Effect of Martensitizing Temperature on Creep Strength of Modified 9Cr Steel*1

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A modified 9Cr-1Mo steel was cooled to a temperature between the Ms point and room temperature from the normalizing temperature and then directly heated to the tempering temperature. It was found that the time to rupture at 650 and 700°C of the steel heat-treated by the new heat treatment increased 2–3 times longer than that of the steel conventionally normalized and tempered. The microstructure of the improved steel was tempered martensite and the size of martensite blocks was larger than for the conventional heat treatment. The hardness of the improved treatment increased 2–3 times longer than that of the steel conventionally normalized and tempered. The microstructure of the improved steel

1. Introduction

A modified 9Cr-1Mo steel1) was specified as Grade 91 (Gr.91) in both ASTM and ASME and is finding increasing applications in power generation industries.2) It has been pointed out that creep strength of some high Cr ferritic steels decreases unexpectedly at long time.3) This phenomenon was confirmed for a certain heat of the modified 9Cr-1Mo steel.4) Therefore, creep behavior of high Cr ferritic steels has been studied continuously in order to secure high creep strength at long time.5,6) When the modified 9Cr-1Mo steel was invented, the tempering temperature was rather low, i.e. 760°C,1) but rather high tempering temperatures for modified 9Cr-1Mo steels also appear in a literature.7) However, evidence for the optimized tempering temperature have hardly found in literature. When strengthening elements, such as Mo, V and Nb, are added too much to modified 9Cr-1Mo steels, delta ferrite is formed, which comes down to that the strengthening effects could not be so large.5,8) The addition of Ni is effective to reduce the amount of delta ferrite. However, Tsuchida et al.9) pointed out that the addition of Ni to Gr.91 caused decreasing the creep strength of the tempered state, because the retained austenite formed in the normalized state by the Ni addition caused the carbon and nitrogen transfer from martensite to austenite. On the other hand, Santella et al.9) reported that retained austenite increased creep strength of weld deposit due to the formation of un-tempered martensite even after the adequate heat treatment. They showed on a basis of thermo-expansion measurements that Mf and Ms points of a standard Gr.91 were about 400 and 200°C, respectively, and martensitic transformation of Gr.91 almost finished at 200°C. They also reported that Ms point of the weld deposit decreased due to micro-segregation caused by the solidification process, and then they estimated that fresh martensite could co-exist with tempered martensite due to the untransformed austenite retained in the weld deposit even after post weld heat treatment. They also reported that when the weld deposit was cooled to 200°C after heating at a normalization temperature and then directly heated at a tempering temperature without cooling down to room temperature, the creep resistance was increased as compared to the creep resistance of the usual weld deposit. These reports show that the effect of retained austenite on creep has not been fully understood. Therefore, samples of a hot rolled plate of Gr.91 were normalized followed by cooling to a temperature below the Ms point, without cooling down to room temperature, and then directly heated to the tempering temperature and the effect of martensitizing temperature on creep strength has been studied. In this paper, minimum temperature, at which martensite transformation takes place, is defined as martensitizing temperature.

2. Experimental Procedure

Starting material of Gr.91 is a 40 mm thick plate (ASME SA387 Grade 91). The chemical composition in mass% is 0.09C 0.33Si 0.45Mn 0.009P 0.004S 0.09Ni 8.4Cr 0.93Mo 0.02Cu 0.18V 0.018Al 0.042N and the balance is Fe. Test blocks of 40 × 20 × 120 mm were machined from the as-received material and were re-normalized at 1150°C for 1 h and tempered at 750°C for 2 h. The normalization temperature was raised as compared to usually used temperatures in order to reduce undissolved MX type carbide-nitride, where M and X denote metallic elements, and C and/or N, respectively. The thermodynamic phase calculations10) show that the amount of MX can be reduced to 0.049% from 0.132% and the amount of Nb in MX, major constituent element, can be reduced to 41% from 80% in total Nb content by raising normalization temperature from 1050 to 1150°C. The amount of V in MX can be reduced to 6% from 29% in total V content by raising normalization temperature. After heating at the normalization temperature the test blocks were moved to a furnace pre-heated at a martensitizing temperature ranging from 450°C to 100°C and kept for 1 h for each, and then directly heated to the tempering temperature as shown in Fig. 1. A test block which was cooled at —196°C...
in order to promote martensite transformation after usual normalization treatment was also prepared and subsequently tempered at 750°C. M_s point of Gr.91 is about 400°C \(^9,11\) and therefore a sample treated at 450°C should be like a usually normalized state. It took about 20 min to heat to the tempering temperature from a martensitizing temperature.

Creep test specimens were machined from each heat treated sample and creep tests were carried out at 650 and 700°C. Vickers hardness was also measured under loading of 10 kg after the tempering. Specimens heat treated as shown in Fig. 1 were used for optical microscopy (OM) and scanning electron microscopy (SEM) observations. Carefully polished bulk specimens were observed with an X-ray diffractometer (XRD) using CuK\(\alpha\) radiation in order to measure the amount of residual austenite and investigate the state of recovery. Electrolytic dissolution of the samples was carried out and the residue was extracted using a polycarbonate filter having pores of 0.1 µm diameter. The extracted residue was analyzed using XRD. The peak profiles of (511) M\(_{23}\)C\(_6\), (220) NbX and (220) VX were measured.

3. Experimental Results

3.1 Effect of martensitizing temperature

Figure 2 shows the Vickers hardness (HV10) and the time to rupture at 700°C and 105.7 MPa as a function of martensitizing temperature. The HV10 of a specimen heat-treated at 450°C was about 400 and the hardness is comparable to the as-normalized state of Gr.91. However, the other specimens, martensitizing temperatures of which are 350°C and below, are considered to be sufficiently recovered by tempering, because the HV10’s of the other specimens are about 200, though a small peak is confirmed at 200°C. On the other hand, although the time to rupture of a specimen heat-treated at 450°C was the longest life and the minimums were observed at 350°C and room temperature, a peak was distinctly observed at 200°C. It can be estimated based on the thermal expansion and contraction curves for Gr.91\(^9\) that M_s point for Gr.91 is about 400°C and the amounts of retained austenite at martensitizing temperatures of 350°C and 200°C are 30 and 10 vol%, respectively. As presented later on, about 3 vol% of retained austenite was observed in the usually normalized state, but the retained austenite disappeared after tempering at 750°C. Therefore, it can be estimated that much more untransformed austenite was left in a specimen martensitized below the Ms temperature of 400°C. If the untransformed austenite is stable after heating at the tempering temperature for 2 h, as pointed out by Santella et al.\(^9\) the untransformed austenite should transform to martensite during cooling to room temperature and thus, much more fresh martensite should be formed when the martensitizing temperature is high. In this case, it is assumed that the higher the martensitizing temperature, including 450°C, the harder and the longer the short term rupture life of the specimens. However, the experimental results shown in Fig. 2 differ from the results obtained by Santella et al.\(^9\) It can be confirmed based on the thermal expansion and contraction curves in the literatures\(^9,11\) that certain amount of untransformed martensite should surely exist in the specimen during martensitizing at 350°C. Therefore, the results shown in Fig. 2 can be interrupted as follows: The untransformed austenite left after the martensitizing treatment changes to a new microstructure during subsequent tempering. The new microstructure causes the peaks in hardness and time to rupture shown in Fig. 2 combining with the tempered martensite, which was formed from the transformed martensite during martensitizing.

The peak temperature of the time to rupture should depend on many factors such as normalizing temperature, tempering temperature, martensitizing temperature and time and creep temperature. Therefore, although further study should be necessary in an engineering sense, in this paper, the strengthening mechanisms are studied focusing on the specimen martensitized at 200°C.

3.2 Creep strength

Figure 3 shows the rupture data of both specimens martensitized at 200°C (Z200 hereinafter) and −196°C (ZLN) as a function of stress comparing to those of the usually normalized and tempered specimens (ZRT). Although the rupture time of ZLN was comparable to that of ZRT, the rupture time of Z200 was twice or three times longer than that of ZRT. Figure 4 shows strain and strain rate vs. creep time curves for ZRT and Z200 tested at 650°C and 150.1 MPa. There was a transition creep region terminating in a minimum creep rate and converting to the acceleration creep region. From the beginning to about 20 h, the creep rate...
of Z200 was slightly lower than that of ZRT. However, the transition creep continued to a later time, the onset of the acceleration creep was delayed and the value of minimum creep rate was obviously lower in Z200. As the result, the time to rupture of Z200 was longer than that of ZRT.

By the way the microstructure of the specimen heat-treated at 450°C (Z450) was un-tempered martensite. In this case, the initial creep rate of Z450 tested at the same condition shown in Fig. 4 was considerably lower than that of ZRT and the onset of the acceleration creep was delayed. Similar results were confirmed in the previous work. As shown in Fig. 2 the initial creep rate of Z200 was comparable to that of ZRT, and therefore, while the microstructure of Z200 could be similar to that of ZRT, it should contain something to delay the onset of acceleration creep. Both rupture elongation and reduction of area of Z200 were in no way inferior to that of ZRT.

3.3 Bulk X-ray and microstructural observations

The X-ray measurement on a polished bulk specimen of the normalized state revealed several weak peaks of austenite beside the major ferrite peaks. The (111) peak of austenite was confirmed at a slightly lower diffraction angle of the major ferrite peak of (110). About 3% of retained austenite was confirmed in the normalized state, assuming the ratio of the integrated intensity, \( \frac{I_{(111)}}{I_{(111)} + I_{(110)}} \), corresponds to the amount of the retained austenite. On the other hand, retained austenite was not detected by the X-ray measurement on a bulk specimen of the tempered state regardless of the martensitizing temperature. Therefore, the retained austenite, which was untransformed at each martensitizing temperature, should be decomposed into ferrite, carbide and nitride during heating to or keeping at the tempering temperature.

Figure 5 shows the (110) diffraction peaks for the polished bulk specimens, the normalized state, ZRT and Z200. Integral breadths of ZRT and Z200 were considerably smaller than that of the normalized state. The integral breadth of Z200 was slightly larger than that of ZRT, which was consistent with the variation in HV10 shown in Fig. 2. Therefore, it can be reconfirmed that the microstructure of Z200 is obviously different from that of ZRT.

The OM images for ZRT and Z200 are shown in Fig. 6. The microstructures for both were tempered martensite and prior austenitic boundaries, packets and blocks of martensite were observed. Both OM images are consist of fine and looked gray structure and looked white structure, however the differences between ZRT and Z200 were not clear. Tempered martensitic structure are clearly seen in the SEM images shown in Fig. 7(a),(b). Coarse particles of 100 nm
precipitated along boundaries and fine particles ranging from 10 to 20 nm precipitated within grains are seen in Fig. 7(c),(d). The coarse precipitates are judged to be mainly $\text{M}_2\text{C}_6$ and the $\text{M}_2\text{C}_6$ precipitated in Z200 were looked to be finer than that of ZRT. If untransformed and fresh martensite existed in Z200, the martensite block structure boundaries of which were free from precipitates would be seen. However, these microstructures were hardly observed by SEM. The massive and looked like white areas are seen on the lower right side of the OM images (Fig. 6). The micro-Vickers hardness values of the white area were not significantly different from the other areas looked like gray in Fig. 6. However, the SEM observations showed that the massive white area was looked like a near-single grain and had substructures growing to the specified crystallographic directions for both ZRT and Z200 as shown in Fig. 7(e),(f). That is, the microstructures of ZRT and Z200 are seemed to be similar tempered martensite, but there should be clear differences between them.

Therefore, since the martensite blocks were clearly observed by OM, the block size was measured by a following method. Ten micrograph images with the magnification of 1800 were prepared for each specimen to measure the size. Two linear lines lying at right angles to each other were drawn for each photograph. The lines were marked at the cross points of the lines and boundaries where differences in the orientation contrast or lines of precipitates were observed. The average block sizes of the steels were then calculated. The block sizes for ZRT and Z200 are shown in Fig. 8. It should be noted that the block boundaries defined in this study also include lines of precipitates within blocks other than large angle boundaries, i.e., prior austenite, packet and block boundaries and therefore, the block boundaries measured in this study include some lath boundaries. Therefore, the average block size defined in this study is neither block width nor block size defined crystallographically. As shown in Fig. 8, the frequency of Z200 at the mode, i.e., $3\ \mu\text{m}$, is obviously smaller than that of ZRT and, on the

Fig. 6  Microstructure of Grade 91 martensitized at (a) room temperature and (b) 200°C.

Fig. 7  SEM microstructure of Grade 91 martensitized at (a),(c),(e) room temperature and (b),(d),(f) 200°C.
contrary, the frequency of Z200 around 10 µm is larger than that of ZRT. The average block sizes of ZRT and Z200 are 4 and 5 µm, respectively. These values are comparable to the block sizes measured based on electron back scattered patterns for similar steels.\textsuperscript{13,14} Therefore, the average block size measured in this study is considered as a measure of the actual block size. That is, the measured block size shown in Fig. 8 indicates that the heat treatment at 200 °C changed the morphology of the martensite blocks as compared to the usually normalized-and-tempered microstructure and the average block size is coarsened by the new heat treatment.

3.4 X-ray observations on precipitates

Typical precipitates in the as-tempered Gr.91 were M\textsubscript{23}C\textsubscript{6}, NbX and VX.\textsuperscript{15} Because TEM measures a limited number of particles, in the present study, the extracted residues were obtained and the particle sizes were analyzed using the XRD method. We have also confirmed that the sizes of particles measured by XRD agreed with the sizes in high Cr steels measured by TEM.\textsuperscript{16}

Figure 9 shows typical examples of the M\textsubscript{23}C\textsubscript{6} (440) peak profile for ZRT and Z200. The observed diffraction peak profiles were asymmetrical and several peaks with a small difference in chemical composition were seemed to overlap each other. Therefore, the observed peak was resolved into two peaks with a normal distribution, as shown in the figure. The bold curves are for Z200. The integral breadths were obtained from these curves. The instrument error was corrected using the standard Si powder with 5 µm in average diameter and the integral breadths were converted to particle sizes of the precipitates using the Scherrer relation\textsuperscript{17} assuming the Scherrer constant $K$ to be unity. The results obtained are presented in the figure. It is confirmed that the particle sizes of M\textsubscript{23}C\textsubscript{6} for Z200 were slightly smaller than those of ZRT, which agrees with the SEM observation shown in Fig. 7.

The sizes of NbX measured by XRD for ZRT and Z200 were rather large, about 70 nm and major part of NbX was considered to be un-dissolved particles. Figure 10 shows the diffraction profiles for ZRT and Z200, which were caused by fine VX particles formed during tempering. The diffraction profiles for ZRT (fine line) and Z200 (bold line) were indicated as the nearby M\textsubscript{23}C\textsubscript{6} (711) peaks are presented having the same intensity. The diffraction profile for the as-normalized state is also shown in Fig. 10 by a gray bold curve and the intensity is presented with suitable intensity, because M\textsubscript{23}C\textsubscript{6} is absent in the as-normalized state. The diffraction angles shown in Fig. 10 were corrected by using a nearby NaCl peak. A diffraction peak was observed at 63.1 degrees for the as-normalized state. The diffraction peak for the un-dissolved NbX was observed near 59 degrees, much lower angle of Fig. 10. On the other hand, for the usually normalized-and-tempered specimen a broad diffraction peak was newly confirmed at 62.9 degrees besides a peak with narrow integral breadth at 63.1 degrees. Based on the Powder Diffraction File (PDF) it is estimated that the peak at a lower angle corresponds to VX which dissolves considerable amount of Nb and/or N. The compound corresponding to the diffraction peak observed at 63.1 degrees for the as-normalized state could be VX particles precipitated during
cooling, but it was judged to be the un-dissolved VX, because its diffraction angle and integral breadth were differ from those of the tempered state. On the other hand, for Z200 only a broad peak at 62.9 degrees was observed and a peak at 63.1 degrees was not observed. It was found from Fig. 10 that the dissolution and disappearance of un-dissolved VX particles was caused by the martensitizing at 200°C and, as the result, finer particles of VX with much more contents of Nb and/or N than the un-dissolved VX were newly formed. It was estimated from the XRD analyses for peaks around 63 degrees that the sizes of newly formed VX were roughly 15 and 13 nm for ZRT and Z200, respectively. However, the peak intensities around 63 degrees were relatively weak, so that the accuracy of size estimation could be insufficient and therefore, the detail examination by TEM was necessary.

4. Discussion

4.1 Strengthening mechanism

It was found from Figs. 9 and 10 that $M_{23}C_6$ and VX for Z200 were finer than those of ZRT. Although the differences in distribution of these precipitates between ZRT and Z200 should be clarified by TEM, the finer precipitates of Z200 should not only be one of the strengthening factors in time to rupture, but also can explain the difference in HV10 between ZRT and Z200 shown in Fig. 2.

Hardness generally depends on grain size, dislocation density etc. When the block size is small, the hardness is large.23 However, Figs. 2 and 8 showed quite the opposite results. Therefore, it is reasonable that the difference in hardness between ZRT and Z200 (Fig. 2) is explained from the differences in the size and distribution of $M_{23}C_6$ and VX (Figs. 9 and 10) or the difference in dislocation density within blocks.

It is generally accepted for creep tests of martensitic steel that recovery progresses at the initial stage of deformation, the width of lath martensite increases, ferritic subgrains are formed and finally, the specimen is ruptured.19,20 It is easily mislead along this consideration that since the block size of Z200 was lager than that of ZRT, the difference in the block size cannot explain the differences in the time to rupture shown in Figs. 2–4. However, the initial large block size of Z200 could stabilize the microstructure and causes to increase the time to rupture by the following reason.

The amount of extracted residue was about 2% for both ZRT and Z200 and the same. Most of the precipitates extracted from ZRT and Z200 were $M_{23}C_6$ and they precipitate preferentially on prior austenitic, packet, block and lath boundaries. All these boundaries were counted as block boundaries in this study. These facts show that the precipitates occupied the block boundaries of Z200 with higher density than in ZRT, assuming similar particle size for both. Figures 7 and 9 showed that the particle size for Z200 was finer than that of ZRT, so the occupation density on the block boundaries of Z200 by precipitates could be higher than the above estimation. The occupation by precipitates with higher density stabilizes the block boundaries of Z200 and restrains the growth of the width of block and/or of lath boundaries. This results in the delay of the onset of accelerating creep. Abe and his colleagues6,21) studied the relation between time to rupture of a high Cr ferritic steel and percentage of occupation near prior austenitic grain boundaries by precipitates and proposed a similar explanation for creep strengthening of high Cr ferritic steel.

It is reported that the size and shape of lath and block of martensite is fine for rapid cooling, because martensite deforms at the speed of sound.22) Assuming a similar result for the steel studied it is expected that the microstructure of ZRT is finer than that of Z200, because the cooling rate for ZRT is faster than that of Z200. It is also reported that bainite decomposition of austenite at martensite/austenite interfaces progressively took place during isothermal aging even above 200°C in hypereutectoid steels.23) Therefore, the results shown in Fig. 8 that the block size for Z200 is larger than that of ZRT are not so unreasonable.

Retained austenite was usually observed as thin films along block boundaries or lath boundaries.24) Since only interstitial elements can move at 200°C, excess C and N in martensite diffuse into the adjacent retained austenite, resulting in the formation of austenite with higher contents of C and/or N for Z200 during holding at 200°C. Direct cooling to room temperature from this state forms the mixed microstructure of the usual martensite and the martensite with higher C and/or N. However, direct heating after holding at 200°C could cause the high density of precipitation such as $M_{23}C_6$ and VX above 500°C preferentially along the boundaries and within the retained austenite with higher C and/or N contents. Coherent precipitation of $M_{23}C_6$ and VX is feasible in the retained austenite before transformation to ferrite resulting in the formation of fine particles within grains. Because precipitation of these compounds is possible at high temperatures above 500°C and the nose point for transgranular precipitation of 0.05%C-18%Cr-8%Ni steel was reported as 700°C 10 min,26) the fine precipitation of $M_{23}C_6$ and VX should occur during not only holding at the tempering temperature but heating.

The untransformed austenite during heating at 200°C is decomposed to ferrite and carbides and/or carbonitrides by subsequent tempering. In this case, it is feasible that a certain orientation relation exists or the same orientation is maintained between the newly decomposed ferrite from the retained austenite and adjacent tempered martensite, which originally transformed to martensite at 200°C and is tempered at 750°C, because Fultz et al.27) observed in 9Ni steel that the austenite/martensite interface was originally quite coherent over 10 nm. Precipitation density on the newly formed boundaries between ferrite and martensite should be lower than that of the higher angle boundaries. Therefore, this mechanism allows the block size of Z200 to be larger than that of ZRT, which delays the onset of acceleration creep and leads to increase the time to rupture.

Moreover, since un-dissolved VX in untransformed austenite is stable, Fig. 10 indicates that un-dissolved VX in transformed martensite could be decomposed during heating at 200°C mechanism of which is discussed later on and so, high density of fine VX precipitates is expected in the transformed martensite during subsequent tempering. As mentioned above V content in the amount of un-dissolved MX is not so large and therefore, the amount of un-dissolved VX is considered to be also not so large. However, it is
inadequate that the dissolution of the small amount of un-dissolve VX did not contribute so much to the formation of fine particles of VX during the tempering, namely the increase in time to rupture, because there are many un-dissolved NbX in the steel. Un-dissolved NbX particles can also dissolve and form newly fine particles of NbX by the same mechanism for the dissolution of the un-dissolved VX and formation of fine VX. However, changes in the diffraction peak profile and shift of NbX near 59 degrees for the as-normalized state, ZRT and Z200 were not clear. The reasons for this may be first that even though fine particles of NbX newly formed during the tempering, when the compositional change in the newly formed NbX is small, the shift in the diffraction peak as shown in Fig. 10 for VX was hardly observed and secondly that rather strong peak from the un-dissolved NbX hindered the weak changes in the peak profile and shift.

$M_{23}C_6$ in Z200 was finer than that of ZRT as shown in Fig. 9. One of the reasons for this is coherent precipitation of $M_{23}C_6$ in retained austenite, carbon concentration of which was increased as mentioned above. Coherently precipitated particles of $M_{23}C_6$ in austenite matrix were generally fine and these $M_{23}C_6$ particles hold partial coherency in ferrite or martensite matrix after transformation due to the Bain relation. On the other hand, $M_{23}C_6$ formed in the matrix of ZRT is generally incoherent and so $M_{23}C_6$ nucleate on boundaries and the growth rate is large as compared to the coherent precipitates.

These circumstances mentioned the above produce the different microstructure in Z200 from ZRT. Figure 11 schematically shows the strengthening mechanism by the new heat treatment.

In the above discussion, it is assumed that retained austenite exists as thin films along block boundaries or lath boundaries, because microstructures examined looked like tempered martensite. However, when the amount of martensite is not so large, retained austenite could be left as islands. The observed lath-like microstructure could be formed from the island-like untransformed austenite by the mechanism such as bainitic decomposition which is helped by internal stress and diffusion of interstitial atoms. Generally the bainitic reaction has not been reported to occur in high Cr steels, because austenite with high Cr content is very stable. However, the precipitation of $M_{23}C_6$ decreases Cr content in austenite, which causes the retained austenite to be unstable. Therefore, it is not denied that bainitic-like decomposition of austenite in Z200 could be possible during heating at 200 °C or tempering. In this case, bainitic structure of Z200 should be coarser than ZRT, which is consistent with the differences in block size shown in Fig. 8.

Using Fig. 10 it was explained that dissolution of un-dissolved VX particles took place in Z200. This should happen during heat treatment at 200 °C, not at tempering temperature, 750 °C. The un-dissolved VX is thermally equilibrated at a normalizing temperature, so that further changes should not occur in austenite. Therefore, the decomposition of un-dissolved VX should occur in newly transformed martensite. This is caused by that a great deal of dislocations introduced by martensite transformation can decompose the un-dissolved VX in martensite and segregate C and N to their cores with the thermal help. Recovery during tempering or creep promotes lowering dislocation density, resulting re-precipitation of VX. It is unusual that the stable precipitates such as un-dissolved VX are thermally decomposing. However, it was clarified experimentally that $\varepsilon$-carbide precipitated in iron was decomposed by heating after cold working. This phenomenon was named “strain temper” and gave the basic understanding for the thermomechanical treatment technologies. Similar phenomena were confirmed on MX in high Cr steels. In the present study, it was suggested that un-dissolved MX (VX and maybe also NbX) is dissolved during heating at 200 °C, a temperature below the Ms point. Hardening resulting from the redistribution of MX occurs in only martensite and therefore, the
hardening due to MX is small for high martensitizing temperatures and also the hardening is small for low martensitizing temperature, because the reaction rate may be low. Moreover, when martensitizing temperature is low, the amount of untransformed austenite and the subsequent transferring of C and N to the untransformed austenite are small, resulting small changes in microstructure nearby the austenite. Therefore, the optimized condition for the martensitizing treatment which corresponds to the peak in time to rupture as shown in Fig. 2 should exist.

In the above, it is estimated that the microstructure of the new heat treatment, Z200, is differ from the conventional one, ZRT. These observations and considerations should be evidenced and supported using other techniques such as TEM. Moreover, optimizing heat treatment, long term creep tests and reexamination on similar steels should be future issues. Anyway, the observations and discussions in this study can explain the improvement in short term creep strength due to the new heat treatment.

### 4.2 Relation among similar heat treatments

Santella et al.\(^8\) already pointed out that creep strength of the weld metal of a modified 9Cr steel was improved by similar heat treatment shown in Fig. 1. They concluded that the improvement for the weld metal was caused by the fresh martensite. They did not surmise the improvement for the mother metal where the amount of retained austenite is little and as the result there may be no open literature for the mother metal. Anyway, it is clear that the improvement in creep strength shown in Figs. 2–4 is caused not by fresh martensite.

Similar heat histories shown in Fig. 1 were applied to improve toughness of ductile cast iron, high carbon tool steel and spring steel and named “Up-quenched Austempering”\(^3\) and “Quenching and Partitioning”.\(^3\) These technologies aim principally at improving toughness; Si-Mn steel is quenched to a bath at about 250 °C after austenitizing, then directly heated to 300–350 °C for tempering, and austenite grains are partitioned by bainitic decomposition during the tempering. However, austenite of high Cr steel is stabilized at low temperatures and bainitic decomposition and as a consequence partitioning of austenite hardly occur in most cases. On the contrary, by applying the new heat treatment to high Cr steel the block size was enlarged as shown in Fig. 8, the particle sizes of M\(_23\)C\(_6\) and VX were finer as compared to the usual normalizing and tempering treatment, and these features improved the creep strength. Therefore, it can be concluded that applying the heat treatment shown in Fig. 1 to high Cr steel is essentially different from the technologies developed for low alloy carbon steel.

### 5. Conclusions

The creep strength of a modified 9Cr steel was improved by applying a new heat treatment: after cooling to a temperature, below the Ms point, in the cooling process of normalizing, the steel is directly reheated to the tempering temperature without cooling to room temperature. The new process decreased the size of precipitates of M\(_23\)C\(_6\) and VX and increased the size of martensite blocks, resulting in a higher density of boundary precipitates. These microstructural features could stabilize the block boundaries and strengthen the matrix, which increases the creep resistance. The improvement is not caused by fresh martensite and a strengthening mechanism for this new heat treatment was proposed. Long term stability of the microstructure should be studied.

### REFERENCES


