

# Martensite transformation, microsegregation, and creep strength of 9 Cr-1 Mo-V steel weld metal

M. L. Santella<sup>1</sup>, R. W. Swindeman<sup>1</sup>, R. W. Reed<sup>1</sup>, and J. M. Tanzosh<sup>2</sup>

<sup>1</sup> Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

<sup>2</sup> Babcock & Wilcox Company, Barberton, Ohio 44203

## Abstract

The 9Cr-1Mo-V (P91) steel is a high strength alloy that normally transforms completely to martensite during air cooling. This means that issues related to the handling of weldments during welding operations, and between the completion of welding and post weld heat treatments are important concerns. Measurements of specimen dilations during controlled thermal cycles were used to follow the martensite transformation in a P91 base metal and a weld deposit. For identical thermal cycles, the base metal transformed completely to martensite after normalizing, but the weld deposit did not. The effect of this difference in transformation behavior was that austenite was retained in the weld deposit after tempering. The retained austenite transformed to martensite upon cooling from the tempering temperature, resulting in small amounts of untempered martensite in fully heat treated weld deposit. An analysis of microsegregation by computational thermodynamics suggested that partitioning of alloying elements increased the range between the martensite transformation start and finish temperatures in the weld deposit, increasing the likelihood of retained austenite in it. Creep testing at 600°C and stresses of 120 MPa and 186 MPa showed that weld deposit specimens with untempered martensite had low creep rates and relatively long rupture lives.

## Introduction

In the USA in the early 1980's, tubing of 9Cr-1Mo-V (P91) steel was introduced into the superheaters of power boilers as a replacement for 300 series austenitic stainless steels [1]. Because P91 steel is a high-strength alloy that normally transforms completely to martensite during air cooling [2], the specification of preheat and post weld heat treating (PWHT) conditions is an important practical matter [3,4]. One aspect of this issue is the handling of weldments between completion of welding and PWHT. Weldments that are cooled to room temperature prior to PWHT will transform more completely to martensite than weldments that are maintained at or above minimum preheat temperature prior to PWHT. Consequently, weldments that are cooled to room temperature are less likely to

contain untempered martensite after PWHT. However, maintaining preheat temperature prior to PWHT is essential for minimizing the probability of hydrogen cracking in weld heat-affected zones. In addition, it makes more efficient use of energy resources, and it may be desirable for practical reasons, depending on the welded component size and the available facilities for material handling and heat treating.

This paper describes the initial analysis and testing of a submerged arc weldment made in 2-in-thick P91 plate and given a PWHT of 8 h at 774°C. The transformation behavior after normalizing and tempering of the weld deposit and a P91 base metal was determined from specimen dilations measured during controlled heating and cooling using a Gleeble™ thermomechanical simulator. Creep testing of weld deposit specimens was done in air at 600°C at stresses of 120 MPa (17.4 ksi) and 186 MPa (27 ksi).

## Experimental Details and Materials

The chemical compositions of the alloys used for this work are given in Table 1. The submerged arc weld was made using Thermanit MTS3 welding filler metal (AWS A5.28, ER90S-B9) and Marathon 543 flux, both products of Böhler Thyssen. The 2-in-thick plate used for the weldment was produced by Bethlehem Lukens Plate and is identified as BLP9Cr in Table 1. The plates were prepared for welding with a single-vee groove using a 60° included angle. A macrophotograph of the weldment is shown in Fig. 1. A total of 44 weld beads was used to complete the weldment. The weldment was given a PWHT of 8 hours at 774°C (1425°F) before being supplied for testing and analysis. Specimens from normalized-and-tempered plate identified as heat 30383 were used to establish baseline transformation behavior for P91 plate. This also permitted more of the weldment to be committed to mechanical test specimens.

A Gleeble™ 3500 thermomechanical simulator was used to determine the  $M_s$  temperatures where martensite starts to form during cooling. The Gleeble specimens used for this study were 6.35 mm (0.25 in) diameter x 108 mm (4.25 in) long rods. In the weld deposit, the rods were cut transverse to the welding direction from near the weld surface. The width of the weld at this location was about 45 mm (1.75 in). This insured that the

**Table 1.** Alloy chemical compositions

ID/heat	Analyzed composition, wt%									
	C	Mn	Si	Cr	Mo	Ni	Nb	V	N	Al
Weld	0.099	0.61	0.17	9.33	0.97	0.80	0.043	0.23	0.051	0.022
BLP9Cr	0.10	0.41	0.33	8.61	0.90	0.14	0.067	0.21	0.056	0.028
30383	0.083	0.46	0.41	8.46	1.02	0.09	0.072	0.198	0.051	0.002



**Fig. 1.** Macro photograph showing a cross-section view of the submerged arc weldment used for testing and analysis. The P91 plate was 2 in thick.

section of the specimen that was actually heated was entirely within the weld deposit. The dilation of the specimens during heating and cooling was measured with an LVDT strain gauge configured to detect changes in specimen diameter. The strain gauge was attached at the same location along the specimen length as the thermocouple. The specimens were heated either in vacuum or argon atmosphere to minimize oxidation during testing. Transformation temperatures were determined by curve fitting procedures at points of significant discontinuity on dilation-versus-temperature data plots.

For mechanical testing, bar specimens with either 6.35 mm (0.25 in) or 9.53 mm (0.375 in) diameters were machined parallel to the welding direction from the weld deposit. These specimens were tested in the as-received, PWHT condition. Other 6.35-mm-diameter specimens were machined transverse to the welding direction near the top of the weld deposit, and they had reduced sections of 25.4-mm-long that were entirely in the weld metal. The transverse specimens were machined from 12.5-mm-thick slices of the original welded plate. These slices were given the following heat treatments:

1. Austenitize for 15 min at 1040°C (1904°F)
2. Air-cool either to room temperature or to 200°C (392°F)
3. Temper either for 30 min at 740°C (1364°F) or for 1 h at 780°C (1436°F)
4. Air-cool to room temperature.

The creep-rupture testing was performed in 12-to-1 lever-arm creep frames following ASTM 139. Testing was done in air

at 600°C using stress levels of 120 MPa (17.4 ksi) and 186 MPa (27 ksi). Extensometers were attached to the specimen shoulders to measure the extension with time.

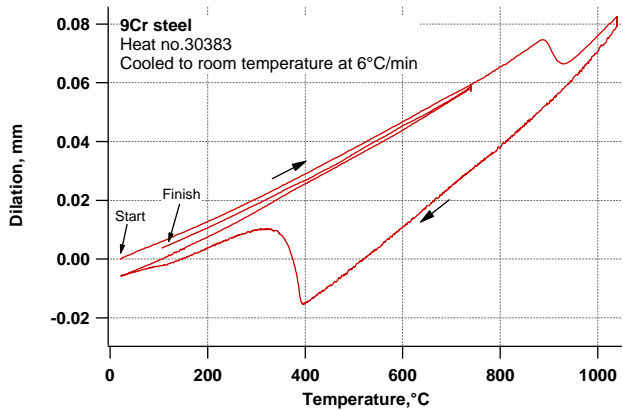
## Results

**Martensite transformation behavior:** The transformation behavior of the submerged arc weld deposit and the alloy 30383 base metal was determined for two similar thermal cycles consisting of:

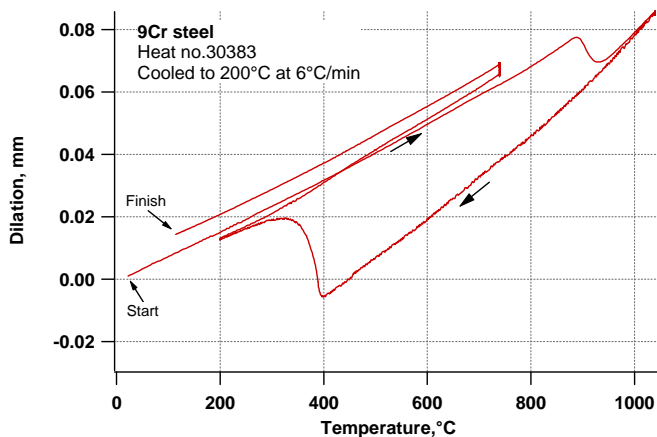
1. Austenitizing for 2 min at 1040°C (1904°F)
2. Cooling to either room temperature or 200°C (392°F)
3. Tempering for 15 min at 740°C (1364°F)
4. Cooling to room temperature at 6°C/min.

The specimen dilation results are shown in Figs. 2 and 3 for alloy 30383, and in Figs. 4 and 5 for the weld deposit. Transformation of the base metal heat 30383 was the same for cooling to either room temperature or 200°C after normalizing. The martensite start temperature,  $M_s$ , for both cases was 393-395°C (739-743°F). In both cases, the martensite reaction in heat 30383 appeared to be completed prior to the tempering portion of the treatment because no other phase transformation was detected. In contrast, the transformation of the weld deposit was influenced by the temperature to which it was cooled following normalizing. In both cases, a secondary martensite reaction was detected in the weld deposit after tempering. The primary  $M_s$  for the weld deposit was 348-350°C (658-662°F). The secondary  $M_s$  was near 400°C (752°F). Also, the magnitude of the dilation associated with the secondary martensite reaction was smaller in the specimen that was cooled to room temperature, indicating that this specimen transformed to a higher fraction of martensite during initial cooling from the normalizing temperature. These results show that the weld deposit is likely to contain some untempered martensite after welding and PWHT.

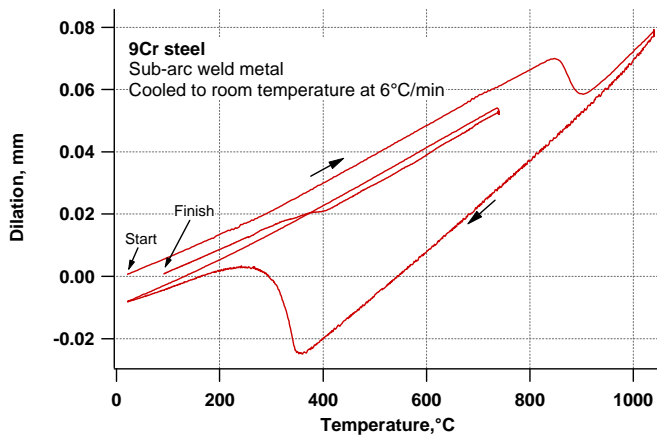
**Creep testing:** Data from the creep tests of the weld deposit are shown in Fig. 6 for the 120 MPa stress level and in Fig. 7 for the 186 MPa stress level. At both stress levels, the creep rates were highest for the as-received PWHT specimens. The creep rates were lowest for specimens that were normalized, cooled to 200°C, and then tempered. Increasing the stress from 120 MPa to 186 MPa also significantly increased the creep rates of all three specimen types. The normalizing and tempering treatments subsequent to PWHT significantly extended the rupture life of the weld deposit at 186 MPa.



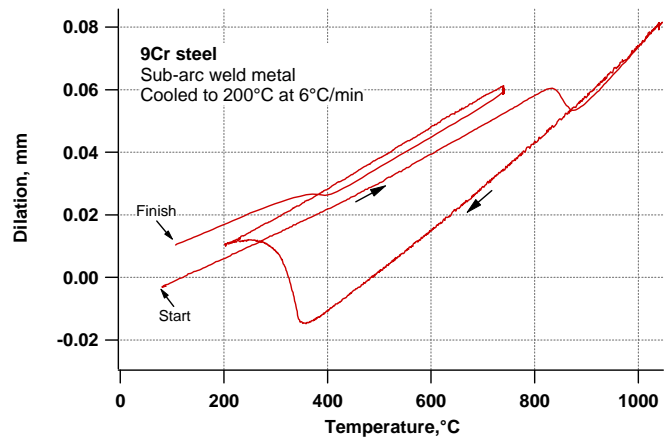
**Fig. 2.** Dilatation response of base metal alloy 30383 specimen cooled to room temperature after normalizing.



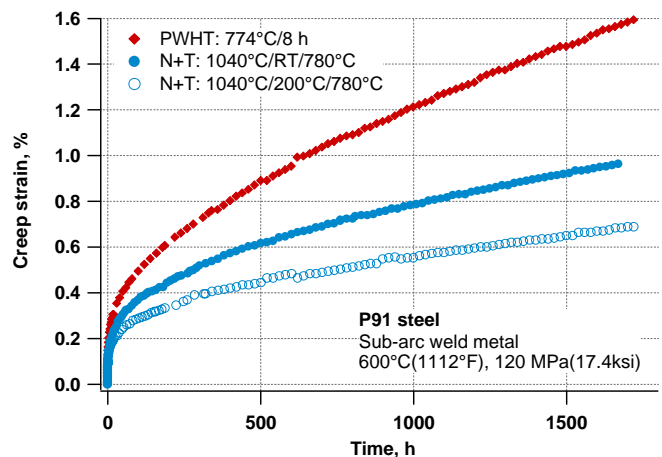
**Fig. 3.** Dilatation response of base metal alloy 30383 specimen cooled to 200°C after normalizing.



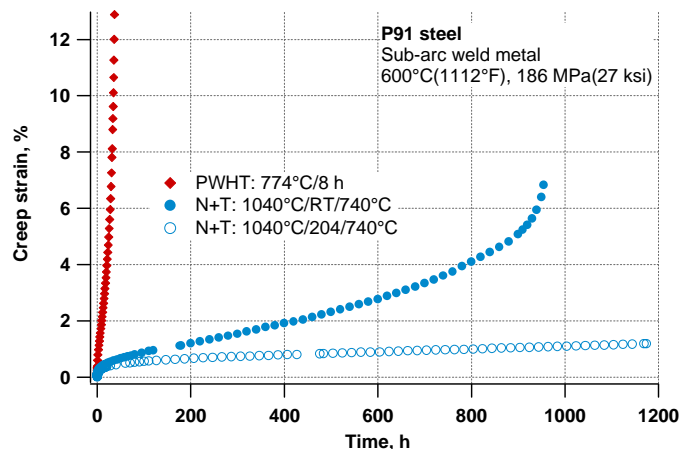
**Fig. 4.** Dilatation response of submerged arc weld deposit specimen cooled to room temperature after normalizing.



**Fig. 5.** Dilatation response of submerged arc weld deposit specimen cooled to 200°C after normalizing.



**Fig. 6.** Plot of creep strain with time for weld deposit specimens tested at 600°C at a stress of 120 MPa.



**Fig. 7.** Plot of creep strain with time for weld deposit specimens tested at 600°C at a stress of 186 MPa.

## Discussion

The  $M_S$  temperatures for heat 30383 and the weld deposit agree well with recently published expressions for the prediction of this transformation start temperature [5,6]. The predicted and measured  $M_S$ 's for heat 30383 are 383°C and 393-395°C; those for the weld deposit are 348°C and 347-350°C. The behavior of

heat 30383 is also consistent with analysis indicating that the temperature below which the martensite transformation is finished,  $M_F = M_S - (180-200^\circ\text{C})$  [5]. Based on this expression, the martensite transformation in heat 30383 should be completed after cooling to about 190-210°C. An  $M_F$  in this range is

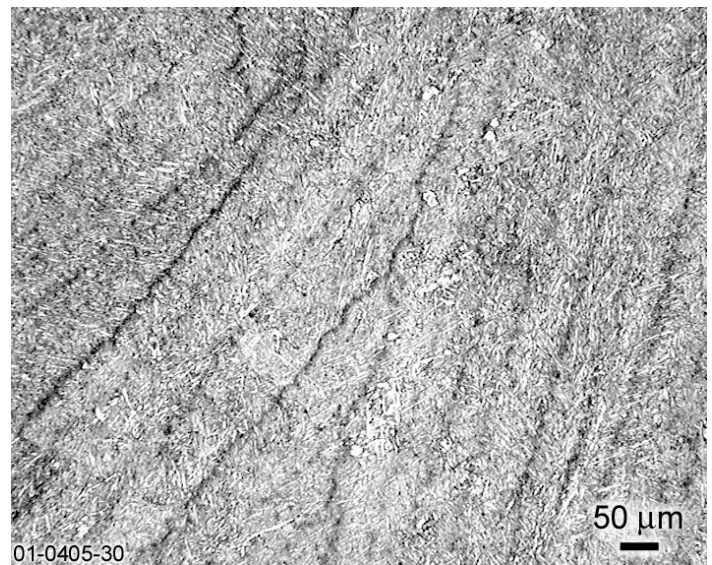
consistent with the dilation measurements shown in Fig. 3. These data show that cooling to 200°C is enough to completely transform to martensite, or at least to a level sufficiently high that further transformation after tempering is undetectable by this experimental technique.

The weld deposit behavior is not consistent with the  $M_F$  prediction of about 150-170°C. According to the  $M_F$  relationship, the martensite transformation in the weld deposit should have been completed upon cooling to room temperature, but not 200°C. The dilation results shown in Figs. 4 and 5 indicate that both normalizing and tempering cycles produced microstructures with retained austenite, some or all of which transformed to martensite at around 400°C upon cooling from the tempering temperature. The higher  $M_S$  after tempering indicates that the martensite formed after tempering transformed from austenite having a lower carbon concentration than the original, as-normalized austenite. Both normalizing and tempering cycles produced some untempered martensite in the weld deposit.

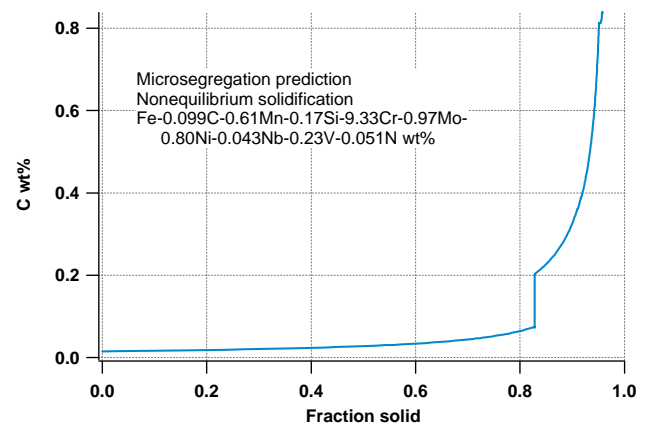
Compared to the P91 plate, the temperature range between  $M_S$  and  $M_F$  is larger in the weld deposit than would be predicted. This may be related to microsegregation in the weld deposit. The microstructure of the weld deposit is shown in Fig. 8, where tint etching was used to reveal the microsegregation pattern that is normally obscured by more common etching techniques. This pattern has a spacing of 50-100  $\mu\text{m}$  which is consistent with the dendrite arm spacing expected in submerged arc welds of steels [7]. The microsegregation of an alloy having the weld deposit composition was further analyzed using computational thermodynamics (ThermoCalc™). The variations of C, Cr, Ni, and Mn with fraction solid were calculated assuming the nonequilibrium solidification (Scheil) conditions of local equilibrium at the liquid-solid interface, no solid diffusion, and complete diffusion in the liquid during solidification [8]. These results are shown in Figs. 9-12. Each of these alloying elements preferentially partitions to the liquid during solidification. According to this prediction, enrichment of the liquid with the combination of C, Cr, Ni, and Mn actually produces a shift in solidification mode from primary ferrite to primary austenite at a solid fraction greater than about 0.83. This event accounts for the discontinuities shown in Figs. 9-12. Experimental data will be required to confirm these predictions. However, there is no question that microsegregation will occur in P91 weld deposits. Because the weld metal composition will not be homogeneous, its transformation behavior to martensite will not be uniform throughout its microstructure, but it will depend on local chemical composition. Interdendritic regions that are enriched in C, Cr, Ni, and Mn will have lower  $M_S$ 's than the nominal composition would imply. These regions would also have lower  $M_F$ 's. One manifestation of these characteristics in P91 weld deposits would be a wider range of martensite transformation temperatures compared to plate material.

The heating and cooling rates used to determine the transformation behavior of the weld deposit do not reproduce exactly those used for normalizing and tempering coupons for preparing creep test specimens. Other variations were used for tempering the creep test specimens. For instance, the dilation test specimens were tempered for 15 min at 740°C (1364°F), but

the creep test coupons were tempered for either 30 min at 740°C or for 1 h at 780°C. Nevertheless, it was expected that the specimens used for creep testing of the weld deposit contained some amount of untempered martensite, and that the amount was greater in the specimens that were only cooled to 200°C prior to tempering. The creep data plotted in Figs. 6 and 7 show that for either tempering condition, lower creep strains developed for cooling to 200°C prior to the tempering treatment. These data suggest that creep rates are lowered in weld deposit microstructures containing small amounts of untempered martensite. It is assumed that the high creep rates experienced by the specimens that were only PWHT are mainly due to the softening associated with their longer tempering time of 8 h. The short rupture life of the PWHT specimen at 186 MPa was also likely due to the more extensive softening caused by the tempering heat treatment.

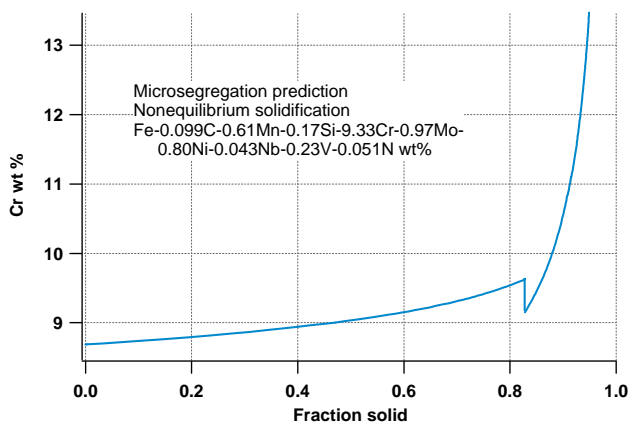


**Fig. 8.** Optical micrograph showing microsegregation in P91 weld deposit.

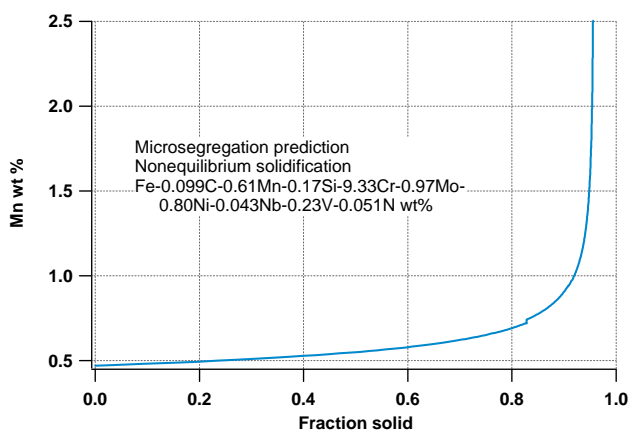


**Fig. 9.** Calculated microsegregation pattern of carbon for alloy with P91 weld deposit chemical composition.

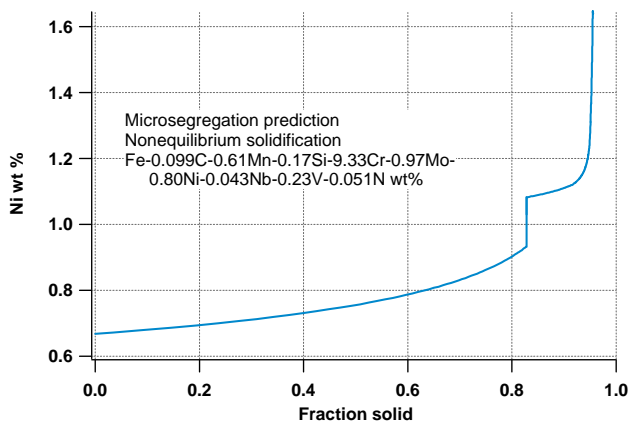




**Fig. 10.** Calculated microsegregation pattern of Cr for alloy with P91 weld deposit chemical composition.



**Fig. 11.** Calculated microsegregation pattern of Mn for alloy with P91 weld deposit chemical composition.



**Fig. 11.** Calculated microsegregation pattern of Ni for alloy with P91 weld deposit chemical composition.

## Summary

Measurements of dilation during controlled thermal cycles were used to follow the martensite transformation in a P91 base

metal and in a weld deposit that was previously post-weld heat treated at 774°C (1425°F) for 8 h. These measurements showed that a secondary martensite reaction occurred during cooling from the normalize-and-temper treatment. This secondary martensite reaction occurred at a higher temperature,  $M_S \approx 400^\circ\text{C}$ , than the primary martensite transformation,  $M_S \approx 350^\circ\text{C}$ . These observations indicate that some austenite was retained in the weld deposit after normalizing and cooling to either room temperature or 200°C, and after tempering. The amount of retained austenite appeared to be greater for cooling to 200°C. The higher  $M_S$  of the secondary reaction indicates that the austenite retained through the full heat treating schedule had a lower carbon concentration than the original, as-normalized austenite. An analysis of microsegregation by computational thermodynamics suggested that partitioning of alloying elements increased the range between the martensite transformation start and finish temperatures in the weld deposit, increasing the likelihood of retained austenite in it.

Creep testing at 600°C at stresses of 120 MPa and 186 MPa indicated that the weld deposit specimens that were austenitized, cooled to 200°C, and then tempered had the lowest measured creep rates. Cooling to 200°C resulted in lower creep rates than did cooling to room temperature. The lower creep rates of the weld deposit were attributed to higher amounts of untempered martensite after full heat treatment.

## Acknowledgement

This research, done at Oak Ridge National Laboratory, was sponsored by the Office of Fossil Energy, Advanced Research Materials Program, (DOE/FE AA 15 10 10 0) U.S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. The encouragement of and helpful discussions with Bill Newell of Euroweld, Ltd. are greatly appreciated. The assistance with metallographic specimen etching provided by George VanderVoort of Buehler Ltd. was invaluable. Technical reviews of the manuscript by S. S. Babu and R. L. Klueh are also appreciated.

## References

1. F. V. Ellis, J. F. Henry, and B. W. Roberts, "Welding, Fabrication, and Service Experience with Modified 9Cr-1Mo Steel," pp. 55-63 in *New Alloys for Pressure Vessels and Piping*, PVP Volume 201, American Society of Mechanical Engineers, NY, 1990.
2. T. Wada, *The Continuous Cooling Transformation Diagram and Tempering Response of 9Cr-1Mo-V-Nb Steels*, J-4672, Climax Molybdenum Company of Michigan, Ann Arbor, MI, 1981.
3. V. K. Sikka, C. T. Ward, and K. C. Thomas, "Modified 9Cr-1Mo Steel – An Improved Alloy for Steam Generator Application," pp. 65-84 in *Ferritic Steels for High-Temperature Applications*, edited by A. K. Khare, American Society for Metals, Metals Park, OH, 1983.

- 
4. G. C. Bodine, C. Chakravarti, C. M. Owens, B. W. Roberts, D. M. Vandergriff, and C. T. Ward, *A Program for the Development of Advanced Ferritic Alloys for LMFBR Structural Application*, ORNL/Sub-4291/1, TR-MCD-015, Oak Ridge National Laboratory, 1977.
  5. L. Béres, W. Irmer, and A. Balogh, "Inconsistency of classification of creep resistant steels in European standard EN 288-3," *Science and Technology of Welding and Joining*, vol. 2, pp. 236-238, (1997).
  6. L. Béres, A. Balogh, and W. Irmer, "Welding of Martensitic Creep-Resistant Steels," *Welding Journal*, vol. 80(8), pp. 191-s-195-s, (2001).
  7. S. A. David and J. M. Vitek, "Correlation between solidification parameters and weld microstructures," *International Materials Reviews*, vol. 35(5), pp. 213-245, (1989).
  8. N. Saunders and A. P. Miodownik, *Calphad (Calculation of Phase Diagrams): A Comprehensive Guide*, Pergamon Materials Series, Volume 1, Elsevier Science Inc., New York, 1998.

This manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.