Microstructure evolution of CLAM steel during creep at 923K

S. Ye, F. Zhao*, **F. Huang, J. He & J. L. Wang**

College of Materials and Metallurgy, Guizhou University, Guiyang, Guizhou 550025, China
Key Laboratory of Guizhou for Mechanical Behavior and Microstructure of Materials, Guiyang, Guizhou 550025, China

Abstract: The microstructure change of CLAM steel during creep testing process was investigated at the temperature of 923K with different stress. The results show that the fragmentation and polygonization of martensite lath, as well as the degeneration of dislocation structure are the main factors to deteriorate the creep performance. The stability of MX precipitates in CLAM steel during high temperature creep is good, but the amount and size of M23C6 precipitates are increased. The Laves phase was not found in all samples, which may be due to the experimental temperature is close to the dissolution temperature of Laves phase. The higher temperature accelerates the microstructure evolution of CLAM steel, which results in the degradation of creep properties.

1. Introduction

Activation Ferritic/Martensitic (RAFM) steels have been selected as the primary structural materials for the demonstration fusion reactor and future fusion power plant due to low coefficient of thermal expansion, high thermal conductivity and adequate corrosion resistance[1-3].Since 1980s, Japan, Europe and the United States to study their own low activation Ferritic/Martensitic steel, such as 9Cr2WVTa, Eurofer-97, JLF and F82H.As one of the RAFM steels, China Low Activation Martensitic (CLAM) steel was developed in Institute of Nuclear Energy Safety Technology (INEST). research institutes and universities have started to study the low activation martensitic steel in China since 2001. The heat treatment process, mechanical properties, anti irradiation properties and welding properties of China low Activation Martensitic steel was studied in a large number of studies and obtained significant results[4].The service condition of CLAM steel is at high temperature condition under a long-term stress, it is very important to study the microstructure evolution of CLAM steel. In the present work, creep deformation and rupture behavior of CLAM steel at 923K was studied and the creep property of CLAM steel and its microstructural evolution were analyzed.

2. Experiment

The CLAM steel used in this study was smelted by vacuum induction melting. After the smelting of peeled for forging, rolling, the final product was a thickness of 21mm plates. Forging process parameters were the initial forging temperature of 1373~1423K, the final forging temperature was above 1123K, the forging ratio was more than 6, air cooling after forging, rolling process interval design method of rolling process to ensure that CLAM steel can obtain relatively uniform structure. Chemical composition (wt.%) of the CLAM steel was shown in Table 1.

Table 1 Chemical composition of CLAM steel(mass fraction,%)

C	Cr	W	V	Ta	Mn	P	Fe
0.091	8.93	1.43	0.19	0.10	0.48	0.05	balance

The plate is cut into a bar with a diameter of 20mm, and then heat treatment is carried out. The heat treatment process of CLAM steel was normalization and tempering at 1253K for 30min followed by air-cooling and 1033K for 60min followed by air-cooling respectively. After the heat treatment of the samples in accordance with the national standard GB/T2039-2012 processed into standard creep specimens such as Figure 1 shape and size, and constant load creep tests were carried out on the model of CMT-B1 type electronic high temperature creep testing machine at 923K in air over a wide stress range of 90~140MPa. Temperature along the specimen was measured using two S-type thermocouples attached to the specimen and was maintained within ±3K throughout the creep test. After the creep test, the creep curves were plotted. The microstructure observation of the specimen was carried out with scanning electron microscope (SEM) and transmission electron microscopy (TEM). Selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) were also used to analysis of precipitates.

The method of metallographic microstructure displays the ratio of $FeCl_3$, HCl and H_2O is 5g, 50ml and 100ml. TEM sample preparation method is as   follows, first mechanical thinning to 60μm, then punch tablets in the size of diameter 3mm and
double thinning, the solution is 5% perchloric acid   while other is alcohol. Thinning temperature is below 253K.
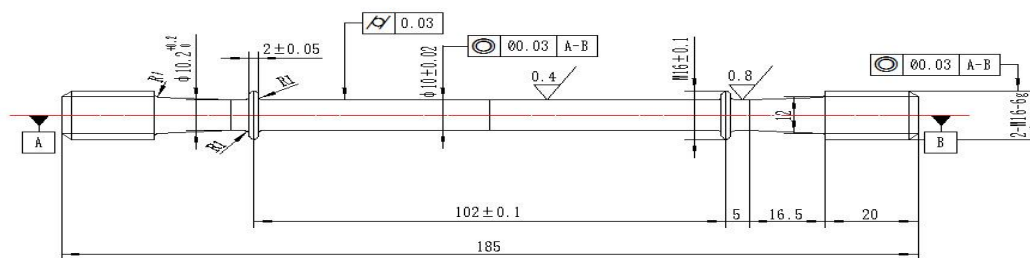

Figure 1 shape and dimensions of creep sample

3. Result and discussion

3.1 *creep curve*

Figure 2 is the creep curve of CLAM steel with different stress at 923K. When the stress is 140MPa creep test in the shortest time, no obvious first stage and steady creep stage, the sample directly into the accelerated creep stage after 4.3 hours test is broken. When the stress is reduced to 110MPa, the creep life is prolonged to 19 hours, no obvious steady creep stage, after a very short first stage of creep then directly into the accelerated creep stage. When the stress is further reduced to 90MPa, the first phase of creep lasted nearly 10 hours. There has an obvious steady creep stage, and the steady creep stage lasts about 100h, then the sample enters the accelerated creep stage. Final creep life increases to 122 hours.
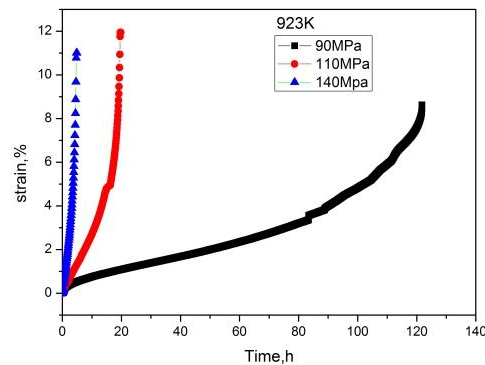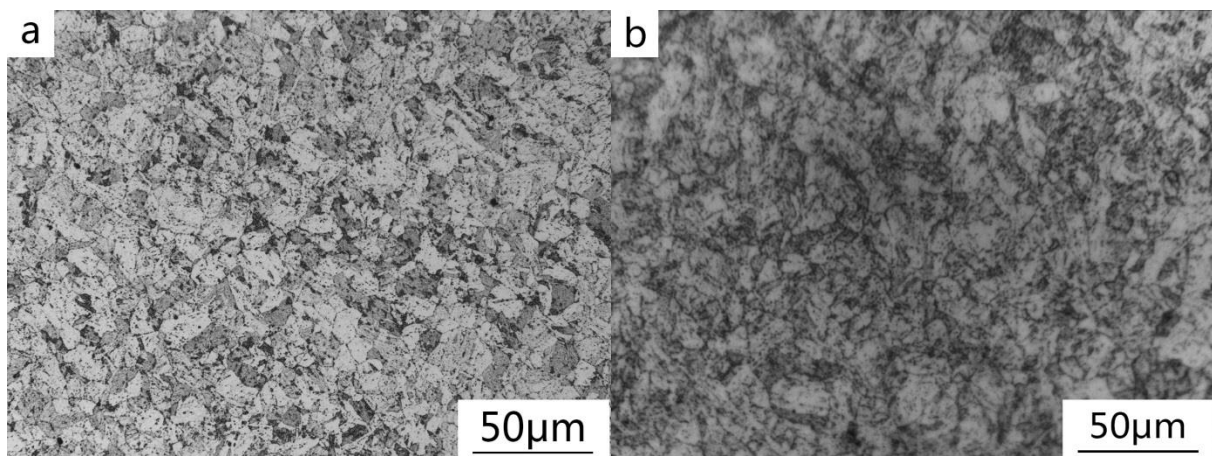
Figure 2 Creep curves of CLAM steel at 923K under different stress

3.2 *Microstructure*

Figure 3 (a) ~ (d) is the original microstructure，creep 10 hours, creep 100 hours and creep fracture specimens under the condition of 923K 90MPa. It can be seen that the original structure of CLAM steel is complete martensite, the grain size is about 7-12 μm. After 10 hours, 100 hours and 122 hours creep, the microstructure morphology changed little. There is no obvious deformation after 10 hours creep. After 100 hours creep, there is a slight deformation of the sample, and the grains are elongated along a certain direction. After 122 hours creep, the fracture specimen is deformed and the grains are elongated.
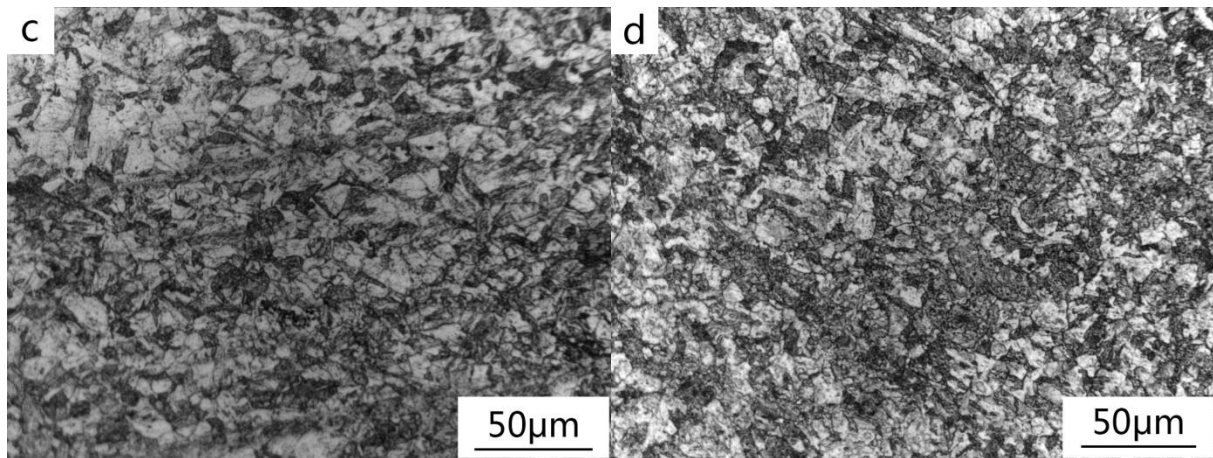
Figure 3 Optical photograph of CLAM steel
(a)original   (b)creep 10hours
(c) creep 100hours   (d) Fracture sample

Figure 4(a)~(d) are scanning electron micrographs of CLAM steel in different states. A large number of small white spots in the picture are precipitates, which are mainly spherical, rod like and irregular. The dispersion is distributed in grain boundaries, subgrain boundaries, lath boundaries and matrix. There are two types of precipitates in 9%-12%Cr steel containing $M_{23}C_6$ and MX[5-8]. Most of the $M_{23}C_6$ carbides are distributed in the vicinity of the original austenite grain boundary and the martensite lath. MX phase is distributed in the vicinity of the martensite lath of the matrix, and the strengthening effect is achieved by the movement of the pinning dislocation. It can be seen that the size of $M_{23}C_6$ is larger and the quantity is more, the MX is small and the quantity is less, the Laves phase is not found in all the samples. The grain size at the grain boundary is larger, and the larger particles in the sample are analyzed by EDS. EDS analysis showed the main elements in alloy are 9.57C，0.56V，26.42Cr，0.59Mn，55.32Fe and 7.54W, and it can be identified as Cr rich $M_{23}C_6$. The EDS analysis of the particles with smaller grain size shows that the composition is 6.23C-0.82V-7.89Cr-3.06Mn-45.18Fe-33.08Ta-3.73W, Ta content is high and does not contain N, can be judged as MX phase of TaC.

The volume fractions of precipitates in the initial state, creep 10 hours, creep 100 hours and creep fracture samples were obtained by statistical analysis. The precipitates in the initial state accounted for 0.11%, and then increased to 0.14% after 10 hours creep. After 100 hours of creep, it can be seen that the size and the number are both increased obviously, and the volume fraction increases to 0.21%.In the creep fracture samples, the coarsening of precipitates is more obvious, the number is more, and the volume fraction of precipitates increases to about 0.25%.The EDS results show that the MX phase of all the samples is very small and the $M_{23}C_6$ is relatively large.
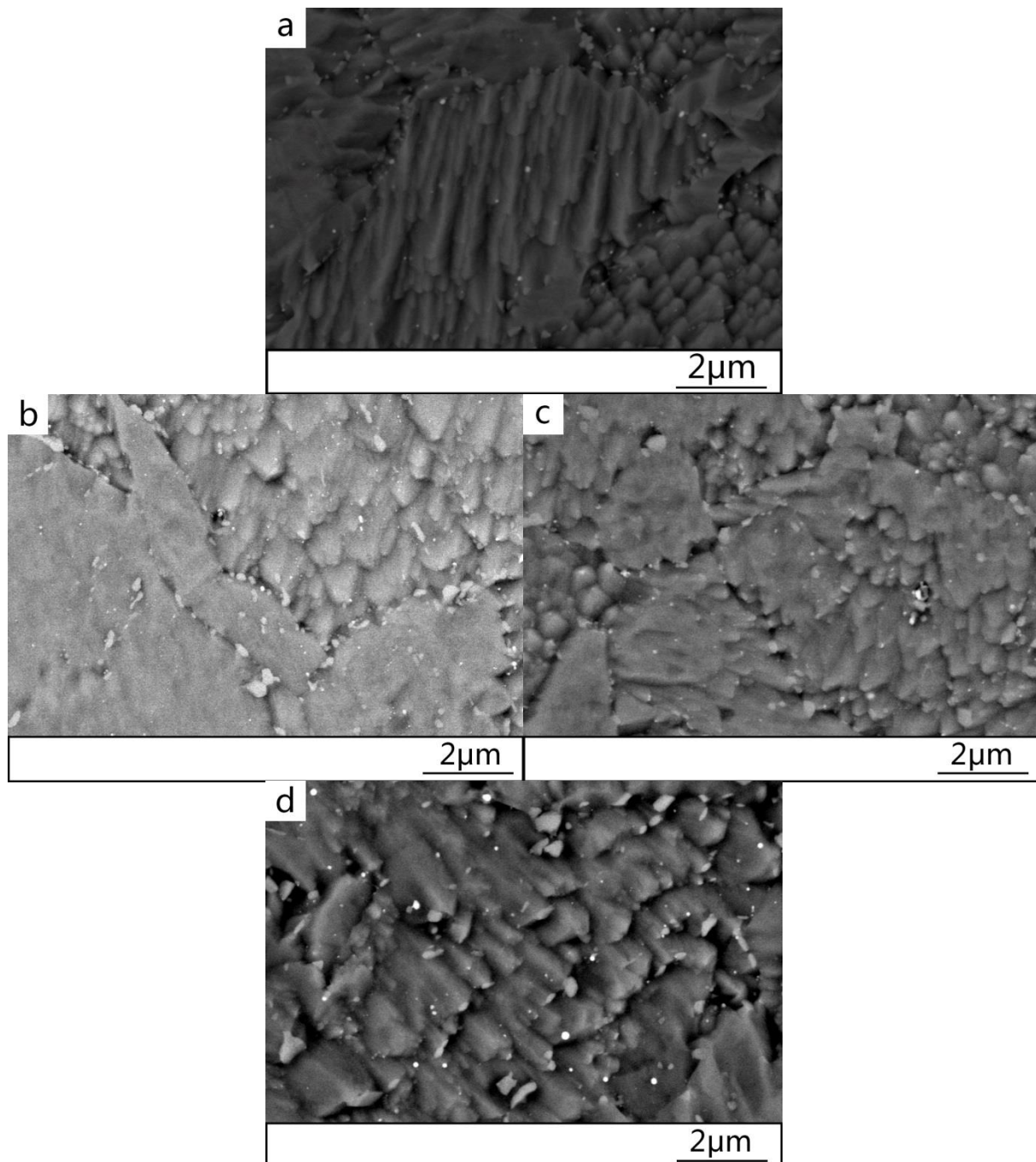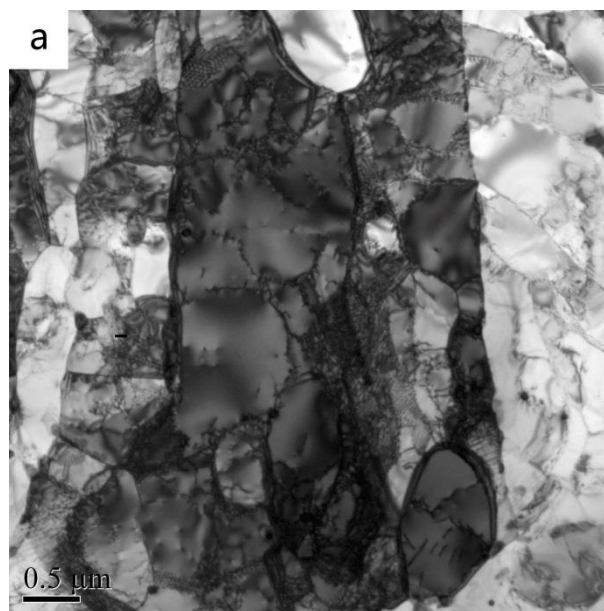
Figure 4 SEM images of CLAM steel at different stage
(a) Initial state   (b)creep 10hours
(c) creep 100hours   (d) Fracture sample

Figure 5 shows the results of transmission electron microscopy, energy spectrum and diffraction pattern of the precipitates. Fig. 5 (a) and (b) are TEM photograph of the original state. The microstructures are mainly lath and bulk martensite, in size of 200nm~400nm. The dislocations are not uniformly distributed in the martensite lath and subgrain, and some dislocations form a dislocation wall, which has a good effect on strengthen. disperse at the grain boundary, sub grain boundary, lath boundary and base, especially at the interface are in large size. The matrix precipitates mainly exist

granular, rod like and irregular in size between 10nm~200nm. The larger size of the precipitates are mainly distributed at the grain boundary, the maximum size is 200nm. Fig.5 (c) and (d) are TEM pictures of the creep fracture. The microstructure is a sub crystal with a size of about 1μm. The grain tends to equiaxed growth and little dislocations. Subgrain structure has two kinds of ways to reply, one is the strain induced recovery from plastic deformation[9-10], the other is static recovery caused by the high temperature service[11]. Both kinds accelerate creep rupture. The carbides are distributed on grain boundaries and sub grain boundaries, the maximum size of which could reach 400nm. Precipitation and subgrain of CLAM steel after creep show coarsening. The origin of creep deformation is caused by dislocation and subgrain boundary migration. The sub grain boundaries are generally formed by dislocation network. The results show that the creep stress affects the recovery of the subgrain.

The precipitates in the matrix are mainly fine particles in size of about tens of nanometers. EDS analysis showed the main elements in alloy are 1.72Ti, 1.52V, 3.76Cr, 30.88Fe and 62.10Ta, which are in atom percent(at%). The content of Ta is higher. The diffraction pattern of calibration measured d1=0.212 nm, d2=0.213nm, and θ=60°. The calculated lattice constant of the precipitate is a=0.58824nm. The diffraction spectrum through look-up table is face centered cubic structure and the zoneaxis shows [111]. The calculated lattice constants of the precipitate is a=0.4266 nm. The PDF card shows the precipitat is TaC, which belongs to MX type carbon nitride. At the same time, there is a high content of Ta element in the steel, and the size of the particles is about 120nm. The relevant literatures infer that it may be TaC particles not completely dissolved in the solid solution phase[12-13]. EDS points show the precipitates on the grain boundary are mainly in composition of 54.65Cr, 34.09Fe and 11.26W (at%). The diffraction pattern of calibration measured d1=0.22222nm d2=and θ=75.05°. The calculated lattice constant of the precipitate is a=1.0189nm. The diffraction spectrum through look-up table is face centered cubic structure and the zoneaxis is [123]. The PDF card proves the precipitate is $M_{23}C_6$.
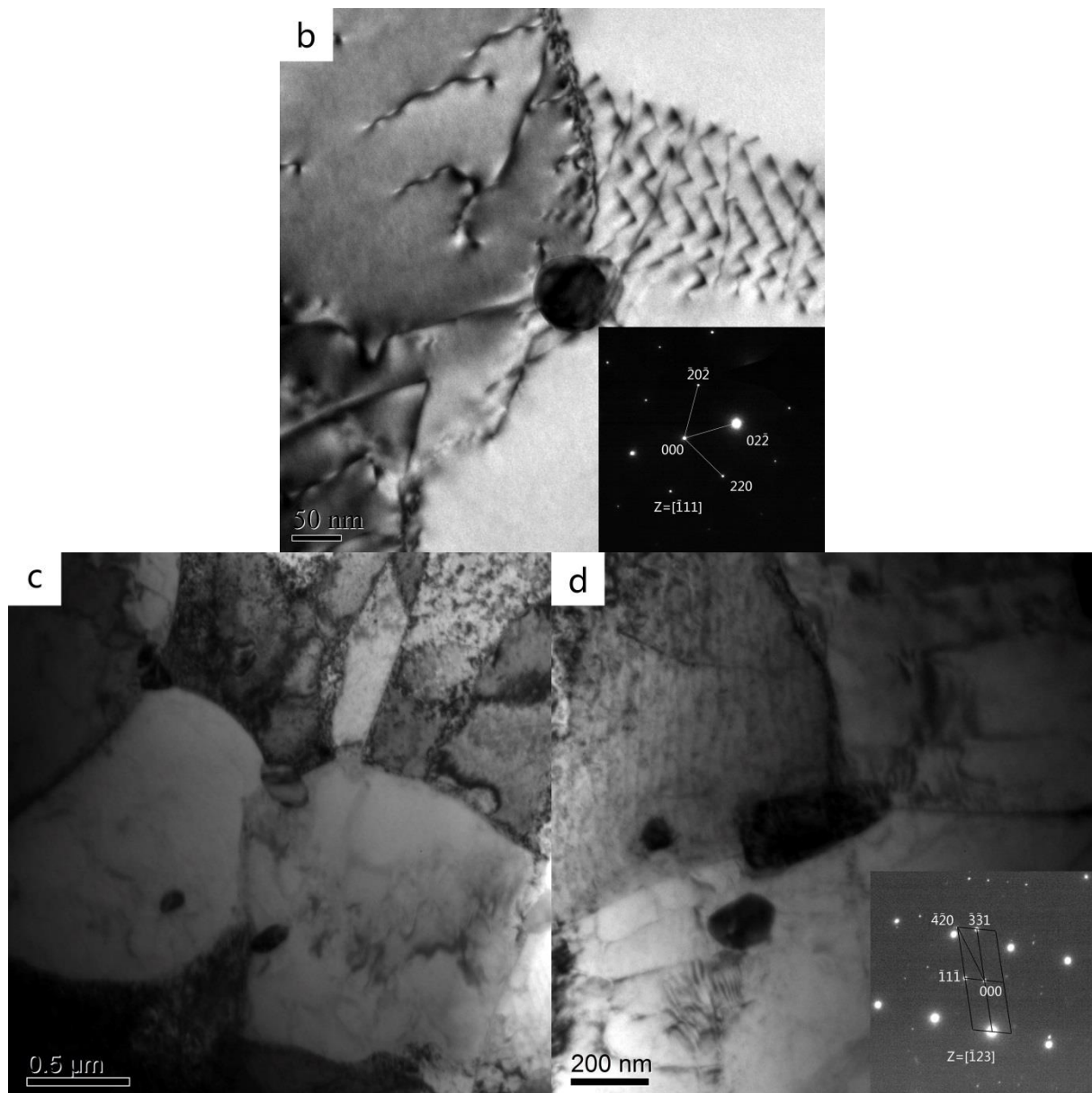
Figure 5 TEM micrographs of CLAM steel
(a) Initial state (b) MX in initial state
(c) Fracture specimens (d) M23C6 in fracture specimen

The microstructure of CLAM steel was changed in the process of high temperature creep.M23C6 coarsening and dislocation density decrease, the martensite will break down and form the subgrain under the action of stress, These changes reduce the creep resistance of CLAM steel. MX is stable in the whole creep test, and the coarsening is not obvious. Because of its strong pinning effect, it is helpful to delay the dislocation annihilation, strengthen the interface, maintain the dislocation strengthening and so on. In the process of creep, VC carbide is also thought to be possible to avoid the occurrence of recrystallization and restrain the migration of grain boundaries[14].

Laves phase can also be precipitated in the process of high temperature creep of CLAM steel. The Laves phase is an intermetallic compound formed by Fe, Cr and W. The Laves phase formed in CLAM steel is Fe_2W. The Laves phase in CLAM steel is similar to $M_{23}C_6$, which can improve the strength of

CLAM steel. The study of Fujio Abe[15] shows that the fine Laves phase precipitates in the creep process cause the decrease of the creep rate, and the steady creep stage is prolonged. The steady state creep phase is mainly a dynamic equilibrium process of a large number of dislocation movement and annihilation. The fine MX phase can stabilize the martensite structure, and the precipitation of fine Laves phase decreases the minimum creep rate. The accelerated creep stage is mainly due to the rapid growth of Laves and $M_{23}C_6$ under high temperature and stress, and the softening of martensite lath leads to the loss of creep strength. However, the Laves phase was not found in this experiment. The reason may be that the dissolution temperature of Laves is close to 923K, and the nucleation of Laves is difficult.

4. Conclusion

(1) A large number of $M_{23}C_6$ was precipitated at grain boundaries during the creep process of CLAM steel, and fine MX was dispersed in the matrix. The increase of the amount of precipitates can effectively improve the creep strength of CLAM steel. No Laves phase was found in this experiment. This is due to the temperature is close to dissolution temperature of Laves phase, and the Laves phase is difficult to nucleation and growth.

(2) In the process of creep, the martensite lath is broken into Subgrain, and the dislocation in the grain is obviously reduced. The degradation of the microstructure at high temperature will lead to the deterioration of the creep performance.

Acknowledgments

References

[1]Tsuzuki, K., M. Sato, & H. Kawashima (2002). Recent Activities on the Compatibility of the Ferritic Steel Wall with the Plasma in the JFT-2 M Tokamak. Journal of Nuclear Materials 307-311: 1386-1390.

[2]Kphyama,A., A.Hishinuma, & D.S. Gelles (1996). Low-activation ferritic and martensitic steel for fusion application. Journal of Nuclear Materials 233-237:138.

[3]Klueh, R.L., D.S. Gelles, & S.Jitsukawa (2002). Ferritic/martensitic steels-overview of recent results. Journal of Nuclear Materials 307-311: 455-465.

[4]Huang, Q.Y, C.J. Li, & Y.F. Li (2007). R&D Status of China Low Activation Martensitic Steel. Chinese Journal of nuclear science and Engineering 27(1):41-50.

[5]Masaki, T., S. Kota, & A. Fujio (2002). Effect of Carbon Concentration on Precipitation Behavior of M23C6 Carbides and MX Carbonitrides in Martensitic 9Cr Steel during Heat Treatment. Metallurgical and Materials Transaction A 4(35):1255-1262.

[6]Abe, F., M. Taneike, & K. Sawada (2007). Alloy design of creep resistant 9Cr steel using a dispersion of nano-sized carbonitrides. International Journal of Pressure Vessels and Piping 84(1-2): 3-12.

[7]Wang, Y.F., K.Y. Zheng, & Z.Y. Wu (2010). Mechanical properties and microstructure stability of T92 steel tubes after long-term exposure to high temperatures. Journal of Chinese Society of Power Engineering 30(4):245-252.

[8]Guo, X.F., J.M. Gong, & Y. Jiang (2011). Research Advances of T92/P92 Steel for Boiler Pipes of USC Power Plants. Pressure Vessel Technology (05):55-61.

[9]Maruyama, K., K. Sawada, & J.I. Koike (2001). Strengthening mechanisms of creep resistant tempered martensitic steel. ISIJ International 41 (6): 641-653.

[10]Blum, W. & G. Gtz (1999). Evolution of dislocation structure in martensitic steels: the subgrain size as a sensor for creep strain and residual creep life. Steel Research 70 (7): 274-278.

[11]Ghassemi, A.H., R. Chen, & K. Maruyama (2009). Static recovery of tempered lath martensite microstructures during long-term aging in 9–12% Cr heat resistant steels. Materials Letters 63 (28):

2423-2425.

[12] Klueh, R.L., D.J. Alexander, & M.A. Sokolov (2002). Effect of chromium, tungsten, tantalum, and boron on mechanical properties of 5–9Cr–WVTaB steels. Journal of Nuclear Materials 304(2–3): 139-152.

[13] Xiao, X., G. Liu, & B. Hu (2013). Effect of V and Ta on the precipitation behavior of 12%Cr reduced activation ferrite/martensite steel. Materials Characterization 82: 130-139.

[14] Kaybyshev, R.O., V.N. Skorobogatykh,& I.A. Shchenkova (2010). New martensitic steels for fossil power plant: Creep resistance. Physics of Metals and Metallography 109 (2): 186-200.

[15] Fujio, A. (2001). Creep rates and strengthening mechanisms in tungsten-strengthened 9Cr steels. Materials Science and Engineering A 319–321 770–773.