embrittlement or microstructural evolution. The same matrix copper level was found before and after the long thermal-aging treatment. In the two welds, a significant decrease of the copper level in the matrix over the nominal bulk composition was found and is due to copper precipitation during the stress-relief heat treatment. This APFIM comparison of the microstructures in all three conditions is consistent with the measured mechanical properties (transition temperature shift); i.e., no significant changes in either the microstructure or the mechanical properties has been observed.

References

1. M. K. Miller and S. S. Brenner, *Res. Mechanica*, **10** 161 (1984).
2. M. K. Miller, J. A. Spitznagel, S. S. Brenner, and M. G. Burke, "Microanalytical Investigations of Light Water Reactor Materials Using the Atom Probe," pp. 523-28 in *Proc. 2nd Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors, Monterey, 1985*, ed. J. T. A. Roberts, J. R. Weeks, and G. J. Theus, American Nuclear Society, La Grange Park, Ill., 1986.
3. M. G. Burke and S. S. Brenner, *J. Physique*, **47-C2**, 239 (1986).
4. S. P. Grant, S. L. Earp, S. S. Brenner, and M. G. Burke, "Phenomenological Modeling of Radiation Embrittlement in Light Water Reactor Vessels with Atom Probe and Statistical Analysis," pp. 385-92 in *Proc. 2nd Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors, Monterey, 1985*, ed. J. T. A. Roberts, J. R. Weeks, and G. J. Theus, American Nuclear Society, La Grange Park, Ill., 1986.
5. M. K. Miller and M. G. Burke, *J. Physique*, **48-C6**, 429 (1987).
6. M. G. Burke and M. K. Miller, *J. Physique*, **49-C6**, 283 (1988).
7. M. K. Miller, M. G. Hetherington, and M. G. Burke, *Met. Trans.*, **20A**, 2651 (1989).
8. M. K. Miller and M. G. Burke, *J. Nucl. Mater.*, **195**, 68 (1992).
9. P. Pareige, J. C. Van Duysen, and P. Auger, *Appl. Surf. Sci.*, **67**, 342 (1993).
10. P. Pareige and M. K. Miller, *Appl. Surf. Sci.*, **67**, 370 (1996).
11. S. L. Hoyt et al., *Transactions of the ASME*, **68**, 571 (1946).
12. R. K. Nanstad, D. J. Alexander, W. R. Corwin, E. D. Eason, G. R. Odette, R. E. Stoller, and J. A. Wang, *Preliminary Review of Data Regarding Chemical Composition and Thermal Embrittlement of Reactor Vessel Steels*, ORNL/NRC/LTR-95/1, Oak Ridge National Laboratory, January 1995.
13. A. W. Pense, R. D. Stout, and E. H. Kottcamp, *Welding J.*, **42**, 5415 (1963).
14. C. Z. Serpan and H. E. Watson, *Nuclear Engineering and Design*, **11**, 393 (1970).
15. C. Z. Serpan, H. E. Watson, and J. R. Hawthorne, *Nuclear Engineering and Design*, **11**, 368 (1970).
16. M. J. Lowe, Jr., *Radiation Embrittlement and Surveillance of Nuclear Reactor Pressure Vessels: An International Study*, ASTM STP 819, ed. L. E. Steele, American Society for Testing and Materials, 146 (1983).

17. M. J. De Van, A. L. Lowe, Jr., and S. Wade, "Evaluation of Thermal-Aged Plates, Forgings, and Submerged-Arc Weld Metals," p. 268 in *Effects of Radiation on Materials: 16th International Symposium*, ASTM STP 1175, ed. A. S. Kumar, D. S. Gelles, R. K. Nanstad, and E. A. Little, American Society for Testing and Materials, Philadelphia, 1993.
18. M. K. Miller and G. D. W. Smith, *Atom Probe Microanalysis: Principles and Applications to Materials Problems*, Materials Research Society, Pittsburgh, 1989.
19. M. K. Miller, A. Cerezo, M. G. Hetherington, and G. D. W. Smith, *Atom Probe Field Ion Microscopy*, Oxford University Press, Oxford, United Kingdom, 1996.
20. M. K. Miller *J. Phys.*, **47-C2**, 493 (1986).
21. K. R. Lawless and A. L. Lowe, Jr., "Further Microstructural Characterization of Submerged-Arc Weld Metals," p. 186 in *Effects of Radiation on Materials: 15th International Symposium*, ASTM STP 1125, ed. R. E. Stoller, A. S. Kumar, and D. S. Gelles, American Society for Testing and Materials, Philadelphia, 1992.
22. K. M. Bowkett and D. A. Smith, *Field Ion Microscopy*, North Holland, Amsterdam, 1970.
23. M. K. Miller, R. Jayaram, and K. F. Russell, *J. Nucl. Mater.*, **225**, 215 (1995).
24. B. Sundman, B. Jansson, and J. O. Anderson, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, **9**, 153 (1985).

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M. G. Vassilaros, NRC Project Manager

11. ABSTRACT (200 words or less)

Atom probe field ion microscopy (APFIM) investigations of the microstructure of unaged (as-fabricated) and long-term thermally aged (~100,000 h at 280°C) surveillance materials from commercial reactor pressure vessel steels were performed. This combination of materials and conditions permitted the investigation of potential thermal-aging effects. This microstructural study focused on the quantification of the compositions of the matrix and carbides. The APFIM results indicate that there was no significant microstructural evolution after a long-term thermal exposure in weld, plate, or forging materials. The matrix depletion of copper that was observed in weld materials was consistent with the copper concentration in the matrix after the stress-relief heat treatment. The compositions of cementite carbides aged for 100,000 h were compared with the Thermocalc™ prediction. The APFIM comparisons of materials under these conditions are consistent with the measured change in mechanical properties such as the Charpy transition temperature.

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