



3 4456 0449291 1

ORNL-5995

# ornl

OAK  
RIDGE  
NATIONAL  
LABORATORY



## Mechanical Properties of a Modified 2¼ Cr-1 Mo Steel for Pressure Vessel Applications

R. L. Klueh  
R. W. Swindeman

OAK RIDGE NATIONAL LABORATORY  
CENTRAL RESEARCH LIBRARY  
CIRCULATION SECTION  
4500N ROOM 175

**LIBRARY LOAN COPY**

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this  
report, send in name with report and  
the library will arrange a loan.

UCN-7969 (3-9-77)

OPERATED BY  
UNION CARBIDE CORPORATION  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

*Fossil  
Energy  
Program*

Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

METALS AND CERAMICS DIVISION

MECHANICAL PROPERTIES OF A MODIFIED 2 1/4 Cr-1 Mo  
STEEL FOR PRESSURE VESSEL APPLICATIONS

R. L. Klueh and R. W. Swindeman

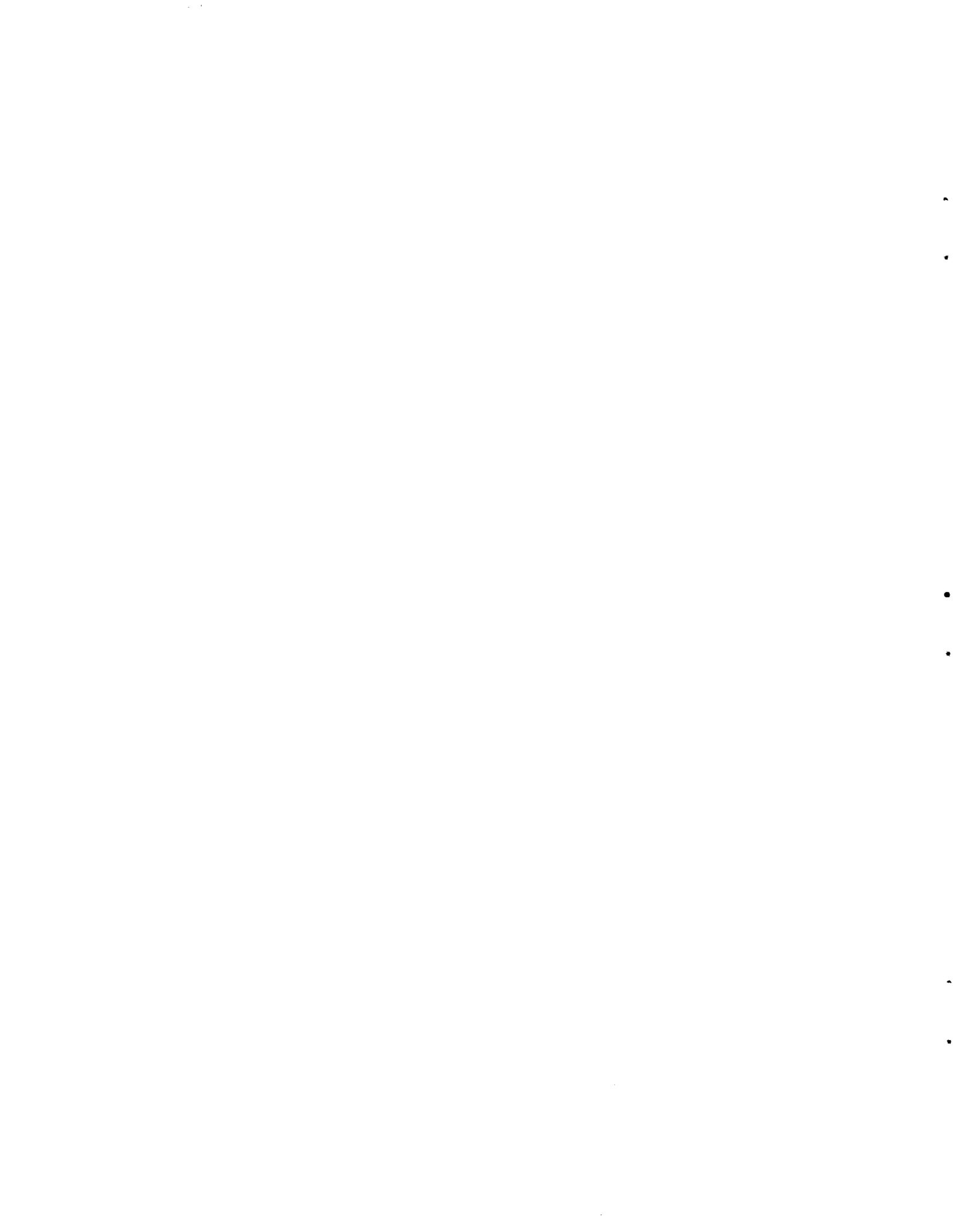
Date Published: December 1983

Prepared by the  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
UNION CARBIDE CORPORATION  
for the Office of  
Advanced Research and Technology Development  
Fossil Energy Materials Program  
U.S. Department of Energy  
under Contract No. W-7405-eng-26

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES



3 4456 0449291 1



CONTENTS

ABSTRACT . . . . .	1
INTRODUCTION . . . . .	1
MATERIAL . . . . .	4
EXPERIMENTAL METHODS . . . . .	5
RESULTS . . . . .	6
HEAT TREATMENT AND MICROSTRUCTURE . . . . .	6
MECHANICAL PROPERTIES . . . . .	16
DISCUSSION . . . . .	25
SUMMARY AND CONCLUSIONS . . . . .	32
ACKNOWLEDGMENTS . . . . .	33
REFERENCES . . . . .	34



MECHANICAL PROPERTIES OF A MODIFIED 2 1/4 Cr-1 Mo  
STEEL FOR PRESSURE VESSEL APPLICATIONS\*

R. L. Klueh and R. W. Swindeman

ABSTRACT

Tensile and creep properties were determined on a V-Ti-B-modified 2 1/4 Cr-1 Mo steel considered to be a candidate alloy for pressure vessel applications for coal liquefaction. The modified 2 1/4 Cr-1 Mo steel had about 0.2% V added for improved elevated-temperature strength and 0.02% Ti for grain refinement. Boron was added to improve the hardenability, thus allowing thicker sections to be quenched and normalized to completely bainitic microstructures. Lower carbon and silicon concentrations were used (~0.1% C and 0.02% Si) than in standard 2 1/4 Cr-1 Mo steel.

The mechanical properties determined on the modified steel after a heat treatment typical for SA-387, grade 22, class 2, indicated high toughness and excellent elevated-temperature tensile and creep strength. The modified steel had substantially better stress-rupture properties than did a standard 2 1/4 Cr-1 Mo steel (both with bainitic microstructures) with equivalent tensile properties — especially at the lowest stresses and highest temperatures. The modified steel had toughness properties superior to those of the standard 2 1/4 Cr-1 Mo steel. Comparative transmission electron microscopy studies of the standard and modified 2 1/4 Cr-1 Mo steels indicated that the differences involve the carbide precipitates and the dislocation substructures present in the steels.

---

INTRODUCTION

The Materials for Coal Conversion Pressure Vessels Task under which this work was conducted has as its primary purpose the development of a basic understanding of the factors that influence the performance of alloys under the hostile conditions expected for high-temperature high-pressure hydrogen service. The scope of the program addresses the three

---

\*Research sponsored by the U.S. Department of Energy (DOE/FE AA 15 10 10 0, AR&TD Fossil Energy Materials Program, Work Breakdown Structure Element ORNL-3.3) under contract W-7405-eng-26 with the Union Carbide Corporation.

main requirements for the development of pressure-vessel materials: a basic understanding of the metallurgy, the production of reliable materials data, and the processing of the data in terms of the development of the constitutive equations and failure criteria for use by designers.

The primary pressure-vessel steel that currently meets the established ASME criteria for pressure-vessel applications to 482°C (900°F) is 2 1/4 Cr-1 Mo steel (SA-387, grade 22). One of the tasks of the program involves the investigation of advanced stronger low-alloy steels that have adequate resistance to hydrogen attack at temperatures to 565°C. We studied a standard 2 1/4 Cr-1 Mo steel, a modified 2 1/4 Cr-1 Mo steel developed by the Japan Steel Works of Muroran, Japan, and several V-Ni-Si-modified 2 1/4 Cr-1 Mo steels produced by the United States Steel Company.<sup>1</sup> Only work on the first two steels is discussed here.

Ishiguro et al. sought an improvement in the strength of 2 1/4 Cr-1 Mo steel by microalloying additions.<sup>2</sup> The objective was a steel with better creep strength for thick sections for use in coal dissolver vessels, desulfurization vessels, and hydrocrackers. These investigators found that a low-silicon 2 1/4% Cr-1% Mo-0.1% C-0.25% V-0.02% Ti-0.002% B steel gave improved creep strength and impact toughness over those for commercial 2 1/4 Cr-1 Mo steel in either the annealed or normalized-and-tempered condition. This modified 2 1/4 Cr-1 Mo steel was also claimed to have superior resistance to temper embrittlement and to have improved weld heat-affected zone properties. Low silicon (0.02% vs 0.2-0.4% for most commercial 2 1/4 Cr-1 Mo steels) was chosen for favorable temper embrittlement response. The authors state that carbon content was restricted to 0.1% so as to

. . . alleviate the deterioration of stress-relief cracking resistance due to the addition of vanadium in conjunction with grain refining effect of titanium.

The ASTM specifications for standard 2 1/4 Cr-1 Mo steel allow 0.15% C (maximum).

The addition of 0.002% B was credited with increasing the hardenability of the alloy, allowing for the formation of "martensite or bainite

or a mixture of the two at a cooling rate as slow as  $10^{\circ}\text{C}/\text{min}$  ( $0.17^{\circ}\text{C}/\text{s}$ )" (ref. 2). On the continuous cooling transformation diagrams given for the modified alloy and a commercial-type 2 1/4 Cr-1 Mo steel with a similar carbon content, the start of the proeutectoid ferrite transformation at  $700^{\circ}\text{C}$  was moved from about 100 to about 2000 s.

Precipitate stability is of prime importance for elevated-temperature strength. Ishiguro et al. give little information on precipitate stability. They state<sup>2</sup> that

. . . the modified steel contains a fair amount of vanadium and titanium which result in the formation of carbides more stable than chromium carbide.

However, no proof of such a precipitate identification was given. When the constitution diagrams for Cr-Mo-V steels published by Andrews et al.<sup>3</sup> are consulted, it appears that at equilibrium a 2 1/4 Cr-1 Mo steel containing 0.25% V would contain  $\text{M}_6\text{C}$  (a molybdenum-rich carbide),  $\text{M}_7\text{C}_3$  (a chromium-rich carbide), and possibly  $\text{M}_4\text{C}_3$  ( $\text{V}_4\text{C}_3$ ) (these diagrams require some interpolation). This ignores the small amount of titanium (0.02%) present in the steel, which could lead to MC. The stability of  $\text{M}_4\text{C}_3$  and MC could then possibly determine the long-term properties.

Ishiguro et al. compared the creep properties of the modified and standard 2 1/4 Cr-1 Mo steel taken from the 1/4-thickness ( $1/4 T$ ) position of a 200-mm plate.<sup>2</sup> The problem with such a comparison is that it was for entirely different microstructures: the modified steel was entirely bainite, and the standard material contained large amounts of polygonal ferrite. The question, then, is whether these differences are due to the titanium and vanadium additions to the modified steel or to the different microstructure caused by the increased hardenability of the modified steel. That is, the modified steel at  $1/4 T$  will be entirely bainite, but the standard 2 1/4 Cr-1 Mo steel will contain appreciable amounts of polygonal ferrite. If the difference is due only to the difference in hardenability, boron (or manganese or nickel) could be added to the standard 2 1/4 Cr-1 Mo steel to increase its hardenability.<sup>4-5</sup>

We determined impact, tensile, and creep-rupture properties on the modified 2 1/4 Cr-1 Mo steel. The results were compared with properties that had previously been determined on bainitic 2 1/4 Cr-1 Mo steel.<sup>6-7</sup>

Such a comparison will allow a determination of the effect of the chemical composition on the properties of the two steels. We also used transmission electron microscopy (TEM) to determine how the properties may be affected by the microstructure.

#### MATERIAL

The material used in these studies came from two heats of steel. The first heat (phase I) was produced as 25-mm plate from a 50-kg vacuum induction melt with the chemical composition given in Table 1. The plate was provided to ORNL in the normalized-and-tempered condition. This heat treatment involved 4 h at 1000°C, air cooling, tempering 5 h at 650°C, followed by air cooling; this will be designated the as-received condition. At ORNL the plate was sectioned, and the part that was tested was subsequently given a second normalize-and-temper heat treatment — a "quality" heat treatment.<sup>2</sup> That treatment was 5 h at 950°C, air cool, followed by 20 h at 690°C, air cool. In the initial development work, the alloy was intended to conform to the ASME SA-387, grade 22, specification, which requires a minimum tempering temperature of 675°C (1250°F).<sup>2</sup> However, in the United States, plate products expected to meet SA-387, grade 22, class 2, properties are often delivered in the stress-relieved condition produced by tempering at 662°C (1225°F). After subsequent fabrication the vessels or components are typically tempered at 690°C (1275°F). The as-received condition (650°C temper) more closely conformed to the stress-relieved condition, and additional heat treatment was required to bring the ultimate tensile strength within an acceptable range. Although the portion of the plate allocated for the phase I exploratory testing was quite small, sufficient steel was available to obtain tensile, creep, and impact properties.

The second heat (phase II) was produced as a 16-ton forging in four thicknesses, 525, 425, 332, and 235 mm (21, 17, 13, and 11 in.), with the chemical composition given in Table 1. The pieces provided ORNL were heat treated by the producer as follows: austenitized at 950°C for 7 h, water

Table 1. Chemical composition of V-Ti-B-modified 2 1/4 Cr-1 Mo steel

Element	Content (wt %)		Element	Content (wt %)	
	Phase I	Phase II		Phase I	Phase II
C	0.14	0.12	Ti	0.032	0.019
Si	0.07	0.02	B	0.0024	0.0022
Mn	0.49	0.50	Al	0.015	
P	0.008	0.005	Sn	0.008	0.010
S	0.007	0.006	As	0.009	0.006
Ni	0.16	0.10	Sb	0.0017	0.0005
Cr	2.34	2.24	Cu	0.08	0.01
Mo	1.00	0.99	N	0.0085	0.0107
V	0.26	0.26			

quenched, tempered 15 h at 650°C, and air cooled. Samples were machined from the 1/4 *T* position of the 425-mm block. After machining, the specimens for the exploratory tests were given a simulated postweld heat treatment of 26 h at 690°C.

#### EXPERIMENTAL METHODS

Tensile and creep tests were made on specimens that had a 6.35-mm-diam by 31.8-mm-long (0.250 × 1.25 in.) reduced section. The tensile testing methods conformed to ASTM Recommended Practice E 21. The creep tests were made in air on lever-arm creep frames with 12:1 ratios. Testing methods conformed to ASTM Recommended Practice E 132. The specimens were heated by a resistance furnace. During test, the temperature was monitored and controlled by three Chromel vs Alumel thermocouples mechanically attached along the specimen gage section. Temperatures were controlled to ±1°C, and the temperature varied less than ±2°C along the gage section. Creep strains were measured with a mechanical extensometer attached to the specimen shoulders, and the extension was read periodically from averaging electrical transducers.

The microstructures of the steels were studied by means of optical microscopy, analytical electron microscopy, and electrolytic extractions. The TEM studies were conducted on specimens cut from tested impact specimens (the portion unaffected by the test). Likewise, electrolytic carbide extractions were made on these specimens.

Electrolytic extractions were produced on samples with an approximate mass of 0.3 g in a solution of 10% HCl-90% methanol at 1.5 V for 5 h. These conditions ensured selective removal of the matrix without any dissolution of carbides. The precipitates were weighed in air, and the weights were converted to weight in vacuum to correct for atmospheric variations. The accuracy of the extraction results was determined by a series of multiple measurements on similar material. A value of  $2\sigma = \pm 0.2$  wt % was found for the range of 0 to 4 wt % precipitates.

Electron microscopy was performed on JEOL 100C and 100CX transmission electron microscopes; the 100CX microscope was equipped with an x-ray energy-dispersive spectrometer (EDS) and modified for analytical work. Extraction replicas on carbon-coated copper grids were used for precipitate analysis to avoid matrix effects in obtaining EDS spectra. Precipitates were identified by a combination of electron diffraction and EDS analysis.

## RESULTS

### HEAT TREATMENT AND MICROSTRUCTURE

The difference in hardenability between the modified 2 1/4 Cr-1 Mo steel and a standard 2 1/4 Cr-1 Mo steel is shown in the comparison of the continuous-cooling transformation (CCT) diagrams determined by Ishiguro et al. (Fig. 1) (ref. 2). To avoid polygonal ferrite in their standard 2 1/4 Cr-1 Mo steel, the cooling rate had to approach 2.5 to 3.3°C/s (150-200°C/min), but the modified steel could be cooled at 0.13 to 0.17°C/s (8-10°C/min) without forming ferrite.

	C	Si	Mn	P	S	Cr	Mo	V	Ti	B	Austenitizing Temperature
2 1/4 Cr-1 Mo-V-Ti-B	.10	.02	.51	.005	.005	2.20	.94	.30	.022	.0023	950°C (1742°F)
2 1/4 Cr-1 Mo	.10	.34	.48	.017	.013	2.16	.96	-	-	-	920°C (1688°F)

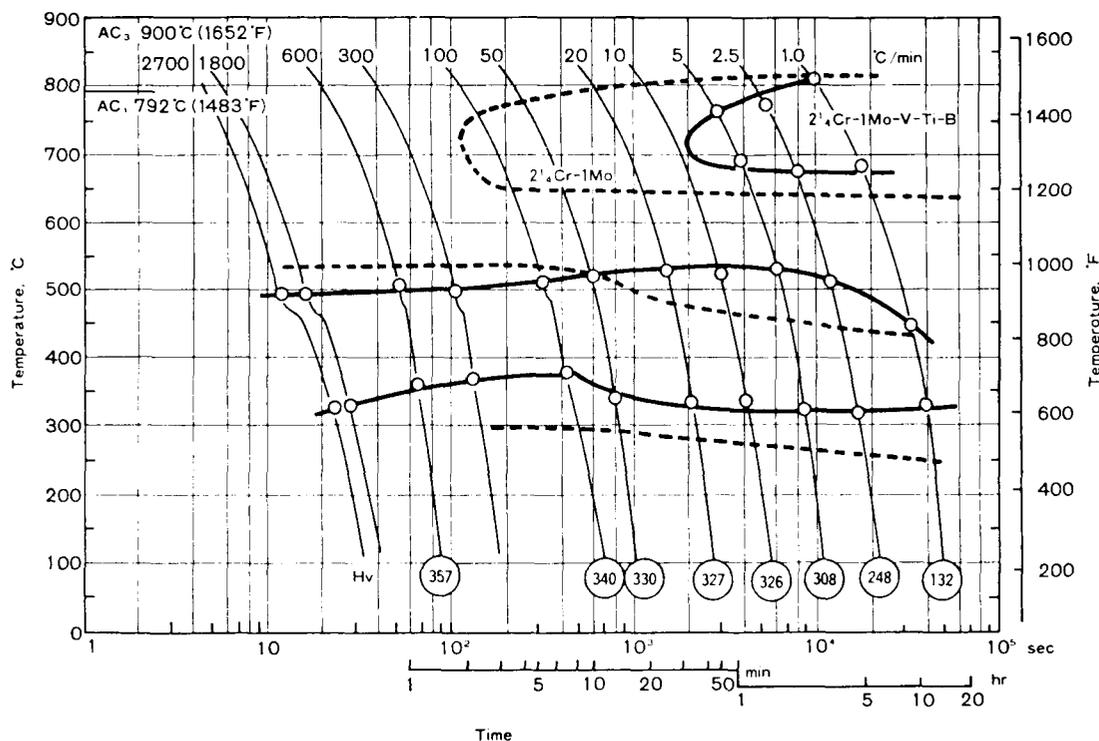


Fig. 1. Continuous-cooling-transformation diagrams for V-Ti-B-modified 2 1/4 Cr-1 Mo steel and standard 2 1/4 Cr-1 Mo steel. The upper boundaries define the region over which polygonal ferrite forms; the lower ones define the region where bainite forms. Source: T. Ishiguro et al., "A 2 1/4 Cr-1 Mo Pressure Vessel Steel with Improved Creep Rupture Strength," pp. 129-47 in *Application of 2 1/4 Cr-1 Mo Steel for Thick-Wall Pressure Vessels*, ed. G. S. Sangdahl and M. Semchyshen, ASTM-STP 755. Copyright, American Society for Testing and Materials, Philadelphia, 1982, reprinted with permission.

As stated above, Ishiguro et al. compared the creep-rupture properties of the modified and standard 2 1/4 Cr-1 Mo steels after both were cooled to simulate the 1/4  $T$  position of a 200-mm plate. This results in the comparison of a bainitic microstructure (for the modified steel) with a steel containing large amounts of polygonal ferrite (for the standard steel). The large difference in hardenability for the two steels gives

rise to such different microstructures. However, the difference in hardenability of the modified 2 1/4 Cr-1 Mo steel presumably depends on the 0.002% B, and such hardenability could be introduced into standard 2 1/4 Cr-1 Mo steel by the addition of 0.002% B. Although there is nothing inherently wrong with this comparison, it would appear more appropriate to compare the properties of the two steels with similar microstructures. We previously determined the creep and tensile properties of a bainitic 2 1/4 Cr-1 Mo steel.<sup>6-7</sup> This report compares the tensile and creep properties of the modified steel with the properties of that bainitic 2 1/4 Cr-1 Mo steel. The bainitic microstructures for the two steels are shown in Fig. 2.

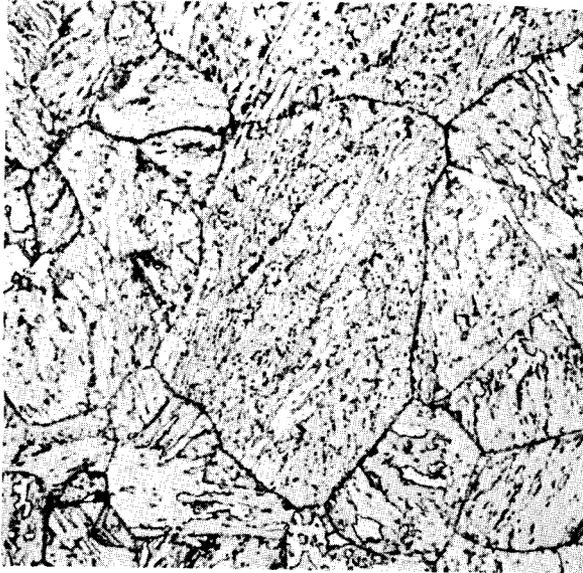
Two heat treatments for the modified steel are discussed in this report. The first, which is a normalize and temper, will be referred to as the "as-received" condition. It consists of an austenitization treatment of 4 h at 1000°C, followed by an air cool; tempering was for 5 h at 650°C. Ishiguro et. al. developed an optimized heat treatment, termed a "quality" heat treatment, which was a second normalize and temper superimposed on the as-received condition.<sup>2</sup> It consists of 5 h at 950°C, an air cool, followed by 20 h at 690°C. Microstructures for the as-received and quality heat treatments are shown in Fig. 2(a) and (b), respectively.

The normalize-and-temper heat treatment for the 2 1/4 Cr-1 Mo steel previously tested<sup>6-7</sup> was not optimized. That heat treatment was: 1 h at 927°C, air cool, followed by tempering 1 h at 704°C [Fig. 2(c)]. The prior austenite grain size of the modified steel is obviously considerably smaller than that of the standard steel.

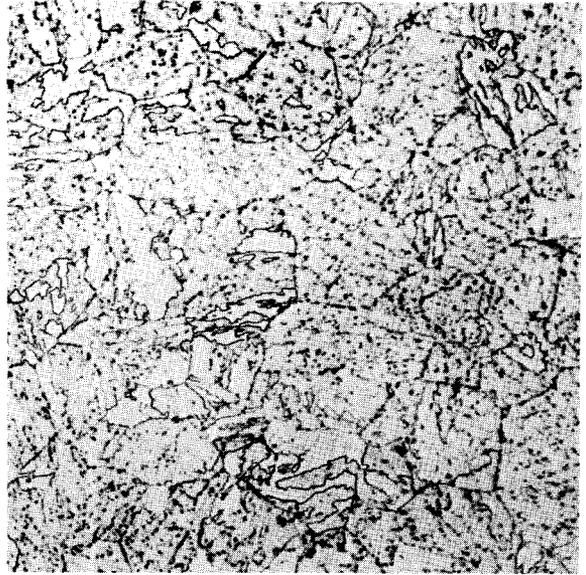
Because the elevated-temperature mechanical properties of these steels are determined by the precipitates, the steels were investigated by TEM, by means of both thin film and replica specimens. When these steels were examined by TEM it was immediately obvious that, despite the optical microstructures of Fig. 2, there is no "uniform" microstructure. Considerable microstructural variation from grain to grain and sometimes within a given grain was found with any specimen.

Y-187412

Y-187408



(a)



(b)

Y-111349



(c)

40  $\mu\text{m}$ 

Fig. 2. Microstructures of V-Ti-B-modified 2 1/4 Cr-1 Mo steel in (a) the "as-received" condition and (b) the "quality" heat-treated condition. (c) Microstructure of a 25-mm-thick plate of standard 2 1/4 Cr-1 Mo steel in the normalized-and-tempered condition.

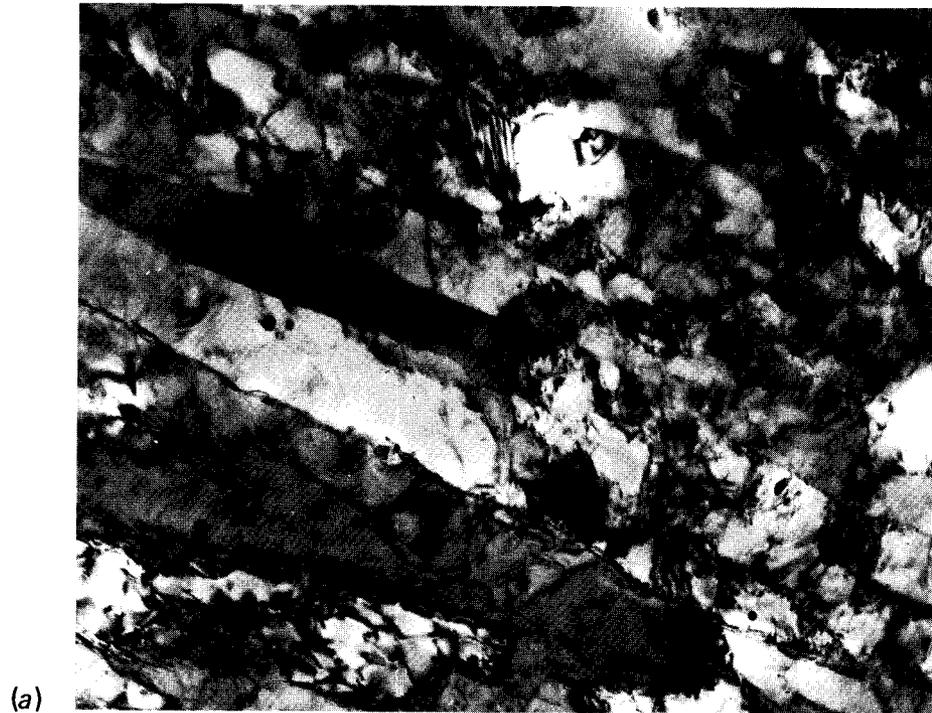
The microstructure of untempered bainite is a highly dislocated lath structure.<sup>8-9</sup> We examined only the normalized-and-tempered structure (i.e., the microstructure tested). After the quality heat treatment, the modified 2 1/4 Cr-1 Mo steel still showed evidence of the high dislocation density as well as some indications of a remaining lath structure [Fig. 3(a)]. The other distinctive feature of the microstructure was the precipitate distribution [Figs. 3(b) and 4]. We observed basically two types of precipitate morphologies: a relatively small number of large, often polygonal, precipitate particles and a high density of much smaller particles. The larger particles were often, but not exclusively, found on grain boundaries. The precipitate distribution was shown quite clearly in the replica studies (Fig. 4).

When the distribution of small platelet-shaped precipitate particles was examined in more detail, it became evident that they were often on dislocations (Fig. 5) and, as discussed later, may have played a role in the evolution of the lath structure. Not all grains contained an indication of the lath structure as clear as that shown in the upper part of Fig. 3(a). In some cases, an elongated cell structure was observed within grains (Fig. 5); this substructure was also associated with fine precipitates. The width of both the lathlike features and the elongated cell structure ranged from 0.3 to 0.7  $\mu\text{m}$ .

The standard 2 1/4 Cr-1 Mo steel had a somewhat different appearance, especially the precipitate morphology (Fig. 6). The large polygonal precipitate particles were again present, but in this case most of the smaller particles were needlelike. On the replicas, the precipitate density in this specimen appeared larger, but this may be because much of the very fine precipitate in the modified 2 1/4 Cr-1 Mo steel was not picked up by the replication technique. Precipitation on dislocations within the grains did not appear to have taken place as in the other steel. The grain size of the standard steel was considerably greater than that of the modified steel.

When the carbides were chemically extracted from the modified 2 1/4 Cr-1 Mo steel and compared with those extracted from standard 2 1/4 Cr-1 Mo steel, slightly more precipitate had formed in the standard

E-41029



E-41033

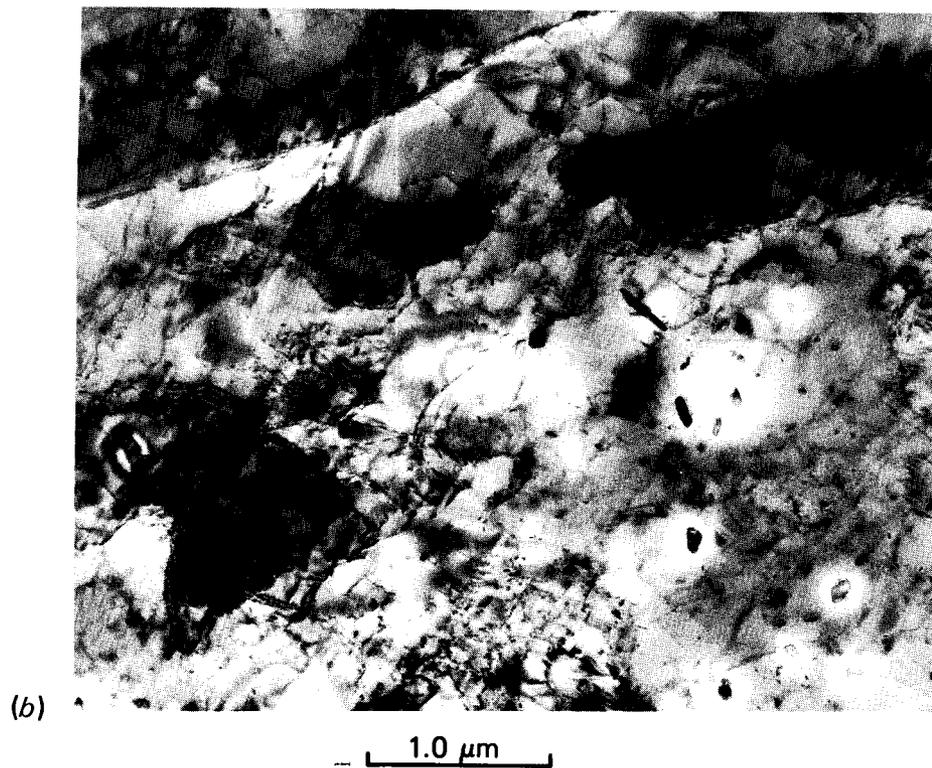


Fig. 3. Transmission electron micrographs that demonstrate the (a) dislocation and (b) precipitate structure of V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

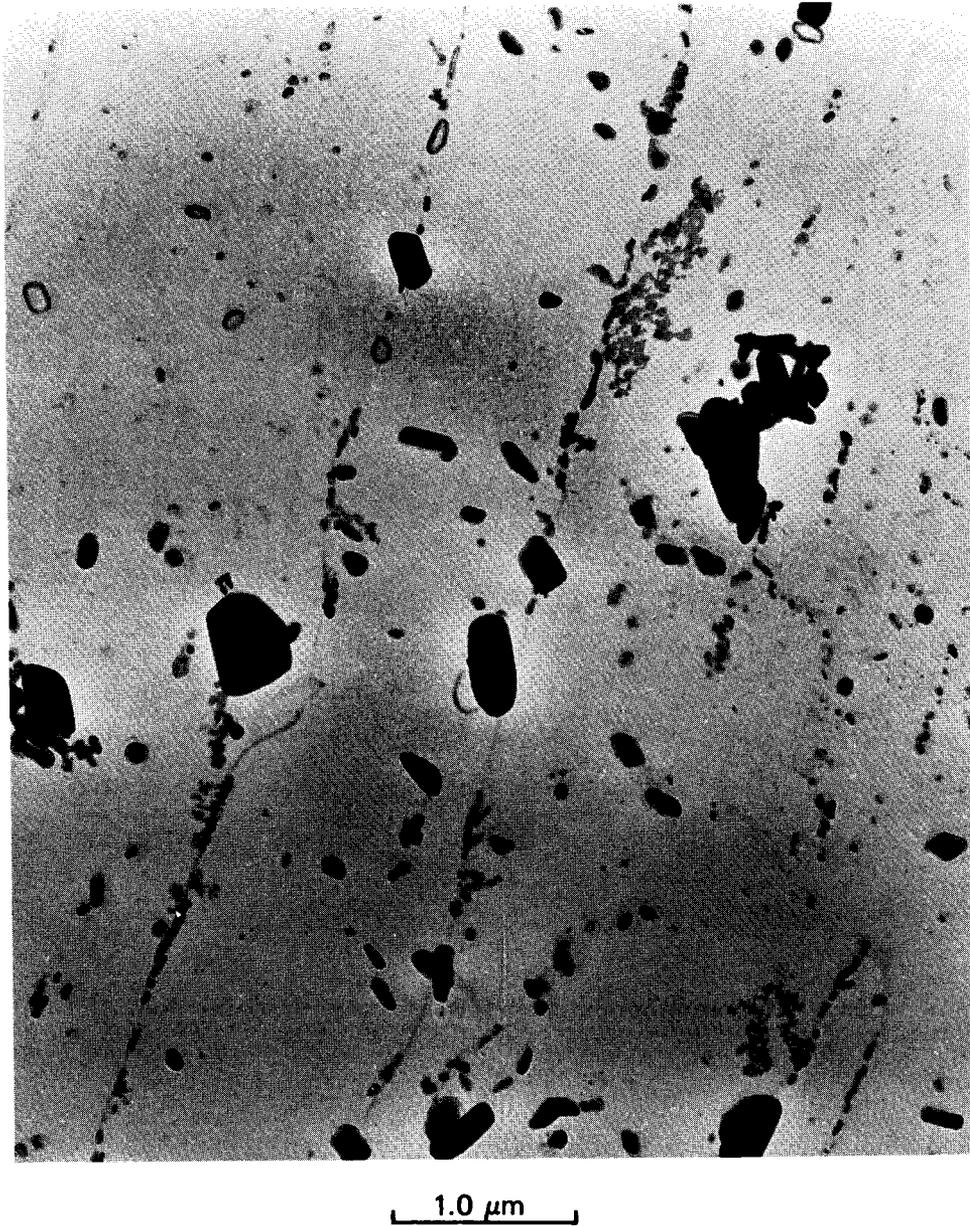
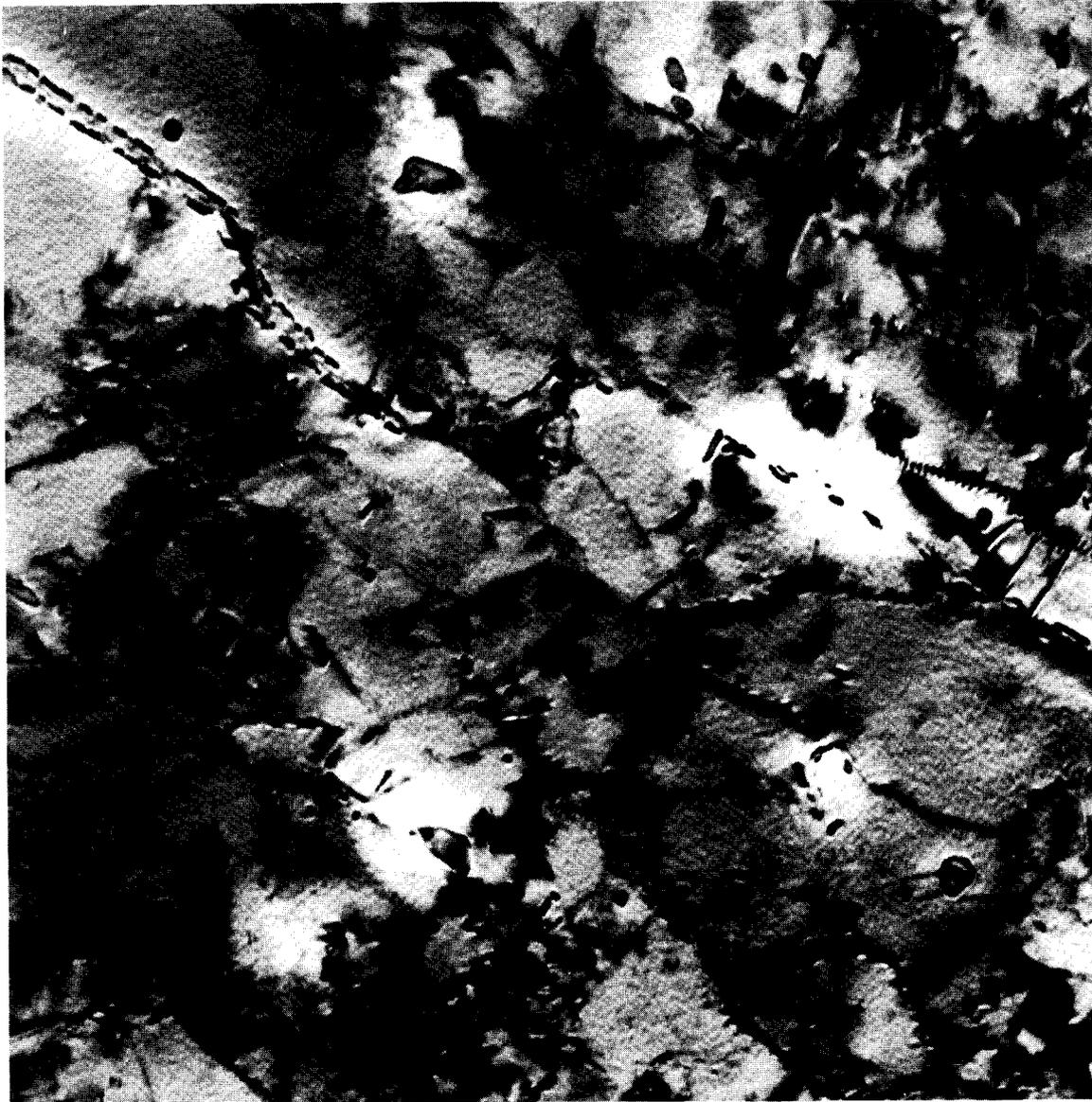


Fig. 4. Transmission electron micrograph of an extraction replica of V-Ti-B-modified 2 1/4 Cr-1 Mo steel.



0.25  $\mu\text{m}$

Fig. 5. Transmission electron micrographs that show the dislocation-precipitate interactions and the substructure within the lath structure of the V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

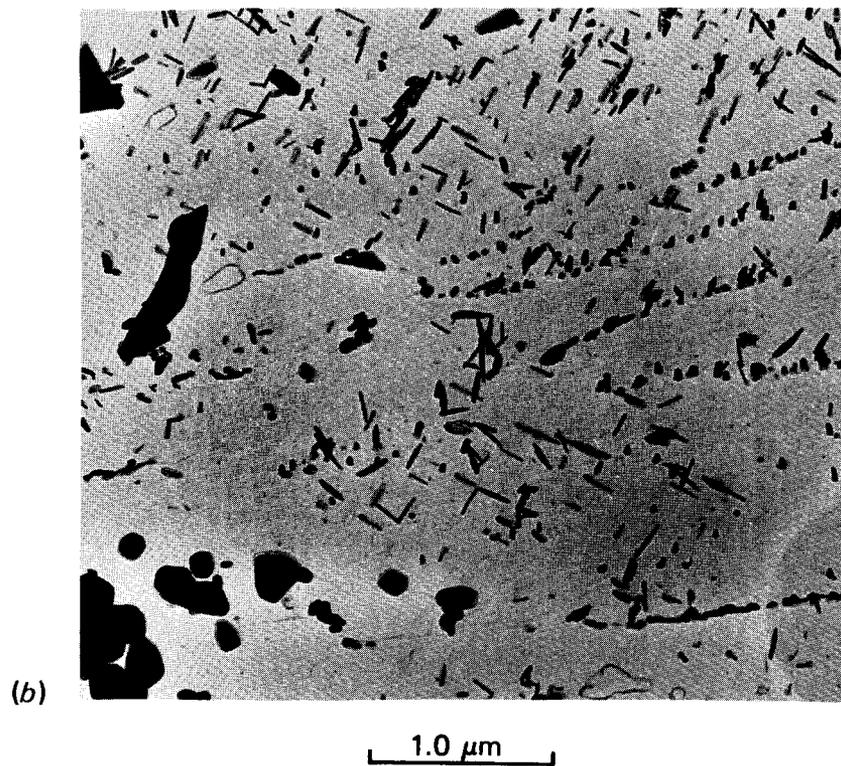


Fig. 6. Transmission electron micrographs of bainitic standard 2 1/4 Cr-1 Mo steel from (a) thin film and (b) extraction replica.

2 1/4 Cr-1 Mo steel (Table 2). Again, we do not know whether all the precipitate was extracted. However, TEM indicated that the average precipitate particle size in the standard 2 1/4 Cr-1 Mo steel was larger than that in the modified steel.

Table 2. Amount of precipitate extracted from modified and unmodified 2 1/4 Cr-1 Mo steel

Steel	Heat treatment			Amount of precipitate (wt %)
	(°C)	(h)	Cool	
Mod 2 1/4 Cr-1 Mo	1000	4	Air	1.08
	650	4	Air	
Mod 2 1/4 Cr-1 Mo	1000	4	Air	1.37
	650	4	Air	
	950	5	Air	
	690	20	Air	
2 1/4 Cr-1 Mo (heat D8681-1)	927	0.5	Quench 0.2°C/s	1.50
	663	6	Air <sup>a</sup>	
2 1/4 Cr-1 Mo (heat D8681-1)	927	0.5	Quench 0.3°C/s	1.60
	663	6	Air <sup>a</sup>	
2 1/4 Cr-1 Mo <sup>b</sup> (heat 20017)	927	1	Air	0.46
2 1/4 Cr-1 Mo <sup>b</sup> (heat 20017)	927	1	Air	1.57
	704	1	Air	

<sup>a</sup>This heat treatment was conducted in a furnace where the cooling rate could be controlled.

<sup>b</sup>Taken from R. L. Klueh, *J. Nucl. Mater* **68**, 294-307 (1977). Specimens were taken from a 25.4-mm-thick plate that had been air cooled.

In addition to extractions from the modified steel given the quality heat treatment (double normalize and temper), extractions were also made on the steel before the last normalize-and-temper treatment. This "as-received" heat treatment developed less precipitate. Extractions were made on several heat treatments of standard 2 1/4 Cr-1 Mo steel, including

two different heats (the extractions on heat 20017 had been done previously<sup>10</sup>). Different tempering treatments for the two different heats, which were given three different cooling rates, still resulted in about the same amount of precipitate (~1.6%). However, note the difference between the amount of precipitate that developed in heat 20017 after normalizing and after normalizing and tempering.

We tried to identify the extracted carbides from the standard and modified steels by x-ray diffraction techniques. Chromium-rich  $M_7C_3$  was the only carbide detected in the standard 2 1/4 Cr-1 Mo steel. The x-ray diffraction of the precipitates from the V-Ti-B-modified 2 1/4 Cr-1 Mo steel indicated the presence of only  $M_{23}C_6$  (~80%) and  $M_7C_3$  (~20%).

The EDS studies on the extraction replicas showed that the large particles in the standard steel were chromium rich, although many of them contained large amounts of iron, which is typical for  $M_7C_3$  (ref. 11), which was detected by x-ray analysis of the extracted carbides. A few of the smaller needles were found to be molybdenum rich, but with some chromium present. These particles are probably  $Mo_2C$ , which may not be present in large enough quantities to be identified in the extracted carbides. The EDS results on the modified steel indicated that all the large precipitate particles (Fig. 6) were chromium rich, usually containing iron and sometimes molybdenum. Both iron and molybdenum can dissolve in large quantities in the chromium-rich  $M_{23}C_6$  and  $M_7C_3$  (ref. 11). The EDS analysis of the very small precipitate particles indicated that they contained primarily vanadium and molybdenum.

#### MECHANICAL PROPERTIES

The Charpy V-notch impact properties of the as-received phase I steel, which had been normalized and tempered (4 h at 1000°C, air cooled, followed by 5 h at 650°C), were compared with those of the steel given the quality heat treatment (the as-received steel given the second normalize-and-temper treatment: 5 h at 950°C, air cooled, followed by 20 h at 690°C) (ref. 12).

The difference was quite striking (Fig. 7). The transition temperature was lower and the upper-shelf energy higher after the second normalize and temper.

As stated above, we feel that it is appropriate to compare the properties of the modified steel with properties of standard 2 1/4 Cr-1 Mo steel having similar microstructure and strength. Figure 8 compares the modified 2 1/4 Cr-1 Mo steel with a standard 2 1/4 Cr-1 Mo steel in a quenched-and-tempered condition with substantial toughness for this material (SA-387, grade 22). Again, there was quite a large difference in properties; the modified steel was substantially tougher than the standard steel as measured by both transition temperature and upper-shelf energy.

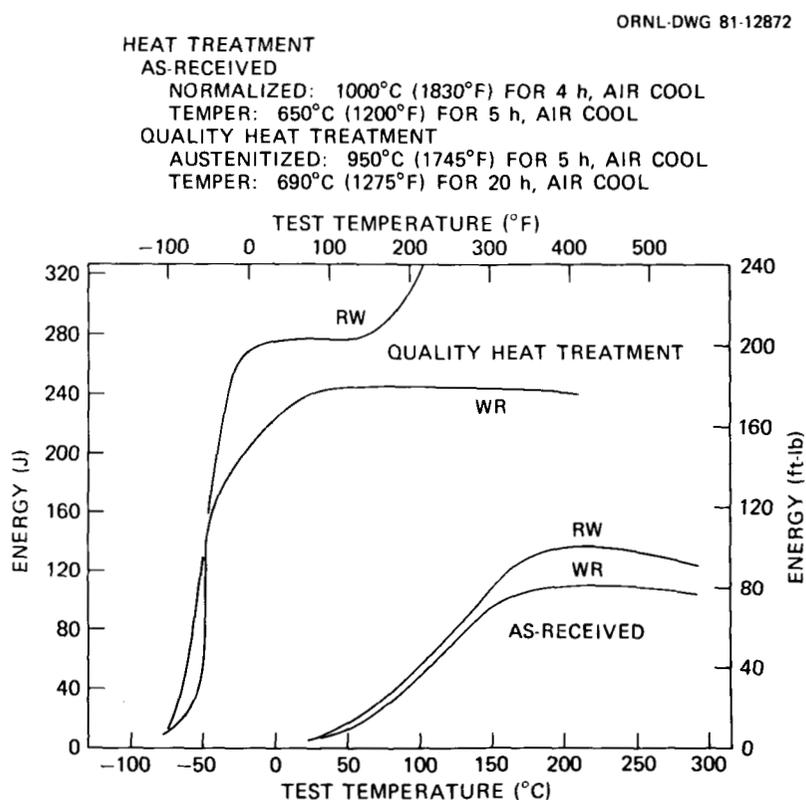


Fig. 7. Comparison of the Charpy V-notch impact properties of the V-Ti-B-modified 2 1/4 Cr-1 Mo steel in the as-received condition (normalized and tempered) and after the quality heat treatment. The RW indicates a specimen taken along the rolling direction with the notch in the width or transverse direction and vice versa for WR.

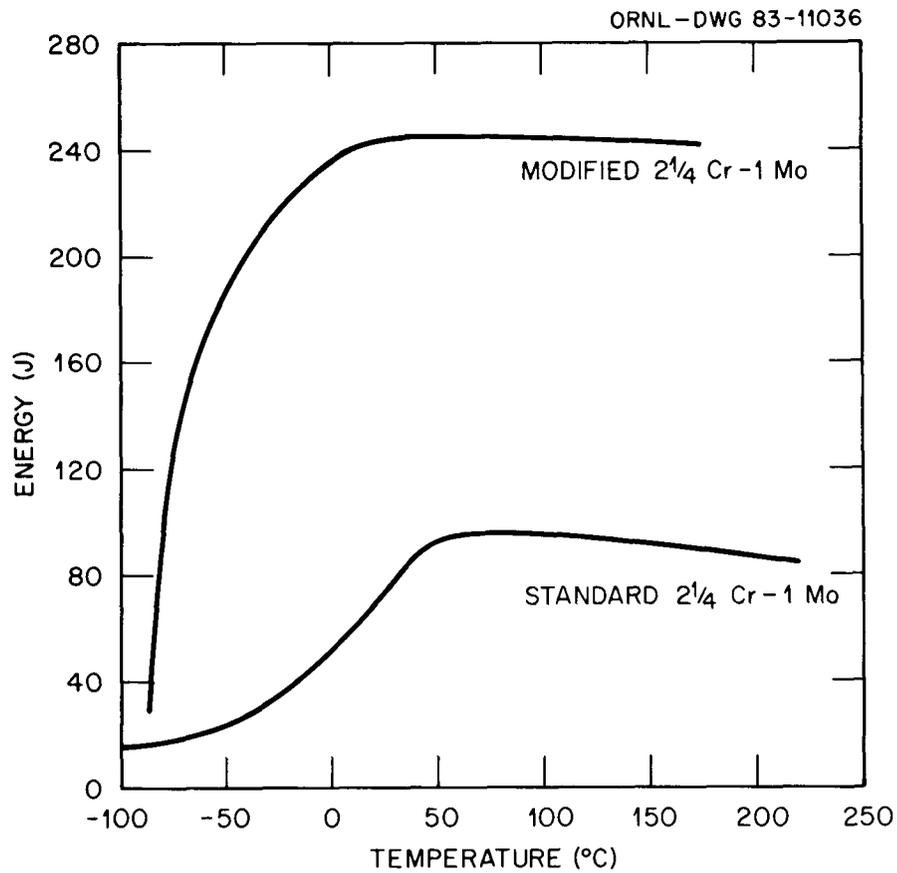
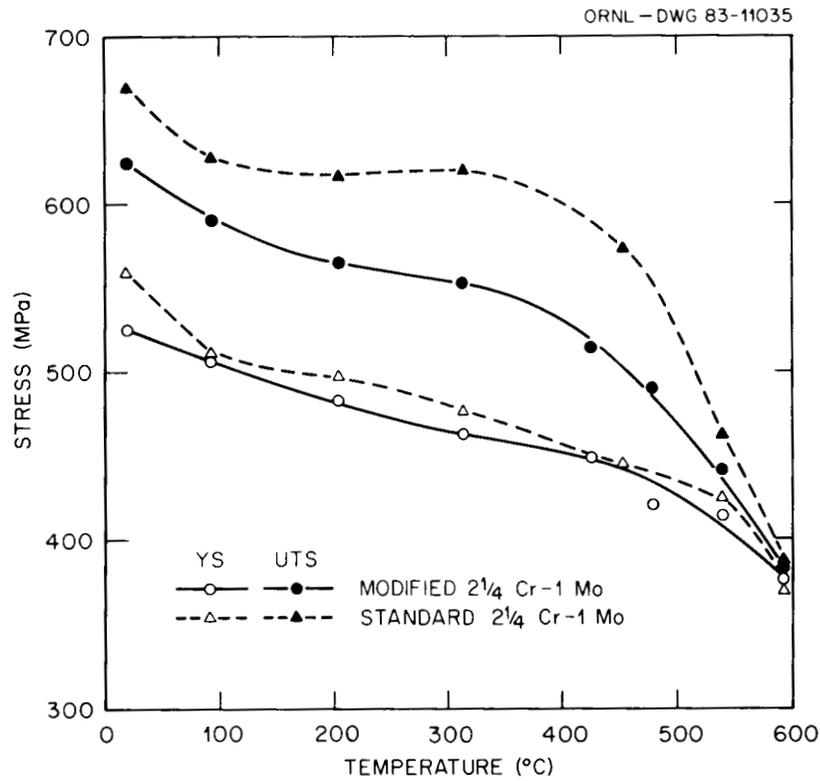
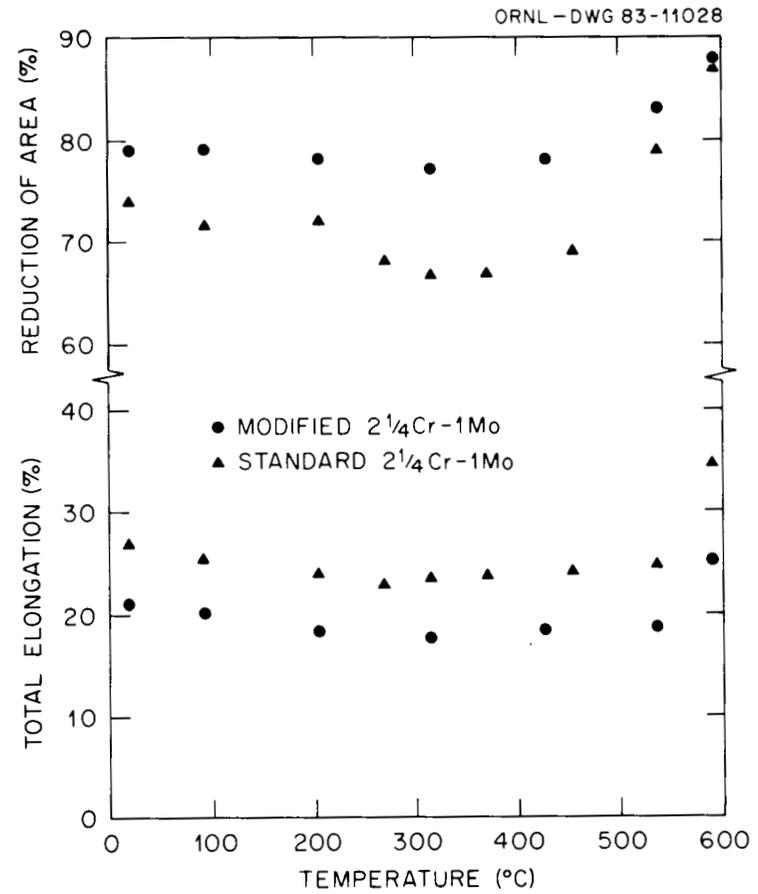


Fig. 8. Comparison of the Charpy V-notch impact properties of the V-Ti-B-modified and standard 2 1/4 Cr-1 Mo steels.

Figure 9 compares the tensile properties between room temperature and 600°C for a normalized-and-tempered commercial 2 1/4 Cr-1 Mo steel from a 25.4-mm plate<sup>6</sup> (heat 20017) and the modified steel with the quality heat treatment (both have tempered bainite microstructures). The yield strengths for the two steels were quite similar over the entire temperature range, but the ultimate tensile strength was considerably higher for the standard steel, especially between room temperature and 500°C [Fig. 9(a)]. The total elongation of the modified steel was slightly greater than that of the standard steel; however, the modified steel had a slightly larger reduction of area [Fig. 9(b)]. This comparison indicates that the tensile properties are quite similar, with a strength advantage for the standard steel.



(a)



(b)

Fig. 9. Tensile properties as functions of temperature for the V-Ti-B-modified 2 1/4 Cr-1 Mo steel with the quality heat treatment and a normalized-and-tempered standard 2 1/4 Cr-1 Mo steel, both in the tempered bainitic condition. (a) Yield strength and ultimate tensile strength. (b) Ductility.

Creep-rupture properties were determined at 482, 510, and 538°C on the modified steel in the quality heat-treatment condition (Table 3). Figures 10 through 12 present the stress-rupture curves, stress-minimum creep rate curves, and ductility-rupture life data. Over the range of temperatures and stresses of these tests, the steel exhibited good strength and adequate ductility. Little or no difference was observed in the behavior of phase I (25-mm plate) and phase II (1/4 T of 425-mm plate) materials.

Table 3. Creep-rupture properties of V-Ti-B-modified  
2 1/4 Cr-1 Mo steel

Specimen <sup>a</sup>	Stress (MPa)	Minimum creep rate (%/h)	Time to tertiary (h)	Rupture life <sup>b</sup> (h)	Elongation <sup>b</sup> (%)
482°C					
I-3	414	$2.9 \times 10^{-2}$	30	44	4.8
I-4	379	$1.9 \times 10^{-3}$	230	336	6.0
I-5	345	$9 \times 10^{-4}$	520	870	10.6
I-6	310	$1.9 \times 10^{-4}$	1400		
II-4	276	$1.1 \times 10^{-4}$	3000		
I-10	241	$3.3 \times 10^{-5}$	8500		
		$7.95 \times 10^{-5c}$			
510°C					
I-6	345	$8.3 \times 10^{-3}$	50	96	17.6
I-7	310	$4.5 \times 10^{-3}$	155	328	9.7
II-1	276	$7.2 \times 10^{-4}$	3750	4899	
II-2	207	$8.6 \times 10^{-5}$			
538°C					
I-13	310	$4.0 \times 10^{-2}$	23	46	17.4
I-14	276	$1.3 \times 10^{-2}$	62	158	17.9
I-11	276	$1.1 \times 10^{-2}$	64	135	8.5
I-8	241	$6.6 \times 10^{-3}$	420	736	15.6
I-9	241	$6.2 \times 10^{-3}$	430	735	19.0
I-A	207	$1.5 \times 10^{-3}$	1920	2796	10.2
II-14	172	$1.5 \times 10^{-4}$			

<sup>a</sup>I, phase I heat; II, phase II heat.

<sup>b</sup>Where data are not given for rupture life or elongation, the tests were not continued to failure.

<sup>c</sup>Nonclassical creep curve with two steady-state stages.

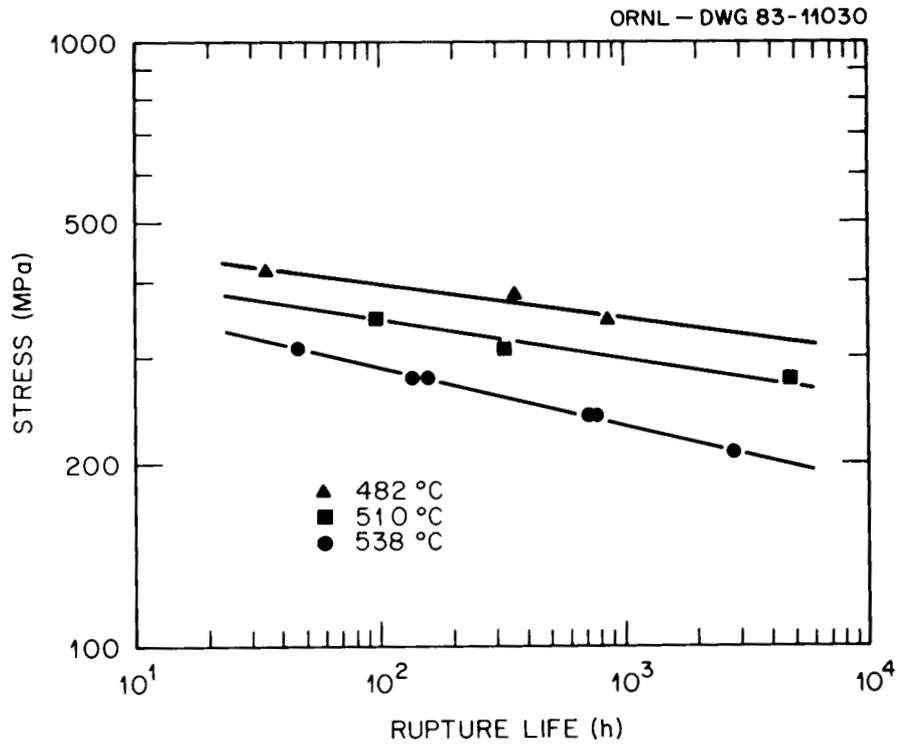


Fig. 10. Stress-rupture curves for V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

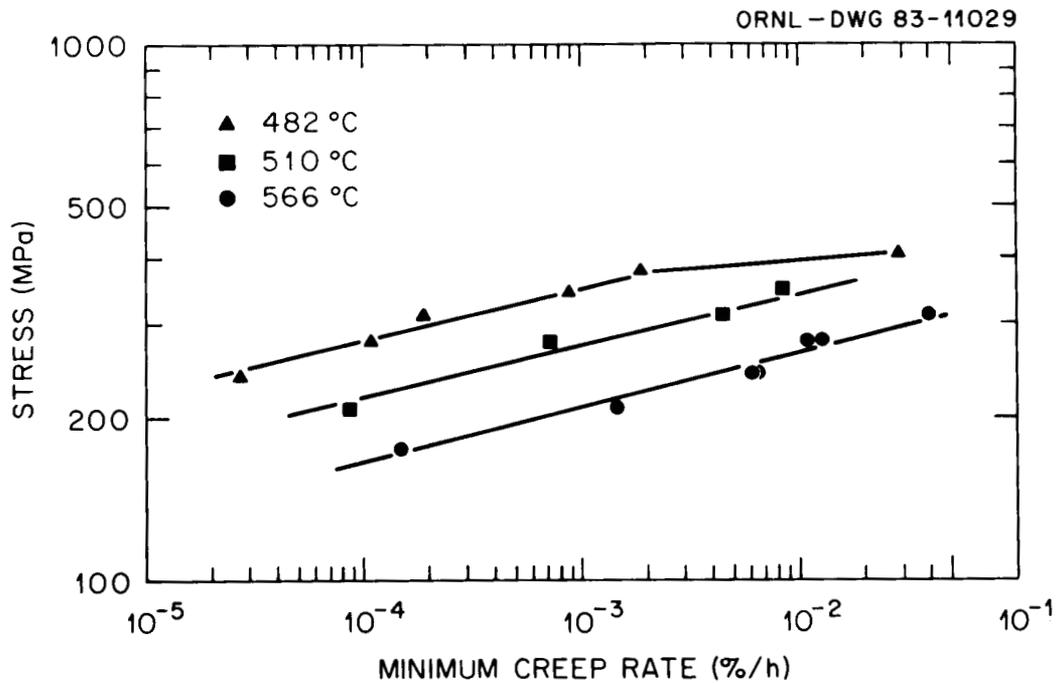


Fig. 11. Stress-minimum creep rate curves for V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

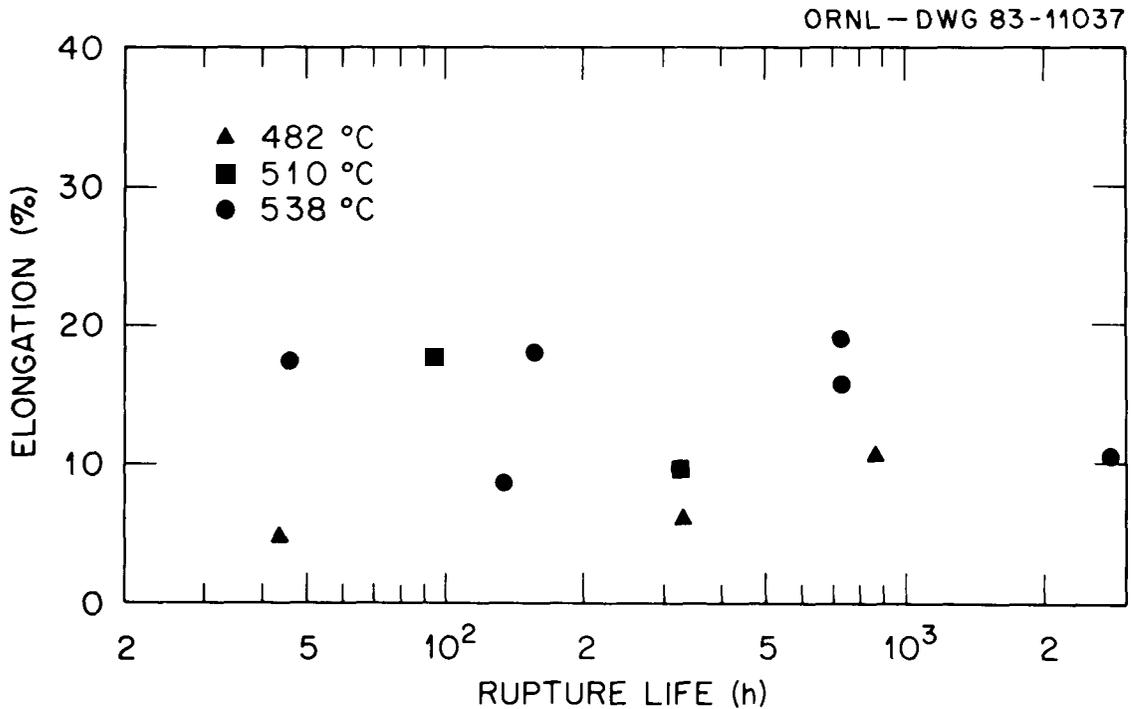


Fig. 12. Variation in rupture elongation with rupture life for V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

The stress-rupture curves for the modified and standard 2 1/4 Cr-1 Mo steels at 482, 510, and 538°C show a definite advantage for the modified steel (Fig. 13). At 482°C, the properties were similar at high stresses (short rupture times), but at low stresses a large difference was observed. A similar divergence of properties was noted at 510°C. At 538°C, this difference was found at all stresses over the range tested.

Creep curves for the modified 2 1/4 Cr-1 Mo steel are shown in Fig. 14. Observations on creep-curve shape revealed two interesting characteristics that have also been observed on standard 2 1/4 Cr-1 Mo steel. Most of the creep occurs with an increasing creep rate (i.e., relatively small primary and secondary stages and an extended tertiary creep stage). Second, the specimen tested at 482°C and 241 MPa had a nonclassical creep curve. This curve had two steady-state stages; the creep rates for both are given in Table 3.

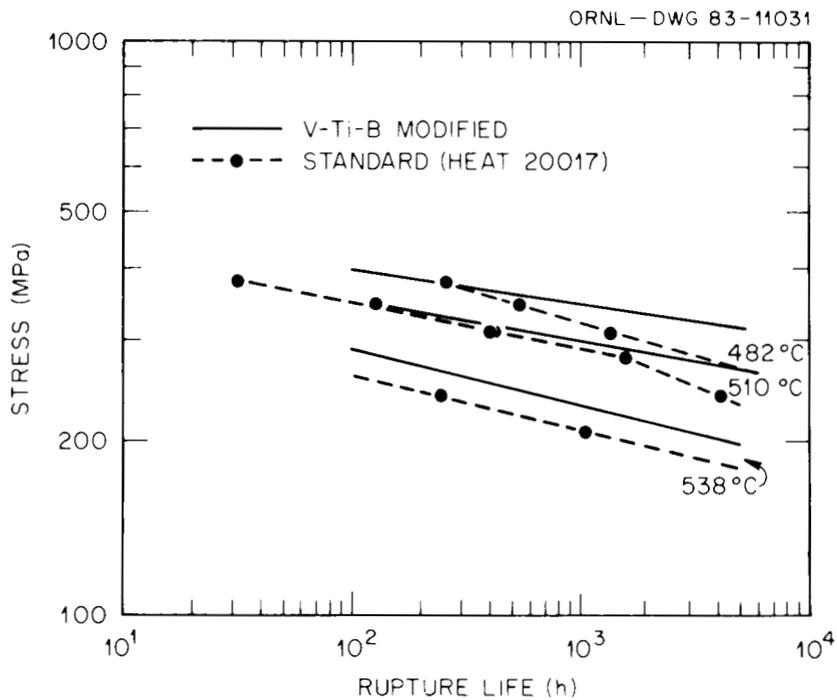


Fig. 13. Comparison of the stress-rupture curves for V-Ti-B-modified and standard 2 1/4 Cr-1 Mo steels with similar tensile properties.

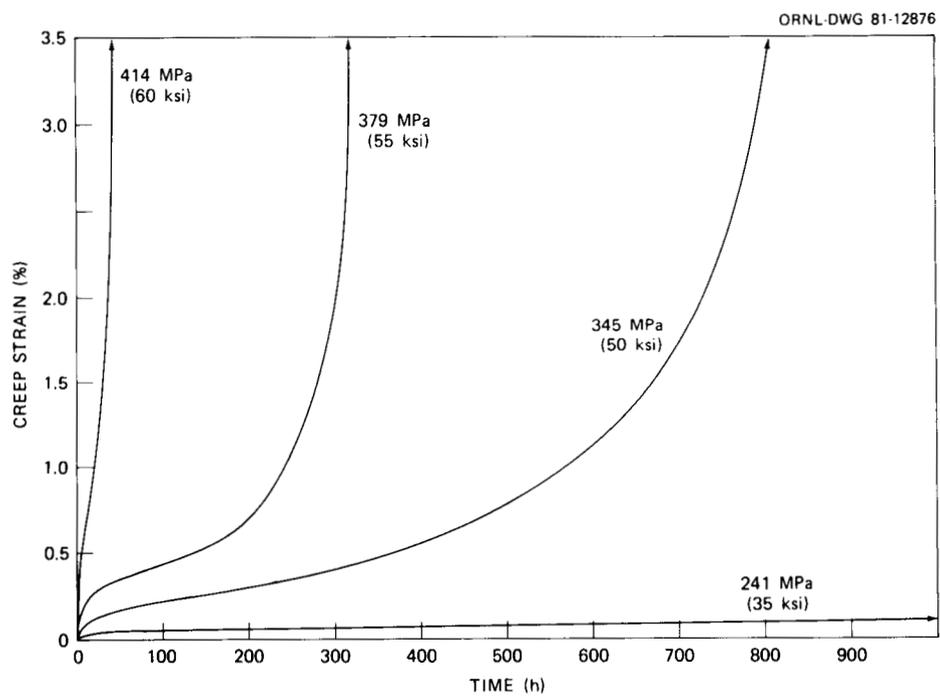


Fig. 14. Creep curves for V-Ti-B-modified 2 1/4 Cr-1 Mo steel at 482°C.

The creep-rupture study on the bainitic 2 1/4 Cr-1 Mo steel<sup>7</sup> found that the time to the onset of tertiary creep  $t_2$  could be related to the rupture life  $t_R$  according to

$$t_2 = At_R^\alpha, \quad (1)$$

where  $A$  and  $\alpha$  are constants with  $\alpha \approx 1$ . For the bainitic steel<sup>7</sup>

$$t_2 = 0.59t_R^{1.006}. \quad (2)$$

Figure 15 shows the tertiary creep data for the modified 2 1/4 Cr-1 Mo steel. These data can be fit by

$$t_2 = 0.35t_R^{1.09}. \quad (3)$$

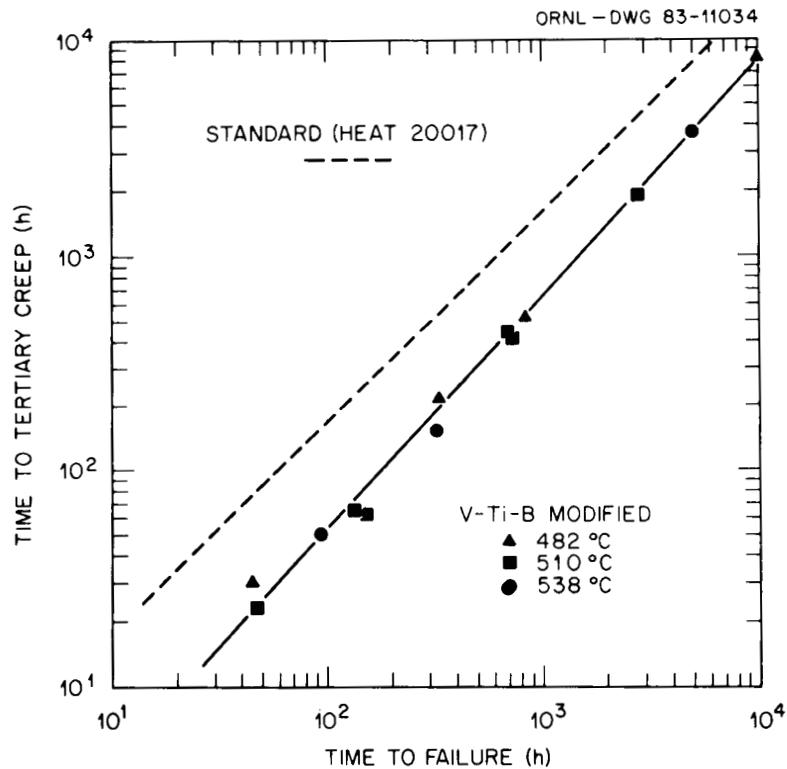


Fig. 15. Time to the onset of tertiary creep plotted against rupture life for V-Ti-B-modified 2 1/4 Cr-1 Mo steel.

Again,  $\alpha \approx 1$ . However, the large difference in the value of  $A$  for the two steels means that for a given rupture life the standard steel has a larger  $t_2$  and thus that considerably less of its creep occurs in the tertiary stage.

Visual observations of fractured specimens indicated that the fractures were of a cup-cone type. This was verified by metallographic examination of selected specimens. All indications were that the fractures were entirely transgranular.

#### DISCUSSION

Although the microstructure of upper and lower bainite appears different under certain viewing conditions, TEM studies show that the morphology of both can be described as consisting of long ferrite laths about  $0.5 \mu\text{m}$  wide.<sup>8-9</sup> The laths contain a relatively high dislocation density and form in parallel packets<sup>9</sup> or sheaves;<sup>8</sup> several packets usually form within a given austenite grain. Low-angle boundaries separate individual laths, and high-angle boundaries separate the packets. The primary distinction between upper and lower bainite is the carbide morphology: In upper bainite, the carbides form as continuous or discontinuous stringers on the lath boundaries; in lower bainite, carbide rods form in parallel arrays within a lath at a  $55$  to  $60^\circ$  angle to the lath axis. Also, a variation of upper bainite retains the high-carbon material in the lath boundaries as austenite, which may form martensite when cooled to room temperature. The retained austenite or martensite then transforms during tempering. This type of bainite has been termed "granular" bainite.<sup>13</sup>

The TEM observations on the V-Ti-B-modified  $2 \frac{1}{4}$  Cr-1 Mo steel indicate that upper bainite has formed in this steel. In those grains in which a lath structure remained, the width was  $0.3$  to  $0.8 \mu\text{m}$ , with carbides along lath boundaries (Figs. 3 and 4). All these features are indicative of an upper bainite morphology. These carbides could have formed from retained austenite or martensite during tempering, thus making this granular bainite. However, granular bainite is generally less lathlike and

has a more blocky appearance — thus, the term "granular."<sup>13</sup> Furthermore, granular bainite is generally associated with higher cooling rates than those used in this study.<sup>13</sup>

The major differences in the microstructure of the V-Ti-B-modified and the standard 2 1/4 Cr-1 Mo steels involved the fine matrix and dislocation precipitates. The modified steel contained a distribution of extremely small platelet-shaped particles, which according to EDS are vanadium rich and are assumed to be vanadium carbide. Todd, Chung, and Parker studied this same steel and also concluded that these small particles were vanadium carbide ( $V_4C_3$ ) particles.<sup>14</sup> They found that the large particles in the microstructure were  $M_{23}C_6$  but gave no indication of the presence of  $M_7C_3$ .

The smaller particles of the standard 2 1/4 Cr-1 Mo steel were considerably smaller than the small particles of the modified steel. These were identified by x-ray diffraction as  $M_7C_3$ ; the EDS studies indicated that  $Mo_2C$  needles were also present. An  $M_7C_3$  precipitate is known to form in bainitic 2 1/4 Cr-1 Mo steel, as shown in the isothermal-transformation diagrams determined by Baker and Nutting.<sup>15</sup> According to these authors, it is generally preceded by  $Mo_2C$ , and, for a steel tempered as this one was, the diagrams indicate that  $Mo_2C$ , and probably  $M_3C$ , should be present. The equilibrium diagrams of Andrews et al.<sup>3</sup> predict the presence of  $M_7C_3$  and  $M_6C$ . The needlelike precipitates observed by TEM are indicative of the  $Mo_2C$  morphology, although  $M_7C_3$  is also known to form in such a morphology.<sup>11</sup> The absence of any  $M_6C$  may be because our steels were well removed from equilibrium [Andrews et al. examined their steels after 1000 h at 700°C (ref. 3)].

The fine precipitates within the matrix of the modified steel were intimately associated with dislocations and with a substructure present within the laths of the tempered bainite. Although large numbers of dislocations were present in the matrix of the standard 2 1/4 Cr-1 Mo steel, the density was much less than that in the modified steel; also, the dislocations in the standard steel did not appear to be as intimately associated with the matrix precipitates.

The x-ray diffraction analysis of the extracted precipitates showed the modified steel to consist of  $M_{23}C_6$  (~80%) and  $M_7C_3$  (~20%). The  $M_{23}C_6$  precipitate agrees with previous observations,<sup>14</sup> although no  $M_7C_3$  was observed in that study. Our analysis of the precipitates did not include determining their distribution in the microstructure (Fig. 6) relative to their morphology and size. Indications are that the large blocky precipitates are the  $M_{23}C_6$  particles and that the  $M_7C_3$  particles are the medium-size precipitate particles — primarily of an elongated rectangular shape.

When the constitution diagrams for Cr-Mo-V steels are consulted,<sup>3</sup> the presence of  $M_7C_3$  in these steels might be expected. For a 2 1/4 Cr-0.25 V (~0.1–0.15% C) steel annealed 1000 h at 700°C,  $M_7C_3$  and  $M_4C_3$  ( $V_4C_3$ ) are found; for this same heat treatment in an alloy with 1% Mo,  $M_7C_3$  and  $M_6C$  are found.<sup>3</sup> The alloys used to construct the diagram<sup>3</sup> differ from the V-Ti-B-modified 2 1/4 Cr-1 Mo steel; the latter alloy contains the strong carbide former titanium and does not approach equilibrium like an alloy that has been annealed 1000 h at 700°C. However, these diagrams indicate that the presence of  $M_7C_3$  in such an alloy might be expected. Furthermore, if these diagrams apply, it would appear that the fine vanadium carbide observed would be unstable. This instability could affect the long-term elevated-temperature mechanical properties.

As noted in the previous section, the dimensions of the lath structure of the tempered bainite of the modified steel were about those expected for upper bainite. Although the standard steel contained some indications of a lath structure, its dimension was up to an order of magnitude larger.

These observations indicate that during the tempering of the modified steel the fine vanadium carbide forms on dislocations, thus locking in the upper bainite lath structure or locking in an elongated cell structure, which develops from the lath structure. In the standard steel, on the other hand, tempering apparently allows for an overall coarsening of the structure, probably because of the difference in the nature of the precipitation process that takes place when the matrix precipitates form. This

coarser substructure for the standard steel superimposed on the originally coarser prior-austenite grain size undoubtedly plays a significant role in the difference in mechanical properties.

The superior toughness of the modified steel after the quality heat treatment must be the result of the finer microstructure produced by that heat treatment. This was seen by optical microscopy, in which the prior-austenite grain size of the as-received steel was much coarser than that of the steel given the quality heat treatment (Fig. 2). The as-received steel is also stronger and therefore not as tough. The very fine precipitate and the substructure developed in the quality heat treatment also contribute to the superior toughness.

A cursory TEM examination of the as-received steel revealed a very high density of fine precipitate particles but gave little indication of a substructure or remnants of the original lath structure such as that observed after the quality heat treatment. This could be interpreted to mean that at the lower tempering temperature (650°C) much of the dislocation structure is "annealed out" before precipitate formation and stabilization, whereas at the higher tempering temperature (690°C) used in the quality heat treatment, more rapid precipitate growth quickly stabilizes that substructure. Another possibility is that the 950°C austenitization temperature during the quality heat treatment (as opposed to 1000°C for the first normalization treatment) is not high enough for all the fine vanadium carbide formed at the 650°C tempering temperature to dissolve. Thus, the remaining precipitates stabilize a dislocation structure in the bainite when the steel is tempered at 690°C. Much more TEM work would be needed to verify this. Although the finer microstructure of the modified steel undoubtedly leads to its superior toughness over the standard steel with the microstructure tested in the present study, it may be possible to develop a microstructure in the standard steel with toughness approaching that of the modified steel.

The elevated-temperature strength of standard 2 1/4 Cr-1 Mo steel has been attributed to two processes: interaction solid-solution hardening<sup>16-17</sup> and precipitate dispersion strengthening, primarily by Mo<sub>2</sub>C (refs. 18 and 19). The effect of these processes on the tensile and creep behavior

has been discussed in some detail for a polygonal ferrite<sup>18-19</sup> and a bainitic ferrite<sup>7,18</sup> microstructure. Because both these processes are felt to play a role in strengthening the V-Ti-B-modified 2 1/4 Cr-1 Mo steel, they are briefly discussed here.

Interaction solid-solution hardening is a solid-solution-hardening effect attributed to the strengthening that results from the simultaneous presence in solution of substitutional and interstitial atoms with an affinity for each other (e.g., C and Mo or C and Cr in standard 2 1/4 Cr-1 Mo steel). As a result of this strong attraction, atom pairs or atom clusters form and subsequently interact with dislocations to form atmospheres. On the basis of results of studies on the ternary Fe-Mo-C and Fe-Cr-C alloys by Baird and Jamieson,<sup>16</sup> interaction solid-solution-hardening effects were attributed to carbon-molybdenum interactions in 2 1/4 Cr-1 Mo steel with a polygonal ferrite microstructure and to carbon-chromium interactions in the bainitic condition.<sup>10,17</sup>

Interaction solid-solution hardening can affect creep curve shape.<sup>19</sup> The resulting curves have been classified as *classical* and *nonclassical*. Classical curves have primary, secondary, and tertiary creep stages. Nonclassical curves have two steady-state stages. A primary and steady-state stage are followed by a stage with an increasing creep rate; instead of increasing to rupture, however, the rate again decreases, going into a second steady-state stage, which finally gives way to an increasing creep rate and rupture. One such curve was observed for the modified steel. For standard 2 1/4 Cr-1 Mo steel, it was concluded that for the first steady-state stage, creep is controlled by interaction solid-solution hardening.<sup>17</sup> Eventually, precipitation removes the supersaturated solution of interacting atoms, and the creep rate increases to a new steady state, in which creep is controlled by atmosphere-free dislocations moving through a precipitate field.

The observation of a nonclassical creep curve for the V-Ti-B-modified steel indicates that interaction solid-solution hardening may also occur in that steel. Undoubtedly, the nature of the interaction solid-solution-hardening process in this steel is different from that observed in standard

2 1/4 Cr-1 Mo steel. For the modified steel, the strongest interaction between interstitial and substitutional solutes should occur between C and V and/or Ti, as opposed to C and Mo and/or Cr in the standard steel. The Fe-V-C and Fe-Ti-C alloys have not been studied as have Fe-Mo-C and Fe-Cr-C (ref. 16).

The observation that a large portion of the creep curve for the V-Ti-B-modified 2 1/4 Cr-1 Mo steel consisted mostly of an increasing creep rate (tertiary creep) is similar to observations on annealed 2 1/4 Cr-1 Mo steel.<sup>19</sup> In that case the observation was explained as being caused by interaction solid-solution hardening.<sup>17</sup> Such creep curves were attributed to nonclassical creep in which only the first steady-state stage was delineated. That is, the first steady-state stage was so long that the second steady-state stage was never observed; by the time the first steady-state stage was finished, the second steady-state stage was so short that it occurred by itself only over a period of time too short to permit identification. Because the end of the second steady-state stage defines the proper start of the onset of tertiary creep,<sup>20</sup> the time and strain to the onset of tertiary creep are underestimated.

This same observation appears applicable for the V-Ti-B-modified 2 1/4 Cr-1 Mo steel. As with the previous results,<sup>20</sup> only when the stress was quite low (long rupture life) was the second steady-state stage identifiable. However, because in this study the test that displayed two steady-state stages (241 MPa at 482°C, Table 3) was discontinued immediately after the second steady-state stage began, the amount of creep before the onset of the true tertiary creep stage was not determined. Nevertheless, this observation indicates that several percent more creep probably occurs before the onset of the true tertiary stage, in which the increasing creep rate denotes a structural instability (i.e., the formation of cracks, voids, or necking, which lower the specimen cross section and thus increase true stress).

Interaction solid-solution hardening affects the tensile properties of standard 2 1/4 Cr-1 Mo steel in addition to its effect on creep. The effect is exhibited as a dynamic strain-aging peak when the ultimate

tensile strength is plotted against temperature.<sup>10,17</sup> The peak occurs between 300 and 450°C, depending on the strain rate. A slight peak is noted for the standard steel in Fig. 9(a); the peak height for this steel becomes more pronounced as the strain rate is decreased.<sup>10</sup> The modified steel shows no indication of a peak at  $2.7 \times 10^{-4}/s$ . This is undoubtedly a manifestation of the difference in the V-C and/or Ti-C interaction, as opposed to the standard steel, in which Cr-C and Mo-C interactions occur.<sup>10</sup> According to carbide stabilities, V and Ti would be expected to interact more strongly with C than do Mo and Cr. The reduced dynamic strain-aging peak may be the result of a small supersaturation of vanadium and titanium relative to their carbides when the steel was cooled from the tempering temperature. Further studies are required to understand these differences. Such studies would prove worthwhile, for, if interaction solid-solution hardening under these conditions were understood in more detail, it could perhaps be applied in the further development of chromium-molybdenum steels.

Although interaction solid-solution hardening is important to the difference in tensile behavior and high-stress creep-rupture behavior of the modified and standard steels, the difference in long-time creep properties depends on the difference in precipitate particle size and distribution in the two steels.<sup>17</sup> As the rupture life increases, the relative amount of time that interaction solid-solution hardening controls the creep process decreases. For such tests, dispersion strengthening by the fine vanadium carbide in the modified steel and molybdenum and chromium carbides in the standard steel determines the creep strength.

The difference in creep-rupture properties of the two steels becomes greatest at the lowest stresses (longest rupture times) (Fig. 14). This observation is similar to observations by Todd, Chung, and Parker on these same two steels.<sup>14</sup> Ishiguro et al. found a larger difference between the modified steel and the standard steel that they tested;<sup>2</sup> however, this difference was due to the different microstructures tested.

The finer distribution of small precipitate particles in the modified steel and the distribution on dislocations would be expected to improve the elevated-temperature strength of the modified steel relative to the

standard steel. In future studies it will be of interest to determine how this relative long-term elevated-temperature superiority is maintained, a determination that will require long-time tests and tests at higher temperatures. Such studies, which are beyond the scope of the present work, should be accompanied by detailed TEM studies.

Previous work has indicated that the addition of chromium beyond 2.25% has no marked strengthening effect.<sup>21</sup> The only reason for adding more chromium is to improve the oxidation and corrosion resistance of the steel (the chromium also increases hardenability). Therefore, for applications to 550°C the present work again demonstrates that it is unnecessary to add the 9 to 12% Cr that is often used.

These observations may be useful to further develop this class of steels. For example, Ishiguro et al., interestingly, found that a 2 1/4 Cr-1 Mo steel with 0.1% C, 0.2% V, and 0.03% Nb (no boron) had tensile, creep, and impact properties comparable to or slightly better than the 0.1% C-0.2% V-0.02% Ti-0.002% B steel that they eventually chose to develop.<sup>2</sup> The only negative comment on the niobium-strengthened steel was that it had insufficient hardenability.<sup>2</sup> However, this was the result of not adding boron. If this observation is coupled with the observation of Brozza, Vacchiano, and Renaldi that a 1 Cr-1 Mo-0.2 V-0.15 Nb-0.003 B steel had properties comparable to those of the modified 2 1/4 Cr-1 Mo steel<sup>22</sup> and that of Sikka, Ward, and Thomas that a 9 Cr-1 Mo-0.2 V-0.06 Nb steel has properties exceeding those with only vanadium added,<sup>23</sup> one must conclude that there is considerable promise for developing a chromium-molybdenum steel with improved elevated-temperature properties (to 650°C) by use of V and Nb for strengthening, B for hardenability, and about 5% Cr for oxidation resistance.

#### SUMMARY AND CONCLUSIONS

Tensile and creep properties have been determined for a V-Ti-B-modified 2 1/4 Cr-1 Mo steel (0.25% V, 0.02% Ti, 0.002% B). The results of the mechanical property determinations were compared with results on

standard 2 1/4 Cr-1 Mo steel. However, although previous investigators compared steels given similar cooling rates during a normalizing heat treatment, we compared steels having similar bainitic microstructures. The difference in microstructure in the Japanese studies was the result of the 0.002% B added to the modified steel. If the boron had been present in the standard steel, a similar hardenability and, hence, a similar basic microstructure should result.

The results generally verified the observations of the Japanese investigators concerning the excellent impact properties and elevated-temperature strength of the modified 2 1/4 Cr-1 Mo steel. The improvement in the mechanical properties of the modified steel was attributed to a fine, relatively stable vanadium carbide precipitate that formed, primarily on dislocations, when the steel was normalized and tempered in accordance with the recommended procedure. This precipitate stabilizes a fine dislocation substructure within the bainite lath structure that developed during normalization, as opposed to the precipitate structure that forms in bainitic standard 2 1/4 Cr-1 Mo steel, which is much coarser and less stable. More work is required to understand the evolution of the carbides during elevated-temperature exposure. Ultimately, the evolution of the carbides will determine the usefulness of this steel at elevated temperatures.

#### ACKNOWLEDGMENTS

We wish to thank the following people who helped in the completion of this work: B. C. Williams carried out the mechanical property tests, C. W. Houck did the optical metallography, W. J. Stelzman helped with discussions on impact properties, R. K. Nanstad and J. M. Vitek reviewed the manuscript, Irene Brodgen and Sigfred Peterson edited the manuscript, Frances Scarboro typed the manuscript, and Debbie Underwood prepared the final copy.

## REFERENCES

1. S. J. Manganello, "Evaluation of 2 1/4 Cr-1 Mo-1/2 Ni and 3 Cr-1 Mo-1 Ni Steels for 12-Inch-Wall Pressure Vessels," pp. 153-77 in *Advanced Materials for Pressure Vessel Service with Hydrogen at High Temperatures and Pressures*, ed. M. Semchyshen, MPC-18, American Society of Mechanical Engineers, New York, 1982.
2. T. Ishiguro et al., "A 2 1/4 Cr-1 Mo Pressure Vessel Steel with Improved Creep Rupture Strength," pp. 129-47 in *Application of 2 1/4 Cr-1 Mo Steel for Thick-Wall Pressure Vessels*, ed. G. S. Sangdahl and M. Semchyshen, ASTM-STP 755, American Society for Testing and Materials, Philadelphia, 1982.
3. K. W. Andrews, H. Hughes, D. J. Dyson, "Constitution Diagrams for Cr-Mo-V Steels," *J. Iron Steel Inst. (London)* 210, 337-50 (1972).
4. T. Funakoshi et al., "Improvement in Microstructure and Toughness of Large Heat-Input Weld Bond of High Strength Steel Due to Addition of Rare Earth Metals and Boron," *Trans. Iron Steel Inst. Jpn.* 17, 426-27 (1977).
5. S. Ueda et al., "Relation Between Precipitation Behavior of Mo-, V-, and Nb-Carbide and Yield Strength in Normalized and Tempered Steel," *Trans. Iron Steel Inst. Jpn.* 20, 765-66 (1980).
6. R. L. Klueh and R. E. Oakes, Jr., "Strain Rate Effects on the Elevated-Temperature Tensile Behavior of a Bainitic 2 1/4 Cr-1 Mo Steel," *J. Eng. Mater. Technol.* 99, 350-58 (1977).
7. R. L. Klueh, "Creep and Creep-Rupture Behavior of a Bainitic 2 1/4 Cr-1 Mo Steel," *Int. J. Press. Vessels Piping* 8, 165-85 (1980).
8. R. W. K. Honeycombe, *Steels: Microstructure and Properties*, Edward Arnold, Ltd., London, 1981.
9. F. B. Pickering, *Physical Metallurgy and the Design of Steels*, Applied Science Publishers, London, 1978.

10. R. L. Klueh, "Heat Treatment Effects on the Tensile Properties of Annealed 2 1/4 Cr-1 Mo Steel," *J. Nucl. Mater.* **68**, 294-307 (1977).
11. J. H. Woodhead and A. G. Quarrell, *The Role of Carbides in Low-Alloy Creep-Resisting Steels*, Climax Molybdenum Company, London, 1965.
12. W. J. Stelzman, R. K. Nanstad, and R. W. Swindeman, "Evaluation of Fracture Toughness of Pressure Vessel Steels," pp. 131-44 in *Fossil Energy Materials Program Quarterly Progress Report for the Period Ending September 30, 1981*, ORNL/FMP-81/4, December 1981.
13. L. J. Habraken and M. Economopoulos, "Bainitic Microstructures in Low-Carbon Alloy Steels and Their Mechanical Properties," pp. 69-107 in *Transformation and Hardenability*, Climax Molybdenum Company, Ann Arbor, Mich., 1967.
14. J. A. Todd, D. W. Chung, and E. R. Parker, "The Effects of Minor Alloy Modifications and Heat Treatment on the Microstructure and Creep Rupture Behavior of 2.25 Cr-1 Mo Steel," pp. 179-91 in *Advanced Materials for Pressure Vessel Service with Hydrogen at High Temperatures and Pressures*, ed. M. Symchyshen, American Society of Mechanical Engineers, New York, 1982.
15. R. G. Baker and J. Nutting, "The Tempering of 2 1/4% Cr-1% Mo after Quenching and Normalizing," *J. Iron Steel Inst. (London)* **192**, 257-67 (1959).
16. J. D. Baird and A. Jamieson, "Creep Strength of Some Synthesized Iron Alloys Containing Manganese, Molybdenum, and Chromium," *J. Iron Steel Inst. (London)* **210**, 847-56 (1972).
17. R. L. Klueh, "Interaction Solid Solution Hardening in 2.25 Cr-1 Mo Steel," *Mater. Sci. Eng.* **35**, 239-53 (1978).
18. K. J. Irvine, J. D. Murray, and F. B. Pickering, "Structural Aspects of Creep-Resisting Steel," pp. 246-75 in *Structural Processes in Creep*, Iron and Steel Institute, London, 1961.
19. R. L. Klueh, "Heat Treatment Effects on Creep and Rupture Behavior of Annealed 2.25 Cr-1 Mo Steel," *Metall. Trans. A* **9A**, 1591-98 (1978).

20. R. L. Klueh, "Tertiary Creep Behavior of Annealed 2 1/4 Cr-1 Mo Steel," *J. Nucl. Mater.* 69, 363-71 (1979).
21. J. Orr, F. R. Beckitt, and G. D. Fawkes, "The Physical Metallurgy of Chromium-Molybdenum Steels for Fast Reactor Boilers," pp. 91-109 in *Ferritic Steels for Fast Reactor Steam Generators*, British Nuclear Energy Society, London, 1978.
22. P. Brozzo, S. Vacchiano, and F. Renaldi, "A New Niobium-Stabilized Ferritic Steel with Improved Creep Strength for Use in Sodium Heated Steam Generators," pp. 200-204 in *Ferritic Steels for Fast Reactor Steam Generators*, British Nuclear Energy Society, London, 1978.
23. V. K. Sikka, C. T. Ward, and K. C. Thomas, "Modified 9 Cr-1 Mo Steel - An Improved Alloy for Steam Generator Application," pp. 65-84 in *Ferritic Steels for High-Temperature Applications*, ed. A. K. Khare, American Society for Metals, Metals Park, Ohio, 1983.

## INTERNAL DISTRIBUTION

- |        |                               |        |                              |
|--------|-------------------------------|--------|------------------------------|
| 1-2.   | Central Research Library      | 31.    | L. E. McNeese                |
| 3.     | Document Reference Section    | 32.    | R. K. Nanstad                |
| 4-5.   | Laboratory Records Department | 33.    | A. M. Nasreldin              |
| 6.     | Laboratory Records, ORNL RC   | 34.    | A. R. Olsen                  |
| 7.     | ORNL Patent Section           | 35.    | P. Patriarca                 |
| 8.     | R. G. Berggren                | 36.    | P. L. Rittenhouse            |
| 9.     | M. K. Booker                  | 37.    | A. F. Rowcliffe              |
| 10.    | R. A. Bradley                 | 38.    | G. M. Slaughter              |
| 11.    | C. R. Brinkman                | 39.    | J. H. Smith                  |
| 12.    | P. T. Carlson                 | 40.    | J. O. Stiegler               |
| 13.    | W. R. Corwin                  | 41-45. | R. W. Swindeman              |
| 14-16. | F. R. Cox                     | 46.    | P. F. Tortorelli             |
| 17.    | D. P. Edmonds                 | 47.    | J. M. Vitek                  |
| 18.    | G. M. Goodwin                 | 48.    | M. H. Yoo                    |
| 19.    | D. O. Hobson                  | 49.    | F. W. Wiffen                 |
| 20.    | J. A. Horak                   | 50.    | R. J. Charles (Consultant)   |
| 21.    | R. R. Judkins                 | 51.    | Alan Lawley (Consultant)     |
| 22.    | J. R. Keiser                  | 52.    | T. B. Massalski (Consultant) |
| 23.    | J. F. King                    | 53.    | R. H. Redwine (Consultant)   |
| 24-28. | R. L. Klueh                   | 54.    | J. C. Williams (Consultant)  |
| 29.    | C. T. Liu                     | 55.    | K. M. Zwilsky (Consultant)   |
| 30.    | H. E. McCoy                   |        |                              |

## EXTERNAL DISTRIBUTION

56. AMERICAN SOCIETY OF MECHANICAL ENGINEERS, 345 East 47th Street,  
New York, NY 10017  
M. R. Green
57. AIR PRODUCTS AND CHEMICALS, P.O. Box 538, Allentown, PA 18105  
K. L. Baumert
58. THE BABCOCK AND WILCOX CO., 20 S. Van Buren Avenue,  
Barberton, OH 44203  
M. Gold
59. BETHLEHEM STEEL CORPORATION, Homer Research Laboratories,  
Bethlehem, PA 18016  
R. L. Bodnar
60. P. M. Brister, Rt. 3, Box 31, Carnesville, GA 30521

61. CHICAGO BRIDGE AND IRON COMPANY, 8900 Fairbanks, N. Houston Rd.,  
P.O. Box 40066, Houston, TX 77040  
J. E. Sims
62. COMBUSTON ENGINEERING, INC., 911 West Main Street, Chattanooga, TN  
37401  
B. W. Roberts
63. COMBUSTION ENGINEERING, INC., Dept. 9001-2226, 1000 Prospect Hill  
Road, Windsor, CT 06095  
C. W. Lawton
64. CORNELL UNIVERSITY, Materials Science, Ithaca, NY 14850  
C. Y. Li
65. ELECTRIC POWER RESEARCH INSTITUTE, 3412 Hillview Avenue,  
P.O. Box 10412, Palo Alto, CA 94303  
Ramaswamy Viswanathan
66. EXXON RESEARCH & ENGINEERING CO., P.O. Box 101,  
Florham Park, NJ 07932  
A. R. Ciuffreda  
G. Sorell
67. G.A. TECHNOLOGIES, Fuels & Materials Division, P.O. Box 81608,  
San Diego, CA 92138  
D. I. Roberts
68. GULF SCIENCE & TECHNOLOGY COMPANY, P.O. Drawer 2038,  
Pittsburgh, PA 15230  
A. G. Imgram  
S. Ibarra
69. W. L. Harding, 82 Wildwood Road, Simsbury, CT 06070
70. JAPAN STEEL WORKS AMERICA, INC., 1980 Post Oak Boulevard,  
Suite 1610, Houston, TX 77056  
S. Mima
71. JAPAN STEEL WORKS AMERICA, INC., 200 Park Avenue,  
New York, NY 10168  
T. Kondo
72. W. E. Leyda, 1192 Overlook Drive, Alliance, OH 44601
73. LUKENS STEEL COMPANY, Coatesville, PA 19320  
R. A. Swift

74. THE METAL PROPERTIES COUNCIL, INC., 345 East 47th Street,  
New York, NY 10017  
Martin Prager
75. MONSANTO COMPANY, 800 N. Lindberg Blvd., St. Louis, MO 63166  
D. P. Peng
76. OAK RIDGE ASSOCIATED UNIVERSITIES LIBRARY, Oak Ridge, TN 37831  
MERT Division
77. RALPH M. PARSONS COMPANY, 100 W. Walnut Street, Pasadena, CA 91124  
W. J. Lochmann
78. R. D. THOMAS & CO., INC., 103 Avon Road, Narbeth, PA 19072  
R. D. Thomas, Jr.
79. R. L. Smith, P.O. Box Box 98, Chassell, MI 49916
80. STANDARD OIL COMPANY (INDIANA), P.O. Box 400, Naperville, IL 60540  
R. W. Howe
81. STEARNS-ROGER ENGINEERING CORP. P.O. Box 5888, Denver, CO 80217  
P. E. Dempsey
82. TENNESSEE VALLEY AUTHORITY, 400 West Summit Hill Drive,  
Knoxville, TN 37902  
M. N. Bressler
83. UNIVERSAL-CYCLOPS SPECIALTY, Steel Division, Metallurgical  
Services, 650 Washington Road, Pittsburgh, PA 15228  
H. L. Black
84. U.S. STEEL CORPORATION, Applied Research Laboratory,  
Monroeville, PA 15146  
S. J. Manganello
85. DOE, OFFICE OF FOSSIL ENERGY, 20 Massachusetts Avenue, N.W.,  
Washington, DC 20545  
S. J. Dapkunas
- 86-87. DOE, OAK RIDGE OPERATIONS OFFICE, P.O. Box E, Oak Ridge, TN 37831  
Office of Assistant Manager for Energy Research and Development
- 88-114. DOE, TECHNICAL INFORMATION CENTER, P.O. Box 62, Oak Ridge, TN 37831