

# Influence of Long-Term Aging and Superimposed Creep Stress on the Microstructure of 2.25Cr-1Mo Steel

N. GOPE, AMIT CHATTERJEE, T. MUKHERJEE, and D.S. SARMA

To understand the influence of high-temperature aging and superimposed creep stress on the microstructural variations in a 2.25Cr-1Mo steel, the shoulder and gage portions of the specimens subjected to stress-rupture tests at 540 °C and 580 °C have been studied by transmission electron microscopy. In the normalized and tempered condition, the steel exhibited a tempered bainitic structure and the carbides were present as  $M_3C$  globules,  $M_2C$  platelets, and  $M_{23}C_6$  rectangular parallelepipeds. Aging the steel at 540 °C for 7022 hours or 17,946 hours resulted in considerable coarsening of  $M_2C$  and caused precipitation of  $M_6C$  carbides. The superimposed creep stress enhanced the  $M_2C$  precipitation. The ferrite matrix exhibited some recovery in the specimens exposed for 17,946 hours. While  $M_2C$  platelets were observed in a few areas after 14,836 hours of aging at 580 °C, this carbide was virtually nonexistent when a stress of 78 MPa was superimposed. Amounts of  $M_{23}C_6$  persisted throughout the tests at both 540 °C and 580 °C. The  $M_6C$  carbide became more predominant after long exposure at 580 °C. The ferrite matrix recovered considerably in specimens subjected to creep stress at 580 °C for 14,836 hours.

## I. INTRODUCTION

A 2.25Cr-1Mo steel has been used for high-temperature service applications in power generation and chemical industries for over five decades. Apart from possessing adequate creep strength, the corrosion resistance of this grade of steel is superior to that of 0.5Mo, 1Cr-0.50Mo, and 1.25Cr-0.50Mo steels. Microstructural changes due to long-term tempering and the creep-deformed structures were investigated a few decades ago using carbon extraction replicas.<sup>[1-4]</sup> Recently, the microstructure of the Cr-Mo and Cr-Mo-V steels exposed to 20 years of service life has been studied to understand the microstructural degradation.<sup>[5-9]</sup> Some investigators used accelerated aging at 630 °C to produce microstructures that simulate 25,000 to 1,000,000 hours of service exposure at 540 °C.<sup>[10]</sup> Though these studies established various structural changes due to prolonged service exposure, the influence of exposure time and temperature *vis-à-vis* that of superimposed creep stress in bringing about the observed microstructural changes is still not clear. Considering the recent interest in predicting the remaining life of the components exposed to the designed life,<sup>[11-12]</sup> a simultaneous study of the two factors becomes important. We have recently reported the results of our investigations on the role of high-temperature exposure time and that of the superimposed creep stress on the microstructures of 1.25Cr-0.5Mo, 1Cr-0.5Mo, and 0.5Cr-0.5Mo-0.25V steels.<sup>[13,14,15]</sup>

Since creep-resistant steels are presently imported by India, Tata Steel embarked on a program of producing 2.25Cr-1Mo grade steel to international specifications.

Stress-rupture tests have been carried out at various temperatures, and the results of these tests have been reported elsewhere.<sup>[16-18]</sup> In the present investigation, the results of a detailed transmission electron microscopy study carried out on both the shoulder and gage portions of the stress-rupture tested specimens of a 2.25Cr-1Mo steel are presented in order to arrive at an understanding of the effects of high-temperature exposure and those of superimposed creep stress.

## II. EXPERIMENTAL

A 2.25Cr-1Mo steel, with the chemistry shown in Table I, was made in a 6-ton electric arc furnace and teemed into a mold fitted with a hot top. The ingot was subsequently rolled to 250 × 250 mm square blooms, and these blooms were machined down to 210 × 210 mm square gothic bars and subsequently rolled to seamless tubes of 215-mm outside diameter and 40-mm wall thickness through a piercing elongator and pilgering process. Longitudinal blanks cut from the tubes were machined down to 25-mm-diameter rounds and austenitized at 950 °C for 1 hour, air cooled, and subsequently tempered at 680 °C for 6 hours.

Stress-rupture tests were carried out at 540 °C, 560 °C, and 580 °C in multipoint creep-testing machines on cylindrical specimens prepared from the normalized-and-tempered rounds. The loading was done with the aim of achieving rupture times of 1000, 3000, and 10,000 hours at each test temperature. The shoulder and gage portions of the specimens that ruptured at 540 °C and 580 °C were selected for a detailed microstructural study. In order to

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Table I. Chemical Composition of the Steel (Weight Percent) Investigated

C	Mn	Si	S	P	Cr	Mo	Fe
0.16	0.55	0.34	0.018	0.017	2.10	1.06	bal.

**Table II. Details of Stress-Rupture Specimens of 2.25Cr-1Mo Steel Used for the TEM Study\***

Temperature (°C)	Stress (MPa)	Rupture Time (h)	Elongation (Pct)	Reduction in Area (Pct)
540	165	7022	27	79
540	132	17,946	50	87
580	98	6526	41	82
580	78	14,836	86	87

\*Normalized and tempered specimens were also examined.

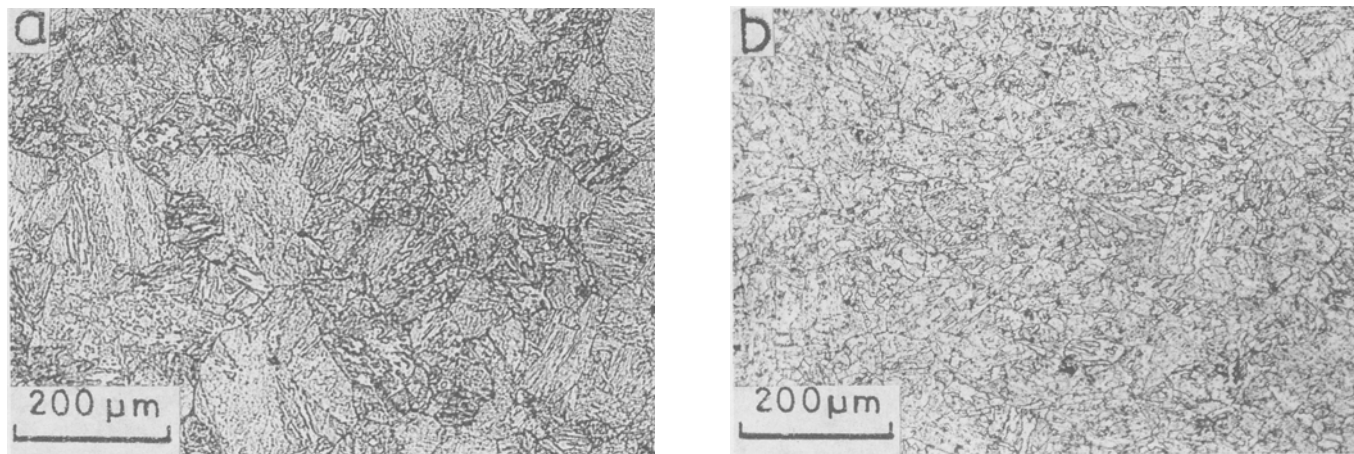


Fig. 1—Optical microstructure of steel: (a) normalized and tempered and (b) stress rupture tested at 580 °C for 14,836 h.

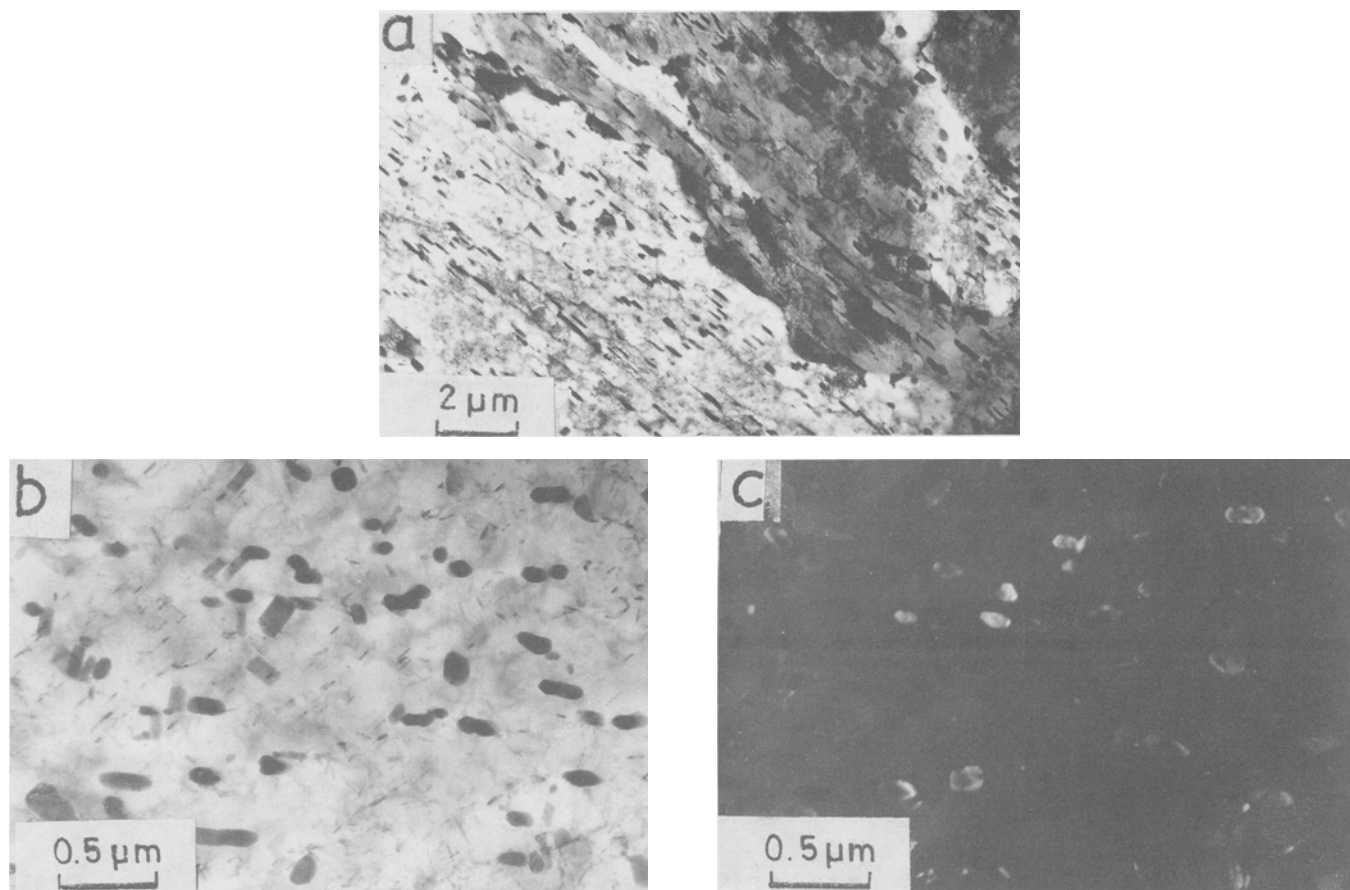


Fig. 2—TEMs of the steel in normalized and tempered conditions: (a) low-magnification BF shows the preferential alignment of rod-shaped carbides; (b) reveals the three morphologies of carbide (1) globular, (2) fine, and (3) rectangular parallelepipeds; (c) DF shows the globular morphology carbide, (d) SAD and (e) schematic representation of SAD identifying the globular carbide as  $M_3C$ ; (f) DF shows the plate carbide; (g) SAD and (h) schematic representation of SAD identifying it as  $M_2C$ ; (i) BF and (j) DF revealing the rectangular parallelepiped morphology of carbide; (k) SAD and (l) schematic representation of SAD identifying it as  $M_{23}C_6$ .

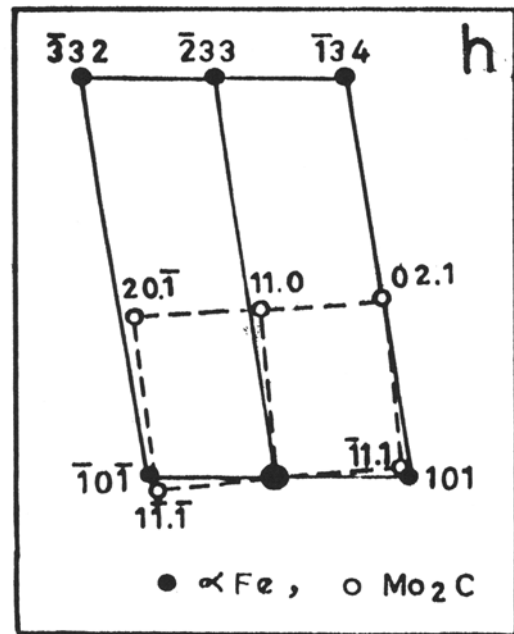
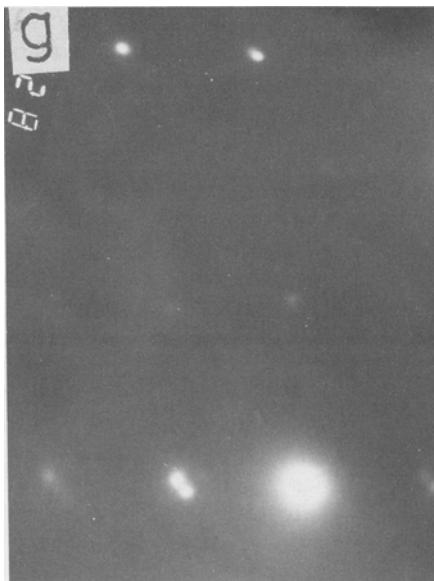
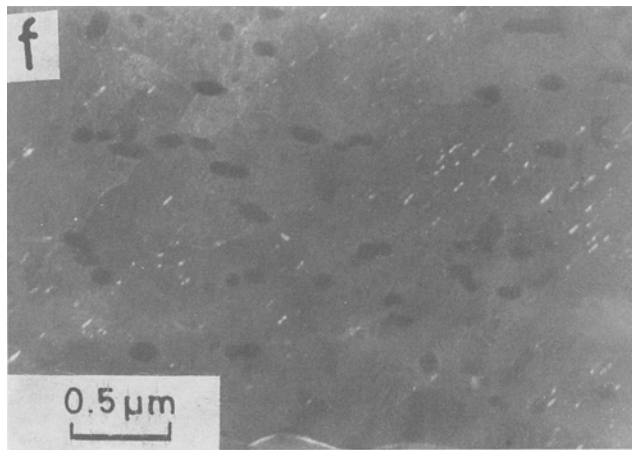
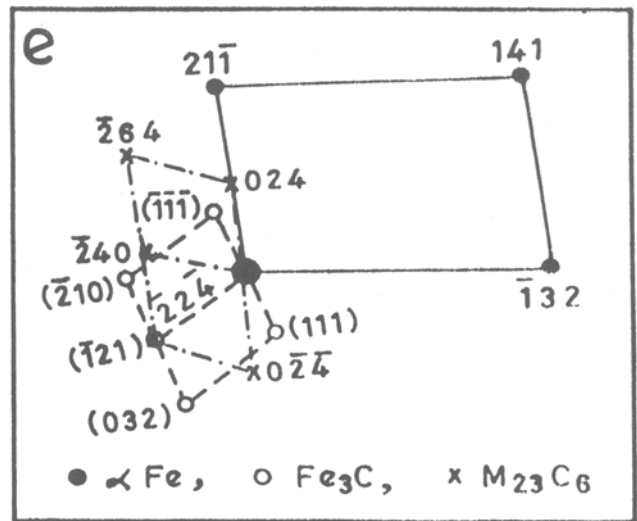


Fig. 2 Cont.—TEMs of the steel in normalized and tempered conditions: (a) low-magnification BF shows the preferential alignment of rod-shaped carbides; (b) reveals the three morphologies of carbide (1) globular, (2) fine, and (3) rectangular parallelepipeds; (c) DF shows the globular morphology carbide, (d) SAD and (e) schematic representation of SAD identifying the globular carbide as  $M_3C$ ; (f) DF shows the plate carbide; (g) SAD and (h) schematic representation of SAD identifying it as  $M_2C$ ; (i) BF and (j) DF revealing the rectangular parallelepiped morphology of carbide; (k) SAD and (l) schematic representation of SAD identifying it as  $M_{23}C_6$ .

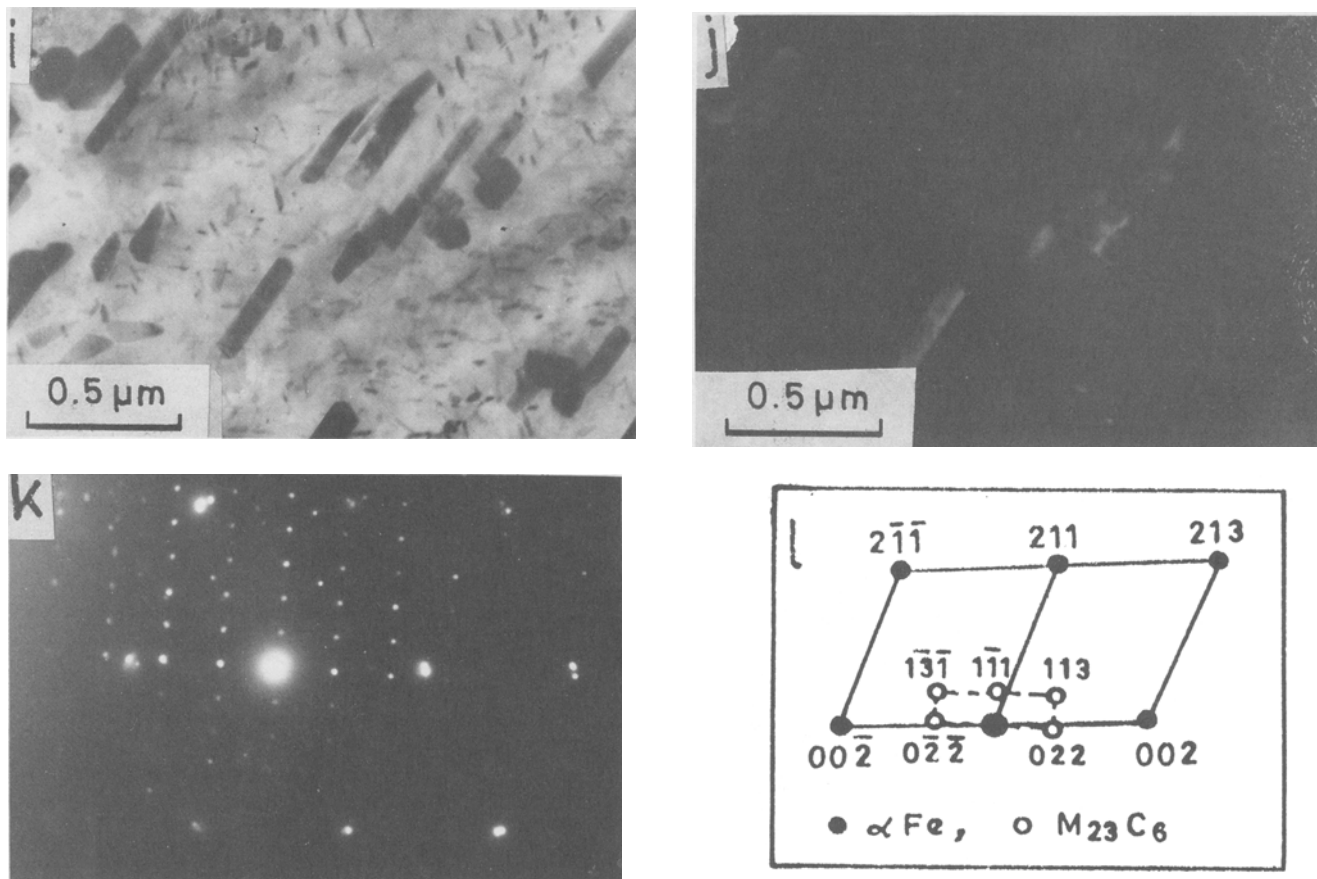


Fig. 2 Cont. — TEMs of the steel in normalized and tempered conditions: (a) low-magnification BF shows the preferential alignment of rod-shaped carbides; (b) reveals the three morphologies of carbide (1) globular, (2) fine, and (3) rectangular parallelepipeds; (c) DF shows the globular morphology carbide, (d) SAD and (e) schematic representation of SAD identifying the globular carbide as  $M_3C$ ; (f) DF shows the plate carbide; (g) SAD and (h) schematic representation of SAD identifying it as  $M_2C$ ; (i) BF and (j) DF revealing the rectangular parallelepiped morphology of carbide; (k) SAD and (l) schematic representation of SAD identifying it as  $M_{23}C_6$ .

understand the effects of exposure time and the superimposed creep stress, the shoulder and gage portions of each specimen were studied. The details of the specimens used for transmission electron microscopic study are shown in Table II.

Heat-treated samples and creep-deformed specimens were mechanically polished and etched with 2 pct nital for optical microscopic examination. Slices of 0.50-mm thickness were cut from the heat-treated and creep-tested specimens at an extremely low speed using an ISOMET low-speed saw. These slices were mechanically ground to less than 0.10-mm thickness, and thin foils were prepared by electropolishing using an electrolyte of 10 pct perchloric acid and 90 pct glacial acetic acid. Thin foils were examined in a JEOL JEM 200 CX transmission electron microscope operating at 160 KV.

### III. RESULTS

#### A. Optical Microscopy

The microstructure of the steel in the normalized and tempered condition, shown in Figure 1(a), reveals that it is fully bainitic. Figure 1(b) shows the microstructure

of the steel after holding at 580 °C for 14,836 hours superimposed with creep stress; the microstructure reveals some recrystallization of the ferrite matrix of bainite.

#### B. Transmission Electron Microscopy

The transmission electron micrographs (TEMs) of the steel in the normalized and tempered condition are shown in Figure 2. Figure 2(a) is a low-magnification TEM showing the tempered bainitic structure; even at this magnification, the preferential alignment of rod-shaped carbides along the lath boundaries of ferrite is seen. Figure 2(b) is a bright-field micrograph (BF) revealing three morphologies of carbide: (1) globular (0.15  $\mu\text{m}$  diameter), (2) fine plate (0.05  $\mu\text{m}$  long), and (3) rectangular parallelepiped shaped (0.5  $\mu\text{m}$  long).

The dark-field micrograph (DF) for the globular morphology carbide of Figure 2(b) is shown in Figure 2(c). The selected area diffraction (SAD) pattern taken from the carbide and its schematic representation are shown in Figures 2(d) and (e), respectively, which identify it as  $Fe_3C$  (this pattern contains reflections from the carbide  $M_{23}C_6$  as well). The DF for plate-shaped carbide revealed in Figure 2(b) is shown in Figure 2(f) and the

SAD, taken from this precipitate and its schematic representation, shown in Figures 2(g) and (h), respectively, identify it as  $\text{Mo}_2\text{C}$ . The following orientation relationship is obtained from this figure:

$$(101)_\alpha \sim 5 \text{ deg } (1\bar{1}\bar{1})\text{M}_2\text{C}$$

$$(233)_\alpha \sim 5 \text{ deg } (11.0)\text{M}_2\text{C}$$

Figures 2(i) and (j), which are the BF and DFs, respectively, reveal the carbides with a rectangular parallelepiped morphology. The SAD taken from this carbide and its schematic representation are shown in Figures 2(k) and (l), respectively, which identify it as  $\text{M}_{23}\text{C}_6$ . The following orientation relationship exists in this figure:

$$(001)_\alpha // (011)\text{M}_{23}\text{C}_6$$

$$(\bar{1}20)_\alpha // (21\bar{1})\text{M}_{23}\text{C}_6$$

This is in agreement with the Nishiyama-Wassermann relationship.<sup>[19]</sup> The TEMs for the shoulder portion of the specimen creep tested at 540 °C for 7022 hours are shown in Figures 3(a) through (c). Figure 3(a) reveals numerous plate-shaped carbides, 0.50- $\mu\text{m}$  long. These are identified as  $\text{M}_2\text{C}$  by selected area diffraction. The coarse carbides (0.2- $\mu\text{m}$  diameter) revealed in this figure have been identified as  $\text{M}_6\text{C}$ . Figure 3(b) is the BF revealing the fine globular  $\text{M}_6\text{C}$  precipitates (0.1- $\mu\text{m}$  size) coexisting with plate-shaped precipitates. The grain boundary carbide shown in Figure 3(c) was identified as  $\text{M}_6\text{C}$ , whereas the rectangular parallelepiped carbides revealed in the same figure were identified as  $\text{M}_{23}\text{C}_6$ . The carbide  $\text{M}_3\text{C}$  has dissolved in the matrix after 7022 hours at 540 °C.

The TEMs for the gage portion of the specimen creep tested at 540 °C for 7022 hours are shown in Figures 4(a) through (e). Figure 4(a) shows numerous  $\text{M}_2\text{C}$  plate-shaped precipitates, 0.4  $\mu\text{m}$  long, coexisting with fine globular carbides identified as  $\text{M}_6\text{C}$ . Figure 4(b) reveals the spheroidization tendency of coarse  $\text{M}_6\text{C}$  carbides, while Figure 4(c) illustrates the grain boundary carbide. The SAD pattern and its schematic representation shown in Figures 4(d) and (e), respectively, identify it as  $\text{M}_6\text{C}$ . The carbide  $\text{M}_3\text{C}$  has dissolved in the matrix after 7022 hours at 540 °C.

The TEMs for the shoulder portion of the creep specimen tested at 540 °C for 17,946 hours are shown in Figures 5(a) through (c). Figure 5(a) shows well-developed (maximum length  $\sim 1.5 \mu\text{m}$ )  $\text{M}_2\text{C}$  precipitates coexisting with fine ellipsoidal  $\text{M}_6\text{C}$  precipitates. Figure 5(b) reveals the significant tendency of coarse  $\text{M}_6\text{C}$  carbide of 0.25  $\mu\text{m}$  size to spheroidize. The ferrite matrix adjacent to grain boundaries has become depleted of plate-shaped carbides. Figure 5(c) demonstrates all the features: plate-shaped carbide  $\text{M}_2\text{C}$ , fine globular carbide  $\text{M}_6\text{C}$ , and rectangular parallelepiped carbide  $\text{M}_{23}\text{C}_6$ .

The TEMs for the gage portion of the specimen creep tested at 540 °C for 17,946 hours are shown in Figures 6(a) through (c). Figure 6(a) reveals numerous plate-shaped  $\text{M}_2\text{C}$  carbides and a rectangular parallelepiped carbide  $\text{M}_{23}\text{C}_6$ . Figures 6(b) and (c) show some well-developed  $\text{M}_2\text{C}$  precipitates (0.8- $\mu\text{m}$  long) and coarse

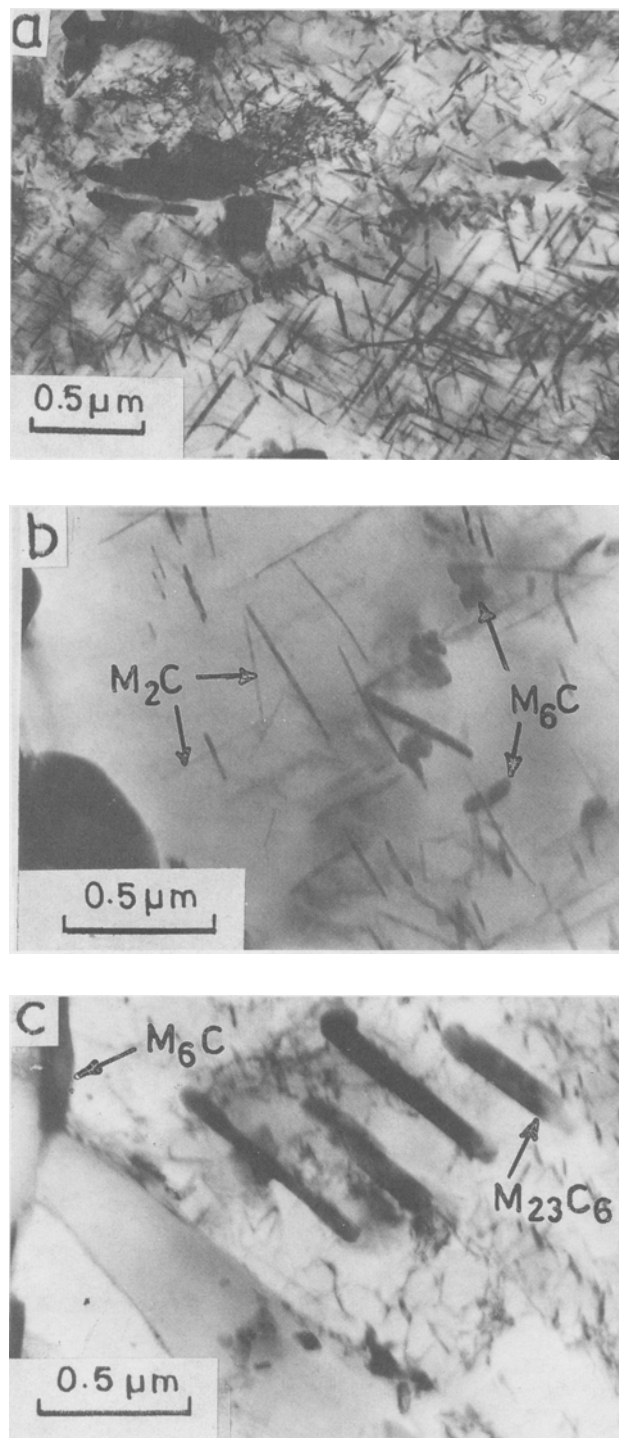


Fig. 3—TEMs for the shoulder portion of the specimen creep tested at 540 °C for 7022 h: (a) the numerous  $\text{M}_2\text{C}$  plate carbides, (b) the fine globular  $\text{M}_6\text{C}$  precipitates coexisting with  $\text{M}_2\text{C}$  precipitates, and (c) grain boundary carbide as well as rectangular  $\text{M}_{23}\text{C}_6$  carbides.

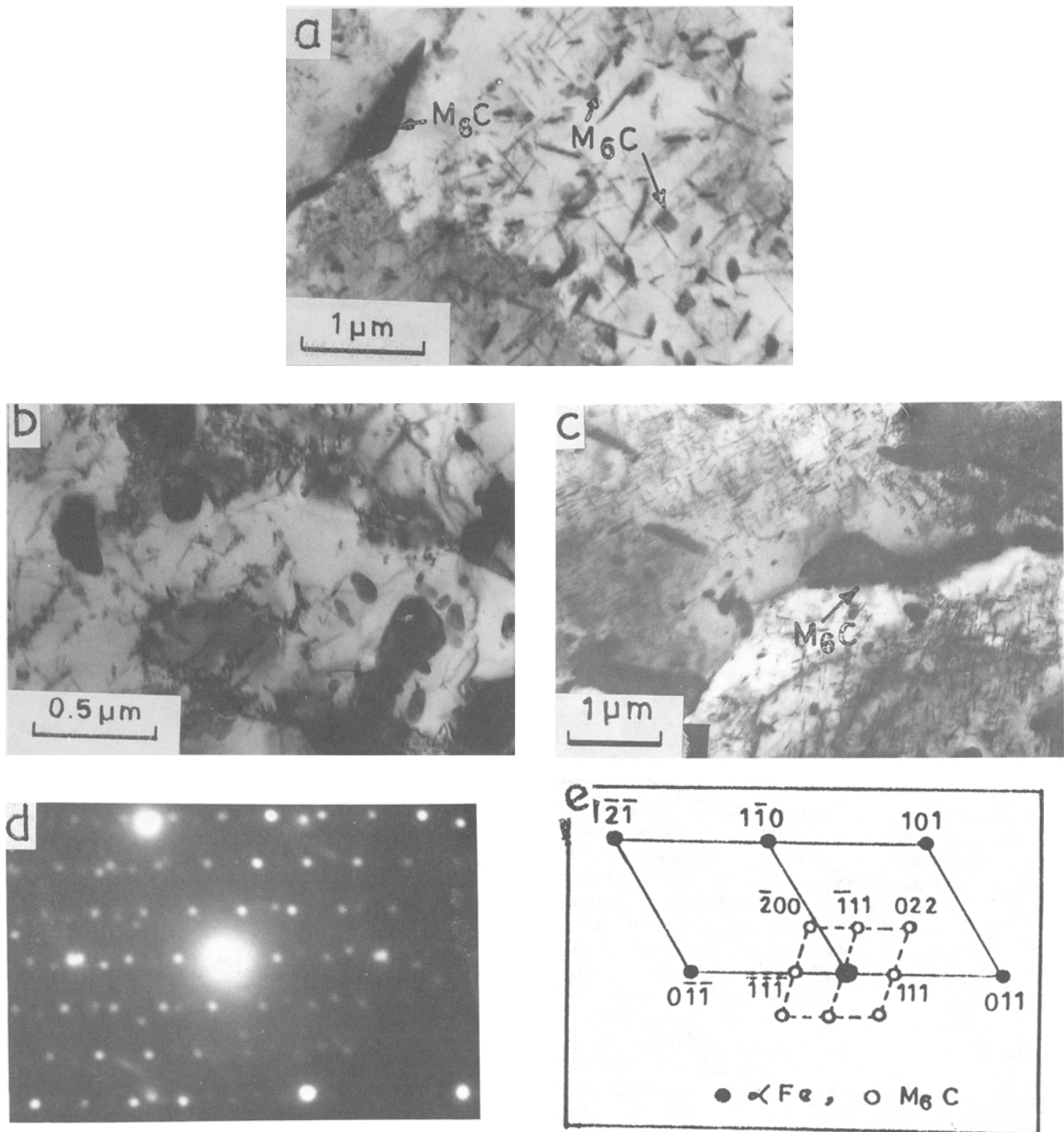


Fig. 4—TEMs for the gage portion of the specimen creep tested at 540 °C for 7022 h: (a)  $M_6C$  precipitate, (b) the spheroidization tendency of coarse  $M_6C$  carbide, (c) the grain boundary carbide, (d) SAD, and (e) schematic representation of SAD identifying it as  $M_6C$ .

$M_6C$  (0.4- $\mu\text{m}$  diameter). Some recovery of ferrite matrix is also revealed in Figure 6(b).

The TEMs for the shoulder portion of the specimen creep tested at 580 °C for 6526 hours are given in Figures 7(a) through (d). Figure 7(a) is a low-magnification TEM revealing a partially recrystallized bainitic structure. The TEM shown in Figure 7(b) dem-

onstrates the two morphologies of carbides, rectangular parallelepiped  $M_{23}C_6$  and globular (coarse as well as fine)  $M_6C$ . Figure 7(c) also shows fine globular carbides, which are identified as  $M_6C$ . The presence of numerous fine  $M_2C$  plates, 0.2- $\mu\text{m}$  long, is revealed in Figure 7(d).

The TEMs for the gage portion of the specimen creep tested at 580 °C for 6526 hours are shown in Figures 8(a)

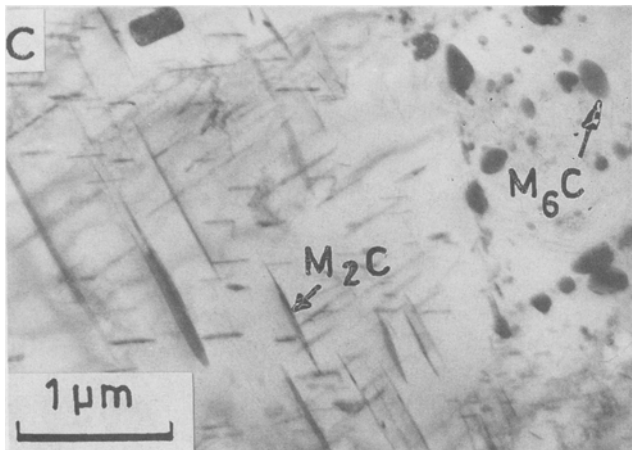
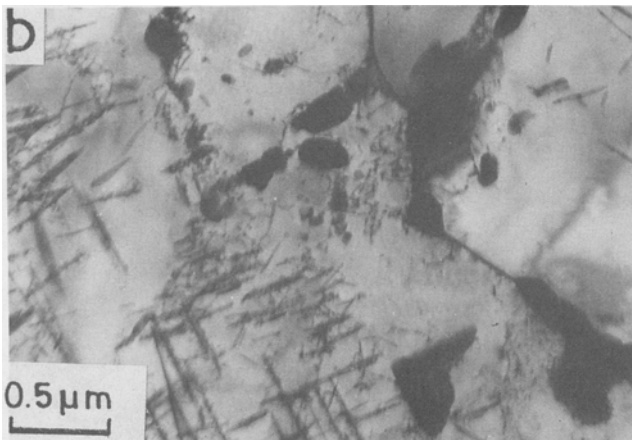
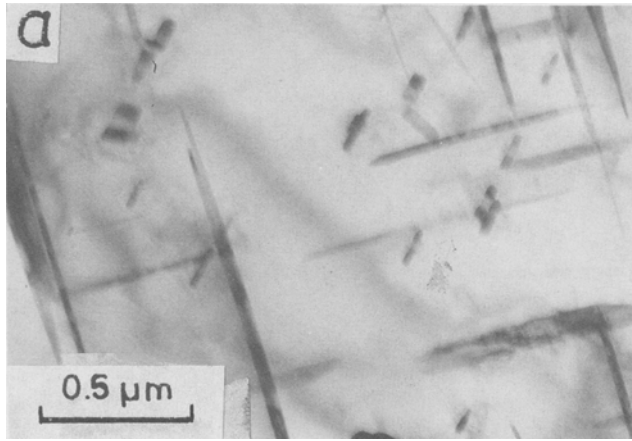


Fig. 5—TEMs for the shoulder portion of the specimen creep tested at 540 °C for 17,946 h: (a) the well-developed  $M_2C$  plate precipitates coexisting with fine ellipsoidal precipitates, (b)  $M_2C$  plate carbide and coarse  $M_6C$  carbide, and (c) all of the features: plate-shaped carbide, fine globular carbide, and rectangular carbide.

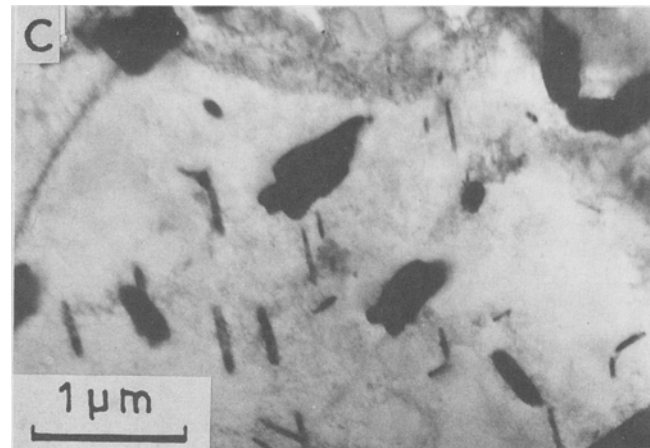
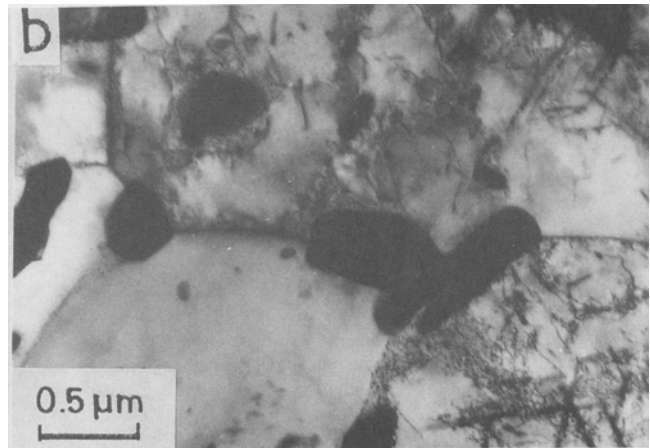
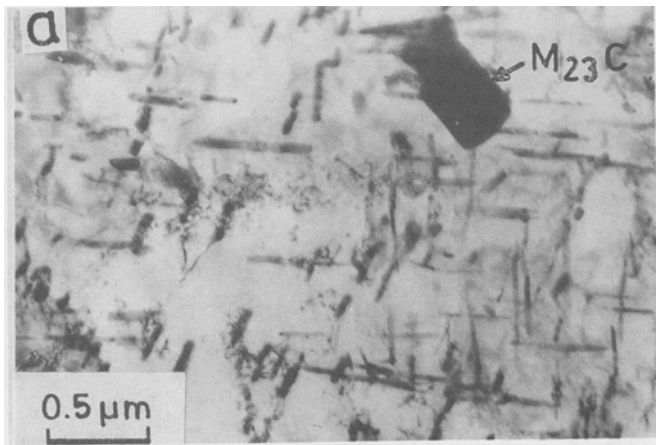


Fig. 6—TEMs for the gage portion of the specimen creep tested at 540 °C for 17,946 h (a)  $M_2C$  carbide, (b) some  $M_2C$  plate precipitates, coarse  $M_6C$  precipitates, and recovery in the ferrite matrix, and (c) coarse  $M_6C$  and  $M_{23}C_6$  parallelepipeds.

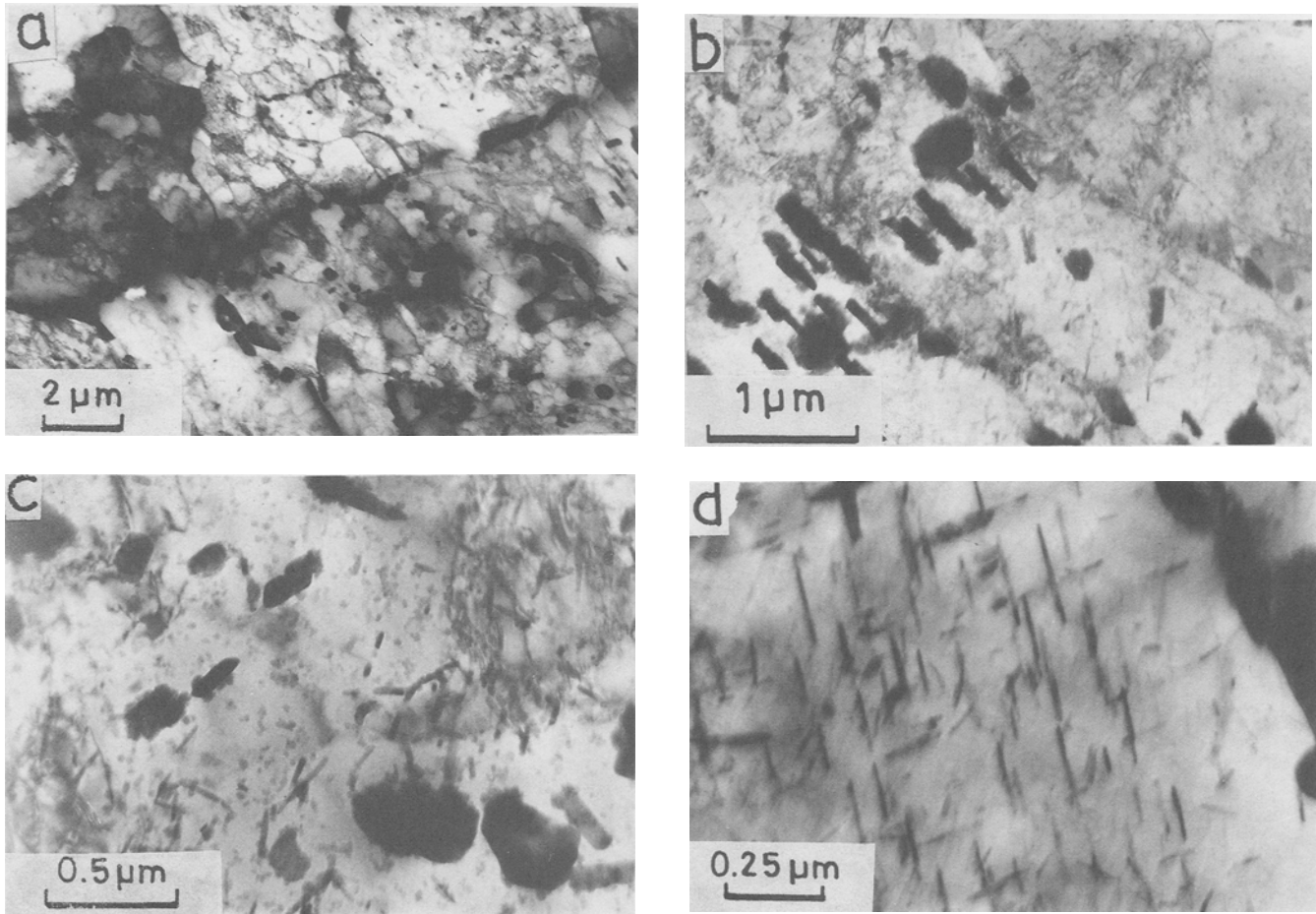


Fig. 7—TEMs for the shoulder portion of the specimen creep tested at 580 °C for 6526 h: (a) low-magnification TEM revealing the recovered bainitic structure, (b) rectangular parallelepiped-shaped  $M_{23}C_6$  and globular (coarse as well as fine)  $M_6C$  carbide, (c) the globular morphology of  $M_6C$  carbides, and (d) the presence of numerous platelets of  $M_2C$ .

through (d). Figure 8(a) illustrates the coarse globular (0.3- $\mu\text{m}$  diameter) carbides as well as extremely fine plates of  $M_2C$ . Figure 8(b) reveals the  $M_{23}C_6$  carbide in its rectangular parallelepiped morphology along with fine plates of  $M_2C$ . Figure 8(c) illustrates numerous  $M_2C$  precipitates of 0.1- $\mu\text{m}$  length. A coarse-grain boundary carbide, shown in Figure 8(d), was identified as  $M_6C$ .

The TEMs for the shoulder portion of specimen creep tested at 580 °C for 14,836 hours are shown in Figures 9(a) through (d). Figure 9(a) is a low-magnification TEM revealing the recovered lath structure containing coarse  $M_6C$  carbides. Figure 9(b) shows a highly recovered ferrite matrix containing several subgrains and coarse  $M_6C$  carbides (0.4- $\mu\text{m}$  size). Figure 9(c) reveals the newly-formed ellipsoidal  $M_6C$  precipitates. Figure 9(d) demonstrates the existence of plate-shaped  $M_2C$  precipitates, 0.3- $\mu\text{m}$  long, in a few areas.

The TEMs for the gage portion of the specimen creep tested at 580 °C for 14,836 hours are shown in Figures 10(a) through (c). Figure 10(a) shows the recrystallized ferrite matrix and also coarse spheroids of  $M_6C$  carbides (0.6- $\mu\text{m}$  diameter), while Figure 10(b) re-

veals the size distribution of  $M_6C$  carbides. Figure 10(c) indicates coarse as well as fine  $M_6C$  carbides along with the  $M_{23}C_6$  carbides in their rectangular parallelepiped morphology. The  $M_2C$  carbide has almost dissolved in this condition, and the ferrite matrix exhibits a recrystallized structure.

#### IV. DISCUSSION

A summary of the transmission electron microscopy results on 2.25Cr-1Mo steel is presented in Table III. The present investigation has clearly shown that in the normalized and tempered condition, the 2.25Cr-1Mo steel studied exhibits a fully bainitic structure and that the tempered bainite has three different types of carbides. The orthorhombic carbide,  $M_3C$ , is present in the nearly spheroidal form, the hexagonal  $M_2C$  as extremely fine and short platelets, and the face-centered cubic  $M_{23}C_6$  in the shape of rectangular parallelepipeds. In addition,  $M_{23}C_6$  was also present at grain boundaries.

Baker and Nutting<sup>[1]</sup> were the first to investigate systematically the sequence of carbide precipitation during tempering of 2.25Cr-1Mo steel using extraction replicas. They also obtained similar microstructures but found that



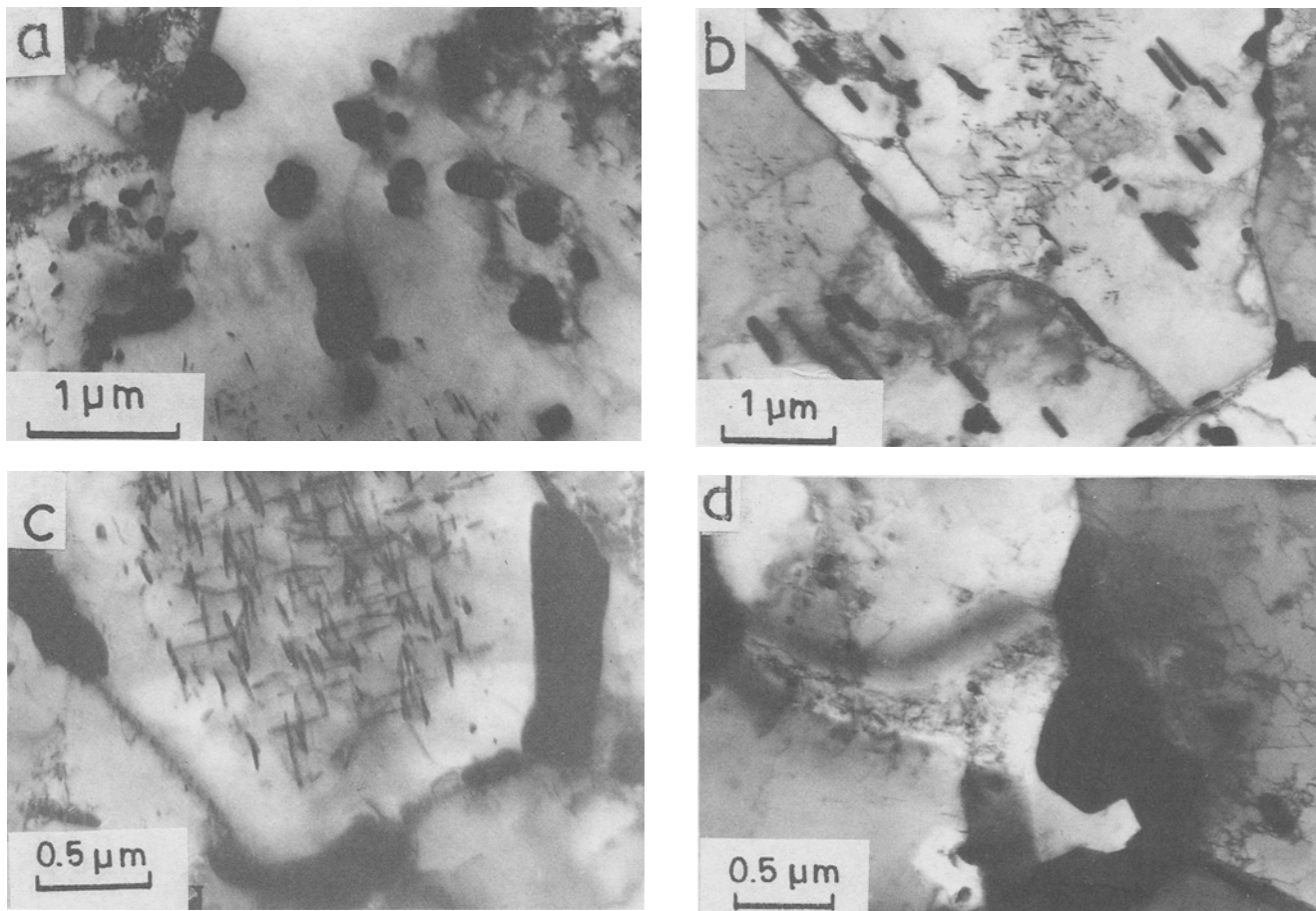


Fig. 8—TEMs for the gage portion of the specimen creep tested at 580 °C for 6526 h: (a) coarse globular  $M_6C$  carbide as well as fine  $M_2C$ , (b) the rectangular parallelepiped  $M_{23}C_6$  along with fine platelets of  $M_2C$ , (c) numerous plate precipitates and coarse  $M_6C$ , and (d) the grain boundary carbide,  $M_6C$ .

the carbides that would be present on subjecting the steel to tempering at 680 °C for 6 hours would be  $Fe_3C$ ,  $Mo_2C$ , and  $Cr_7C_3$ . The morphologies of the first two carbides are similar to those observed in the present work, and that of  $Cr_7C_3$  is similar to that of  $M_{23}C_6$  observed in the present investigation.

Murphy and Branch<sup>[3]</sup> also studied normalized and tempered 2.25Cr-1Mo steel and found evidence of  $M_3C$  and  $M_2C$  with an occasional presence of  $M_{23}C_6$ . They also observed that the normalized structures for different heats of 2.25Cr-1Mo steels exhibited different volume fractions of ferrite and bainite, and that as the bainite content increased, the size of cementite particles decreased. The fineness of the cementite spheroids observed in the present work is, thus, in accordance with the finding of Murphy and Branch.<sup>[3]</sup>

Pilling and Ridley<sup>[20]</sup> also observed rodlike precipitates which were similar in morphology to the  $M_{23}C_6$  carbides observed in the present work and indicated that they could be either  $M_{23}C_6$  or  $M_6C$ . They identified the fine needle carbide as  $Mo_2C$ . Baker and Nutting<sup>[1]</sup> and Wada<sup>[21]</sup> reported the presence of fibrous  $M_2C$  carbide in the normalized and tempered condition of 2.25Cr-1Mo

steel in cases where ferrite was observed along with bainite. In the present case, the microstructure was entirely bainitic, and the absence of free ferrite is probably responsible for the absence of fibrous precipitates.

In cases where  $Cr_7C_3$  was reported by earlier investigators, some detected its presence by streaking in electron diffraction patterns (not by obtaining reciprocal lattice reflections of this carbide).<sup>[21]</sup> In the present investigation, we could obtain the selected area diffraction patterns from each of the morphologies of the carbides, and by this technique, we could establish the presence of  $M_3C$ ,  $M_2C$ , and  $M_{23}C_6$ . Similarly, Yukitoshi and Nishida<sup>[2]</sup> confirmed the presence of  $M_3C$ ,  $M_2C$ , and  $M_{23}C_6$  only in the normalized and tempered condition and could not get enough evidence for  $Cr_7C_3$  and  $M_6C$ . The present results are in excellent agreement with this work. There has also been some evidence to suggest that while the carbide  $M_7C_3$  is formed in chromium steels, the addition of molybdenum would result in an increased tendency to form  $M_{23}C_6$  at the expense of  $M_7C_3$ .<sup>[22]</sup>

Although there have been earlier investigations on the microstructure of 2.25Cr-1Mo steel subjected to creep or long-term service exposure, no information is avail-

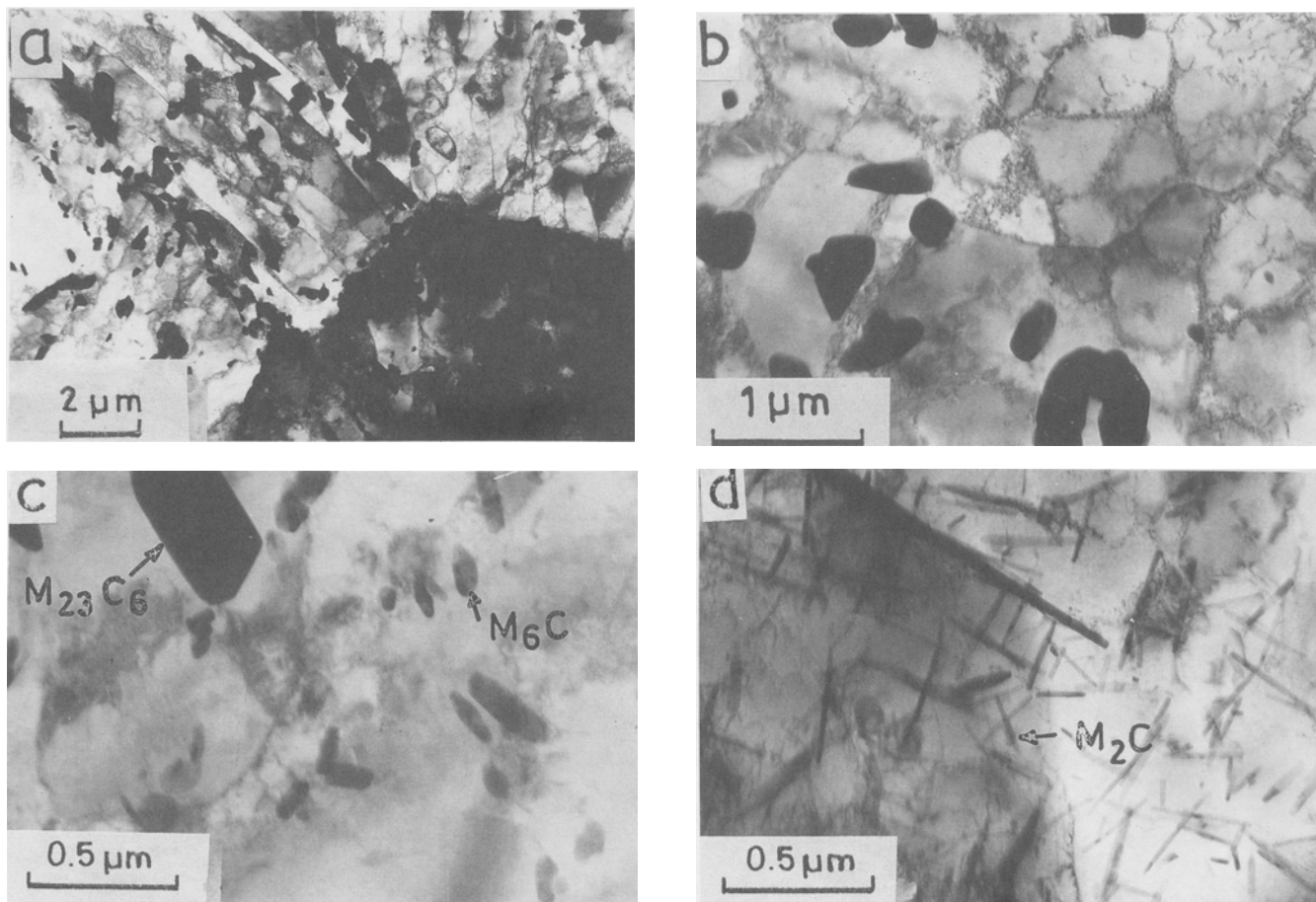


Fig. 9—TEMs for the shoulder portion of the sample creep tested at 580 °C for 14,836 h: (a) a low-magnification TEM revealing the recovered lath structure containing coarse carbide, (b) the mostly coarse  $M_6C$  carbides and recrystallization of ferrite matrix, (c) the newly formed ellipsoidal  $M_6C$  precipitates, and (d) the existence of  $M_2C$  plate precipitates.

able on the individual contribution of the high-temperature exposure time on the microstructure and that of the superimposed creep stress. The present investigation is aimed at isolating these effects to arrive at an understanding of the long-term tempering effects and the role of creep stress in altering these microstructural variations.

The present work shows that aging the 2.25Cr-1Mo steel at 540 °C for 7022 hours considerably coarsened the  $M_2C$  carbide, and it increased in length from about 0.05  $\mu\text{m}$  in the normalized and tempered condition to 1.5  $\mu\text{m}$  after 17,946 hours of exposure at 540 °C. The superimposed creep stress surprisingly restricted the length of these platelets to 0.8  $\mu\text{m}$ ; however, these platelets are more profuse in the latter case. Another effect of 540 °C aging is that the  $M_3C$  carbide dissolved in the matrix, and in its place,  $M_6C$  carbide was observed as globular carbide. There was no noticeable change in  $M_{23}C_6$  carbide occurring as rectangular parallelepipeds either in the shoulder or gage section of the specimens tested at 540 °C up to 17,946 hours. The ferrite matrix showed some signs of recovery only in specimens exposed for 17,946 hours, with or without the creep stress. Interestingly, the length of the  $M_2C$  platelets exposed at 580 °C is much less than the corresponding ones at 540 °C, both in the shoulder portion and the gage section of the steel.

While the  $M_2C$  plates grew up to 0.30  $\mu\text{m}$  long after 14,836 hours aging at 580 °C, this carbide is virtually absent when 78 MPa stress is superimposed on it. The  $M_6C$  carbide became more prominent, both within the ferrite matrix and at the grain boundaries, after long exposure with or without the creep stress. The onset of recrystallization is clearly visible, the extent of which has become more prominent in specimens subjected to creep stress at 580 °C for 14,836 hours.

Murphy and Branch<sup>[3]</sup> carried out a detailed investigation of the microstructural changes taking place during the creep of 2.25Cr-1Mo steel. They reported that the  $M_3C$  carbide rapidly spheroidizes and begins to transform to  $M_{23}C_6$  and  $M_6C$ . The present results are in agreement with this finding, as  $M_3C$  is observed only in the normalized and tempered condition and not in any other creep-tested sample, either in the shoulder or the gage section. Murphy and Branch<sup>[3]</sup> also reported that  $M_2C$  carbides would dissolve gradually in the matrix during creep testing at 566 °C for 15,000 hours. The present investigation reveals that the  $M_2C$  carbide grows to about 1.5  $\mu\text{m}$  at 540 °C after 17,946 hours, and at 580 °C, it would grow initially in size before the dissolution process starts. The size of the  $M_2C$  carbide came down to 0.3  $\mu\text{m}$  after 14,836 hours at 580 °C in the shoulder

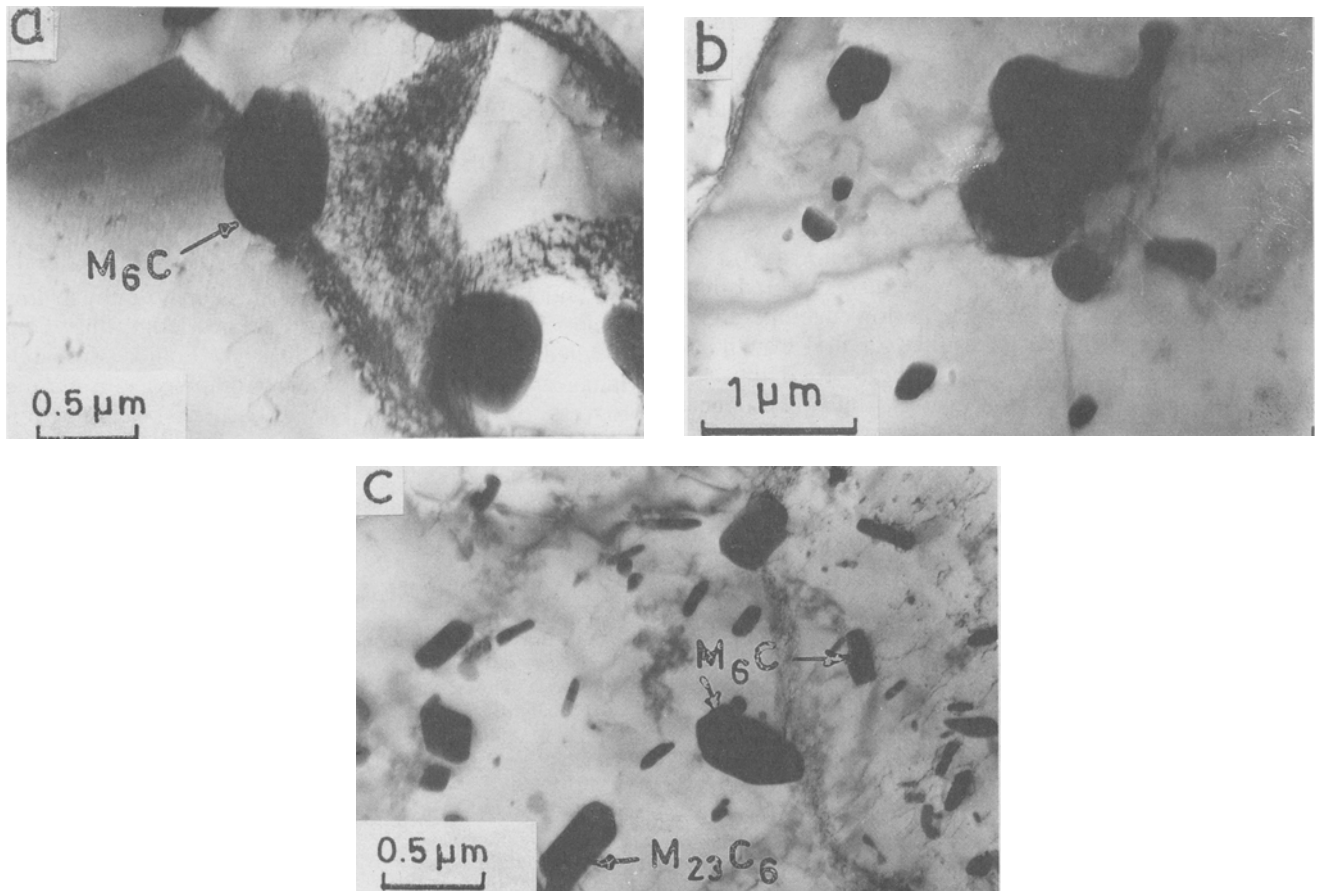


Fig. 10—TEMs for the gage portion of the steel creep tested at 580 °C for 14,836 h: (a) the recrystallized ferrite matrix and the coarse spheroids of  $M_6C$  carbides, (b) the size distribution of  $M_6C$  carbides, and (c) the coarse as well as fine  $M_6C$  carbides along with  $M_{23}C_6$  carbides in their rectangular parallelepiped morphology.

Table III. Summary of Transmission Electron Microscopy Results on 2.25Cr-Mo Steel

Temperature (°C) (Rupture time, h)	Specimen Location	Carbide Type and Morphology				Ferrite Matrix
		$M_3C$	$M_2C$	$M_{23}C_6$	$M_6C$	
As heat treated	—	globular, 0.15 $\mu\text{m}$	fine platelets 0.05- $\mu\text{m}$ long	rectangular parallelepiped, 0.50- $\mu\text{m}$ long 0.70 $\mu\text{m}$	absent	tempered bainitic structure
540 (7022)	S	absent	0.50- $\mu\text{m}$ long		globular, 0.20 $\mu\text{m}$	tempered bainitic structure
540 (7022)	G	absent	0.40- $\mu\text{m}$ long	1.0 $\mu\text{m}$	0.30 $\mu\text{m}$	tempered bainitic structure
540 (17,946)	S	absent	1.50- $\mu\text{m}$ long	0.80 $\mu\text{m}$	0.25 $\mu\text{m}$	$\alpha$ reveals tendency to recover
540 (17,946)	G	absent	0.80- $\mu\text{m}$ long	0.80 $\mu\text{m}$	0.40 $\mu\text{m}$	$\alpha$ reveals tendency to recover
580 (6526)	S	absent	0.20- $\mu\text{m}$ long	0.80 $\mu\text{m}$	0.30 $\mu\text{m}$	$\alpha$ reveals tendency to recover
580 (6526)	G	absent	0.10- $\mu\text{m}$ long	0.80 $\mu\text{m}$	0.30 $\mu\text{m}$	$\alpha$ reveals tendency to recover
580 (14,836)	S	absent	0.30- $\mu\text{m}$ long in a very few areas	0.80 $\mu\text{m}$	0.40 $\mu\text{m}$	$\alpha$ recovery is substantial
580 (14,836)	G	absent	absent	0.60 $\mu\text{m}$	0.60 $\mu\text{m}$	$\alpha$ recrystallizes

Note: S = shoulder; G = gage;  $\alpha$  = ferrite.

portion, and the corresponding gage section was totally free from this carbide.

The recovery and recrystallization process was also more prominent in the gage section than the shoulder when tested at 580 °C, suggesting that creep stress exerted a significant increase in the rate of recovery and recrystallization of bainitic ferrite.

Wada<sup>[21]</sup> has reported that the only carbides observed in a 2.25Cr-1Mo steel after long-term exposure at 600 °C to 650 °C were  $M_6C$  and  $M_{23}C_6$ . He also reported that service exposure for 12 years in the lower temperature range of 500 °C to 570 °C resulted in the growth of needlelike carbides. Abdul-Latif *et al.*<sup>[10]</sup> used the accelerated aging at 630 °C for various times to produce microstructures which simulate 25,000 to 100,000 hours of service exposure at 540 °C. They reported a lower volume fraction of acicular carbide as compared with the as-received material. They found that the general trend was an increase in molybdenum content of the carbide as the service duration was increased. The majority of the carbides have face-centered cubic structure which was either  $M_{23}C_6$  or  $M_6C$ , and they indicated that the former carbide has the alloying elements in the ratio of 65Fe-23Cr-12Mo, compared to 20-Fe-3Cr-77Mo for the  $M_6C$  precipitates. They reported that the acicular carbides were not  $M_2C$  but either  $M_{23}C_6$  or  $M_6C$ . Clear evidence has been obtained in the present work by selected area diffraction that the acicular carbides are, in fact,  $M_2C$  of hexagonal symmetry. It should, however, be understood that carbide structures produced at 630 °C may not be identical to those produced by long-term aging at a lower temperature, like 540 °C or 580 °C used in the present work, even if the morphologies are similar.

#### IV. CONCLUSIONS

The transmission electron microscopy studies of the heat-treated and stress-rupture samples of 2.25Cr-1Mo steel, tested in the temperature range of 540 °C to 580 °C, have revealed the following:

1. In the normalized and tempered condition, carbides occur in three morphologies: (1) plate,  $M_2C$ , (2) globular,  $M_3C$ , and (3) rectangular parallelepiped,  $M_{23}C_6$ .
2. Aging the steel at 540 °C for 7022 and 17,946 hours resulted in a lengthening of the  $M_2C$  platelets and led to the dissolution of  $M_3C$  and precipitation of  $M_6C$ . The superimposed creep stress does not seem to have much of an effect in short-term (7022 hour) testing at 540 °C, but in the long-term (17,946 hour) test, it resulted in the reduction of the length of  $M_2C$  but increased its density.
3. Aging at 580 °C for 6526 hours resulted in a slight lengthening of  $M_2C$ , but holding at 580 °C for 14,836 hours resulted in the disappearance of the  $M_2C$  plates in most of the areas. The superimposed creep stress resulted in the dissolution of  $M_2C$  precipitates after 14,836 hours.
4. The superimposition of 78 MPa stress on the steel at 580 °C for 14,836 hours promoted the formation of

$M_6C$  and resulted in significant recovery and recrystallization of the ferrite matrix.

5. The rectangular parallelepiped carbide, identified as  $M_{23}C_6$ , in the normalized and tempered condition, did not change morphology under any test conditions studied in the present work.

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