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Changes in Precipitates of Modified 9Cr-1Mo Steel During Long-term Creep Deformation at 873K and 923K

Kenta SUZUKI, Graduate Student, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, JAPAN
Shinji KUMAI, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, JAPAN
Hideaki KUSHIMA, Kazuhiro KIMURA and Fujio ABE, Frontier Research Center for Structural Materials, National Research Institute for Metals, 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305-0047, JAPAN

Degradation of a Mod.9Cr-1Mo steel during long term creep deformation is caused by heterogeneous recovery preferentially occurred at vicinity of prior austenite grain boundary (PAGB). In order to understand a mechanism of preferential recovery, changes in precipitates during long term creep deformation at 873K and 923K have been investigated. Precipitates of $M_{23}C_6$, Nb(C,N) and V(C,N) have been observed in both the as tempered condition and all the creep ruptured specimens, except for no Nb(C,N) in the specimen creep ruptured after 41,425.2h at 923K-50MPa. Laves phase (Fe_2Mo) has been observed in the specimen creep-ruptured at 873K. Moreover, precipitation of modified Z-phase (Cr(Nb,V)N), has been observed in the specimen creep-ruptured after more than several thousands hours at the both temperatures. Precipitation of modified Z-phase preferentially takes place at the vicinity of PAGB. Tendency of decrease in a number density of MX carbonitrides with increase in a number of modified Z-phase particles was observed. The coarsening rate of modified Z-phase is much larger than those of $M_{23}C_6$, Nb(C,N) and V(C,N). It has been concluded that precipitation and coarsening of modified Z-phase is one of the reasons that promote a preferential recovery at the vicinity of PAGB.

1. Introduction

Improvement of energy efficiency in power generation is strongly demanded from a global environment point of view, especially to save fossil resources such as oil, coal and natural gas and to suppress the CO_2 emission. From such reason, a lot of researches and developments on high strength ferritic creep resistant steels have been carried out [1]-[4]. Mod.9Cr-1Mo steel [5], that is one of the high strength ferritic creep resistant steels, has been widely used in power plant for high temperature structural components such as header and main steam pipe. Many investigations have been performed on the relationship between microstructure and strength property of a Mod.9Cr-1Mo steel [6]-[15]. Recently, Kushima et al. have reported that degradation of Mod.9Cr-1Mo steel during long term creep deformation has been caused by heterogeneous recovery of tempered martensite microstructure preferentially occurred at vicinity of prior austenite grain boundary (PAGB), in contrast to homogeneous progress in recovery during short term creep at the higher stress condition [13]. Furthermore, precipitation of modified Z-phase (Cr(Nb,V)N) [16] has been found in the Mod.9Cr-1Mo steel creep ruptured in the long term region, and it has been supposed to be one of the factors which promote preferential recovery at the vicinity of PAGB [14],[15].

In this study, changes in tempered martensite microstructure and precipitates with progress in creep deformation have been investigated on a Mod.9Cr-1Mo steel and the correlation between those, especially on the effect of precipitation of modified Z-phase, has been discussed, in order to understand a mechanism of preferential recovery occurred at vicinity of PAGB.

2. Experimental Procedure

The material investigated is a Mod.9Cr-1Mo steel (ASME SA-213 T91), which is the same material used in the previous work [13]-[15]. Chemical composition (mass%) and heat treatment condition are shown in Table 1. Heat treatment condition is normalizing for 10minutes at 1323K and tempering for 30minutes at 1038K. Creep specimen with 6mm in diameter and 30mm in gauge length have been taken from a boiler and heat exchanger tube with about 8mm in wall thickness. Specimens both crept for 3,000 and 7,900h at 873K-120MPa and creep ruptured at 923K up to about 40,000h and 873K-120MPa (t_r=12,858.6h) were subjected for microstructural observation.

Analysis of precipitates was performed on carbon extracted replicas which were prepared from both crept and creep-ruptured specimens, using a field emission transmission electron microscope (FE-TEM) with an energy dispersive X-ray spectroscopy. Microstructural observation was also conducted on thin foils that were prepared from the steel in the as tempered condition and the crept specimens for 3,000h and 7,900h, and the creep-ruptured one after 12,858.6h at 873K-120MPa.

Table 1 Chemical composition (mass%) and heat treatment of the Mod.9Cr-1Mo steel studied.

C	Si	Mn	P	S	Ni	Cr
0.09	0.29	0.35	0.009	0.002	0.28	8.70
Mo	Cu	V	Nb	Al	N	Fe
0.90	0.032	0.22	0.072	0.001	0.044	Bal.

Normalizing : 1323K/10min. → Air cooling
Tempering : 1038K/30min. → Air cooling

3. Results and Discussion

3.1 Microstructural change during creep deformation

Figure 1 shows schematic illustration on the effect of heterogeneous recovery on creep deformation behaviour of Mod.9Cr-1Mo steel proposed by Kushima et al. [13]. It has been supposed that recovery of tempered martensite microstructure progressed homogeneously at the higher stress condition in the short term region, however, heterogeneous recovery preferentially occurred at a vicinity of PAGB promotes the onset of tertiary creep stage at the lower stress condition in the long term region.

Bright field TEM images on (a) steel in the as tempered condition, the specimens crept for (b) 3,000h and (c) 7,900h, and (d) the specimen creep ruptured after 12,858.6h at 873K-120MPa are shown in Figure 2. Conditions of crept for 3,000h and 7,900h at 873K-120MPa correspond to ***A*** point, at the onset of tertiary creep stage, and ***B*** point, in the tertiary creep stage, in Figure 1, respectively. Typical tempered martensite microstructure is observed in the as tempered condition (Fig.2 (a)), the lath width is about 0.3 μ m and the dislocation density is very high. In the creep ruptured specimen (Fig.2 (d)), significantly recovered microstructure which is wholly covered with coarse subgrain with a few μ m in diameter is observed. On the other hand, progress in recovery is observed only at the vicinity of PAGB in the specimen crept for 3,000h (Fig.2 (b)), and the microstructure within grain is still fine similar to that in the as tempered condition. In the specimen crept for 7,900h (Fig.2 (c)), extension of recovered region along the PAGB is observed. Preferentially recovered region at vicinity of PAGB was observed at the onset of tertiary creep stage and heterogeneous progress in recovery during tertiary creep stage was clearly demonstrated by the extension of recovered region along PAGB.

Creep rate vs. time curve at 873K-120MPa and changes in mean diameter of the precipitates are shown in Figure 3. Mean diameters of Nb(C,N) and V(C,N) were described as MX, since no significant difference in size of those two phases was observed. $M_{23}C_6$ and MX type carbonitrides were detected in the as tempered condition. Precipitation of Laves-phase and modified Z-phase were observed in the crept specimens.

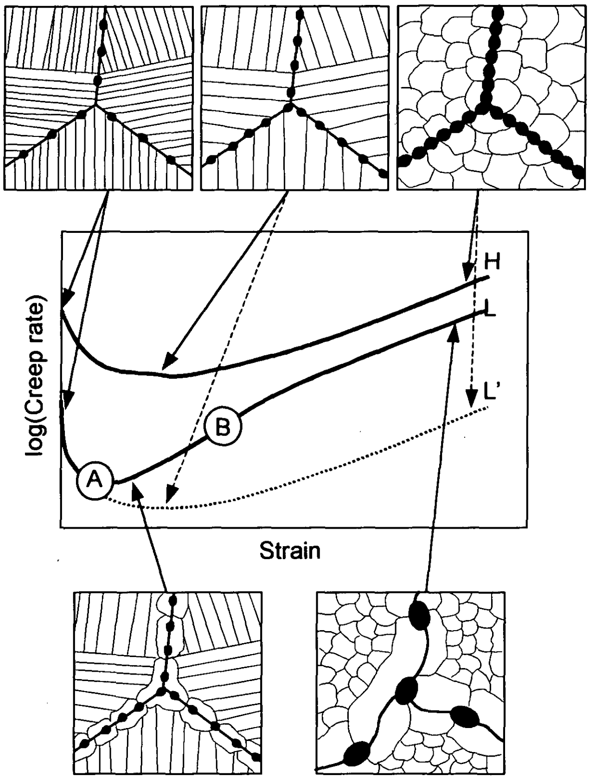


Figure 1 Schematic illustration on the effect of heterogeneous recovery on creep deformation behaviour of Mod.9Cr-1Mo steel.

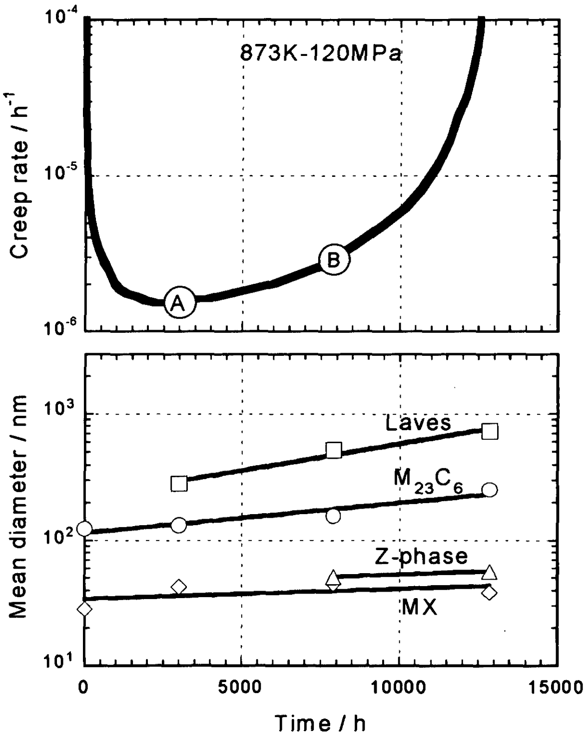
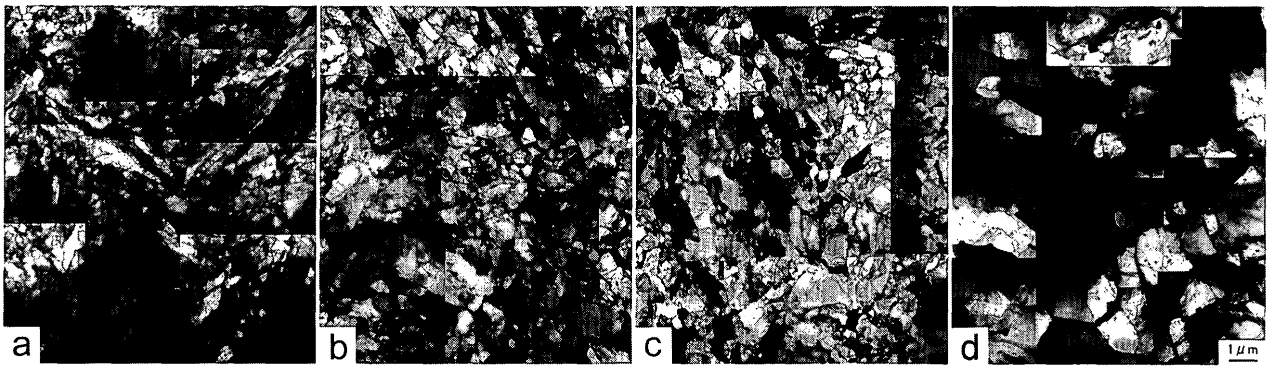


Figure 3 Creep rate vs. time curve at 873K-120MPa and changes in mean diameter of $M_{23}C_6$, MX, Laves-phase and Z-phase with creep deformation at 873K-120MPa.



a) as-tempered b) t_i = 3,000h c) t_i = 7,900h d) t_r = 12,858.6h

Figure 2 Bright field TEM images of Mod.9Cr-1Mo steel (a) in the as-tempered condition, crept for (b) 3,000h and (c) 7,900h, (d) creep ruptured after 12,858.6h at 873K-120MPa.

3.2 Precipitates in the creep ruptured specimen

Results of EDX analysis on each precipitates of the steel in the as tempered condition and the specimen creep ruptured after 5,409.5h at 923K-80MPa are shown in Figure 4 and Figure 5, respectively. For the steel in the as tempered condition, compositions of the precipitates are clearly divided into three groups of $M_{23}C_6$, Nb(C,N) and V(C,N), as shown in Fig.4. On the other hand, additional precipitate of modified Z-phase to the same three types precipitates found in the as tempered condition, was detected in the specimen creep ruptured after 5,409.5h at 923K-80MPa (Fig.5).

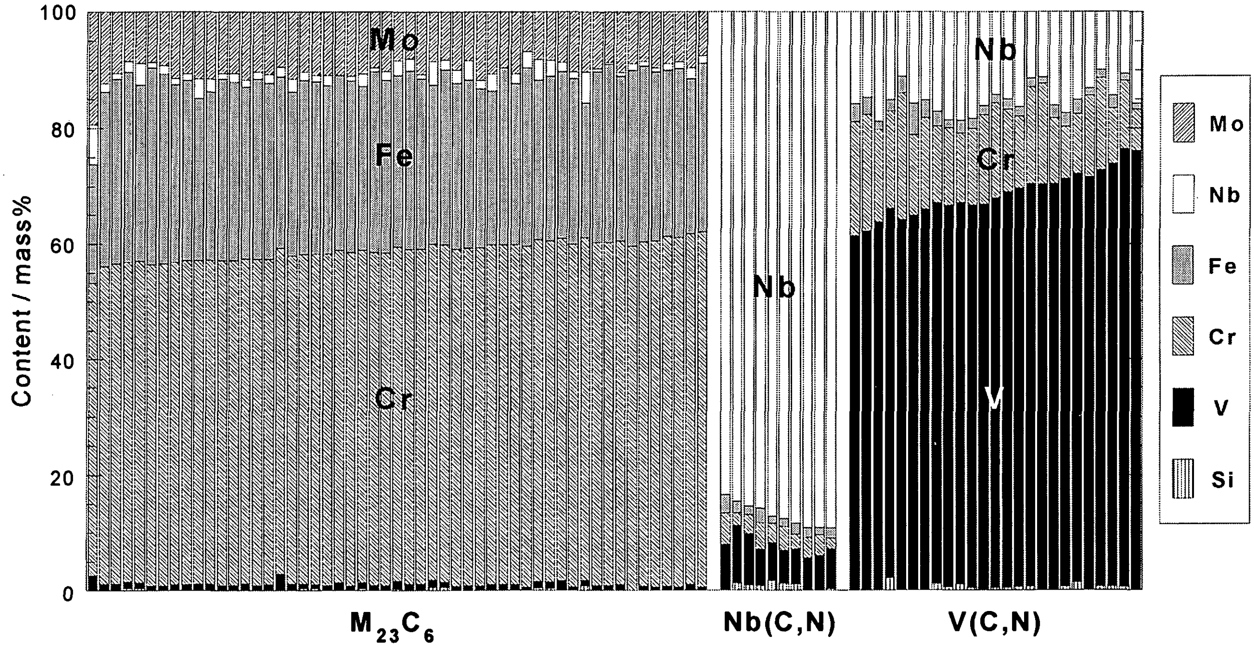


Figure 4 Results of EDX analysis on the precipitates in the as-tempered specimen.

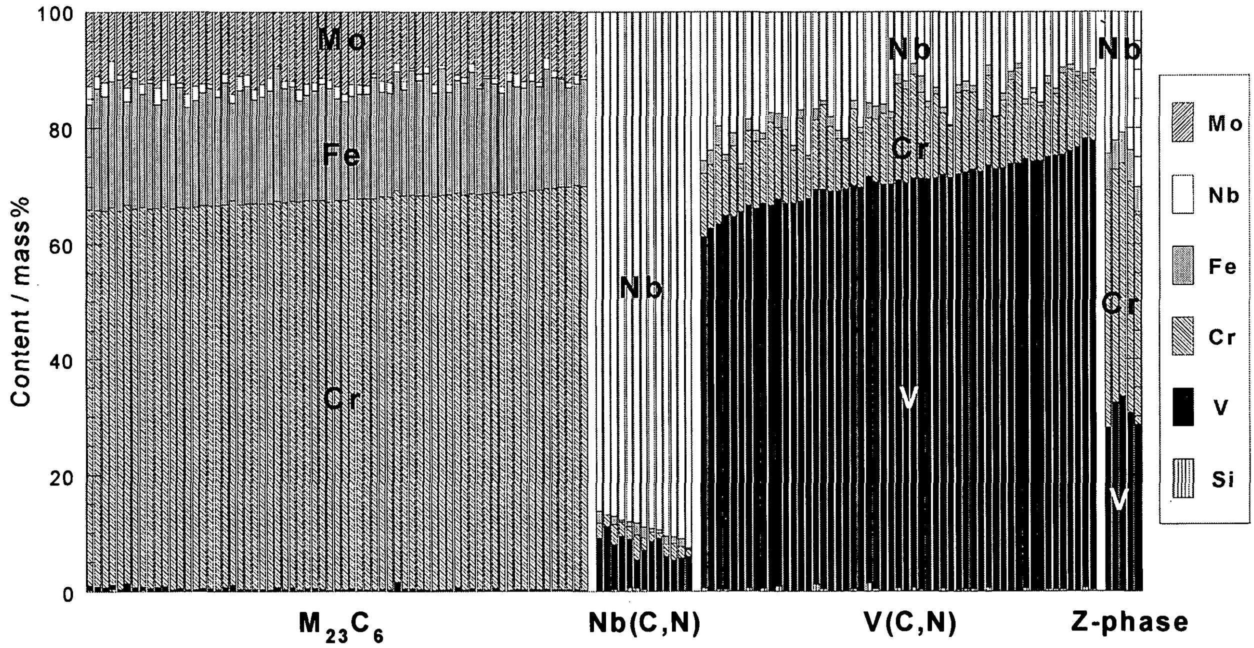


Figure 5 Results of EDX analysis on the precipitates in the specimen creep ruptured after 5,409.5h at 923K-80MPa.

Species of the precipitates detected by EDX analysis in the as tempered condition and the specimens creep ruptured at 873 and 923K were summarized in Figure 6. As shown in Fig.4, three types precipitates of $M_{23}C_6$, Nb(C,N) and V(C,N) exist in the as-tempered condition. Laves-phase precipitates during creep deformation at 873K, but not at 923K. Precipitation of modified Z-phase was detected after creep deformation for several thousands hours at both temperatures. Modified Z-phase was found more frequently at vicinity of PAGB than within grain. Moreover, tendency to decrease in number of MX type carbonitrides with increase in time to rupture was observed at 923K, and no Nb(C,N) was detected in the specimen creep ruptured after 41,425.2h at 923K-50MPa.

3.3 Changes in precipitates

Figure 7 shows changes in average chemical composition of $M_{23}C_6$ with increase in time to rupture. Increase in Cr content from about 60 to 70mass% and decrease in Fe content from about 30 to 20mass% with increase in time to rupture was observed at both temperatures. Such obvious changes in average chemical composition were observed only for $M_{23}C_6$ and Laves-phase.

Figure 8 shows the changes in number fraction of V(C,N) and Nb(C,N) carbonitride precipitates with increase in time to rupture at the both temperatures. No obvious change in number fraction of those is observed at 873K, however, it shows tendency to decrease in a number fraction of Nb(C,N) with increase in time to rupture at 923K. Number fraction of Nb(C,N) in the MX type carbonitrides is about 30% in the as tempered condition, and it decreases with increase in time to rupture at 923K to 0% in the specimen creep ruptured after 41,425.2h. Decrease in total number of fine MX precipitates was also observed on carbon extracted replicas with increase in time to rupture at 923K. It seems that decrease in number fraction of Nb(C,N) particles means not increase in number of V(C,N) precipitates, but earlier disappearance of Nb(C,N) than V(C,N) with decrease in total number of MX precipitates, due to a small amounts of Nb(C,N) precipitates.

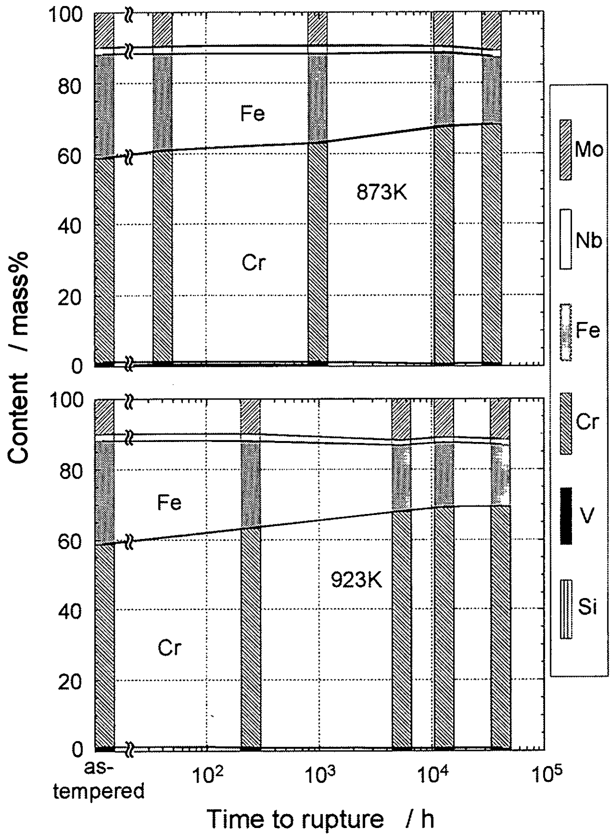


Figure 7 Changes in chemical composition of $M_{23}C_6$ with increase in time to rupture at 873 and 923K.

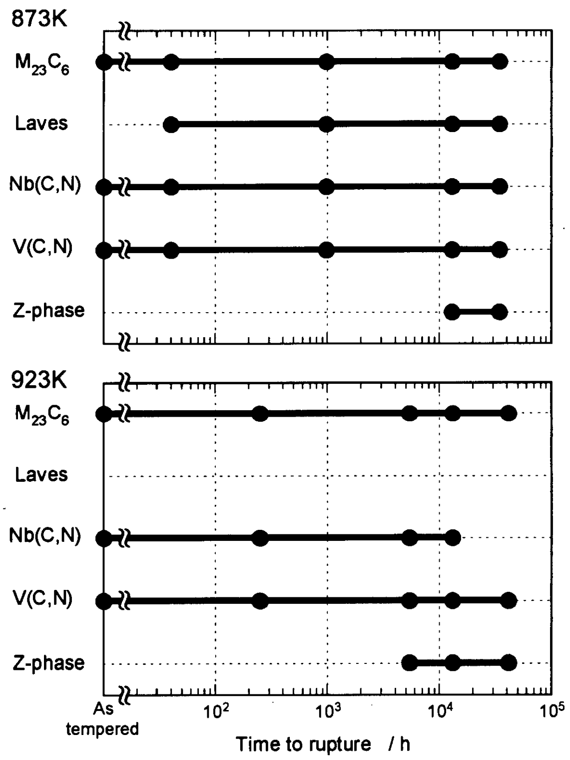


Figure 6 Changes in type of precipitates with increase in time to rupture at 873 and 923K.

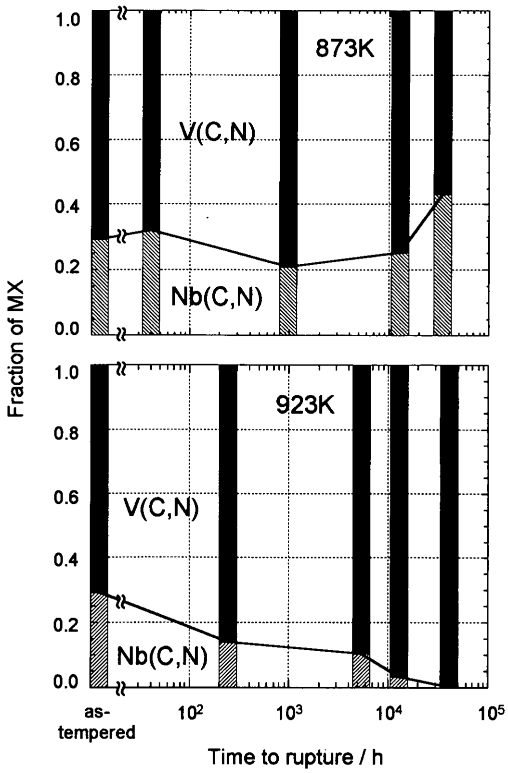


Figure 8 Changes in fraction of Nb(C,N) and V(C,N) with increase in time to rupture at 873 and 923K.

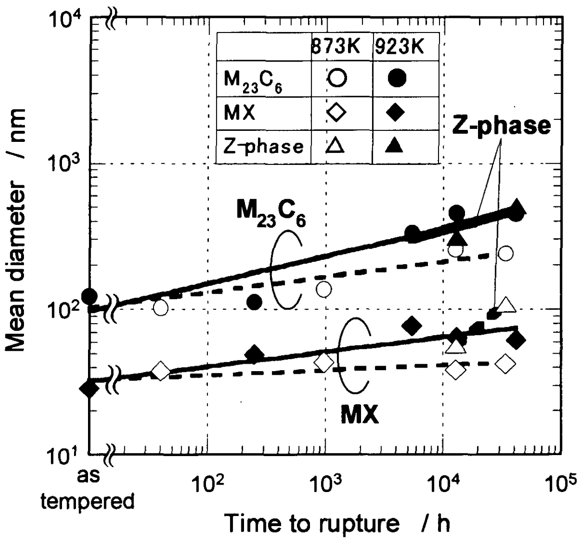


Figure 9 Changes in mean diameter of precipitates with increase in time to rupture at 873 and 923K.

Changes in mean diameter of the precipitates with increase in time to rupture at 873 and 923K are shown in Figure 9. Mean diameters of Nb(C,N) and V(C,N) were described as MX, as same as Fig.3. Mean size of $M_{23}C_6$ is larger than that of MX and coarsening rate of all the precipitates are accelerated by increase in temperature from 873 to 923K, especially on modified Z-phase. Coarsening of modified Z-phase at 923K is very fast in comparison with those of the other precipitates, since precipitation of it starts after several hundreds or several thousands hours of creep deformation. Such significantly quick coarsening of modified Z-phase should affect a distribution of MX type carbonitrides, because modified Z-phase is a complex nitride in a form of Cr(Nb,V)N [16], and, therefore, coarsening of modified Z-phase needs resolving of MX type carbonitrides. Consequently, decrease in number of MX precipitates and disappearance of Nb(C,N) with progress in creep deformation at 923K is thought to be caused by precipitation and quick coarsening of modified Z-phase. It has been concluded that precipitation and coarsening of modified Z-phase which has been more frequently occurred at vicinity of PAGB, has been one of the important factors promoting preferential recovery at vicinity of PAGB.

4. Conclusion

The metallographic studies on the evolution of microstructure during long term creep deformation of a Mod.9Cr-1Mo steel at 873 and 923K have shown that;

1) Under creep condition of 873K-120MPa, preferential recovery at vicinity of PAGB was observed at the onset of tertiary creep stage. Heterogeneous progress in recovery and precipitation of modified Z-phase during tertiary creep stage was also clearly demonstrated.

2) Precipitation of modified Z-phase was detected more frequently at vicinity of PAGB after creep deformation for several thousands hours at 873 and 923K.

3) Decrease in number of MX type carbonitrides with progress in creep deformation and disappearance of Nb(C,N) precipitate after long term creep deformation were observed at 923K.

4) Coarsening of modified Z-phase at 923K was found to be very quick in comparison with those of the other precipitates such as MX and $M_{23}C_6$.

5) It has been concluded that precipitation and coarsening of modified Z-phase which has been occurred more frequently at vicinity of PAGB, has been one of the important factors promoting preferential recovery at vicinity of PAGB.

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