Journal of Alloys and Compounds 579 (2013) 599–605

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Effects of carbide precipitate on the mechanical properties and irradiation behavior of the low activation martensitic steel

P.P. Liu, M.Z. Zhao, Y.M. Zhu, J.W. Bai, F.R. Wan, Q. Zhan *

School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 11 July 2013
Accepted 12 July 2013
Available online 20 July 2013

Keywords:
Precipitates
Dislocation loops
Radiation hardening
High resolution transmission electron microscopy
Scanning transmission electron microscopy

ABSTRACT

Precipitates may be induced during the processing, heat treatment and reactor operating and will play a key role in determining the properties of materials. The effects of precipitates on the mechanical properties and irradiation behavior of the low activation martensitic steel have been investigated using transmission electron microscopy combined with tensile test. Two types of China low activation martensitic (CLAM) specimens (with and without Si) were chosen as the model materials. The significant microstructural difference between the two CLAM specimens was the distribution of fine (Ta, W, V) C precipitates which can strengthen materials. Nano-indentation test revealed that the fine (Ta, W, V) C precipitates promoted by adding silicon can also decrease the irradiation hardening ratio of CLAM steel because the MC precipitates with high interface-to-volume ratio could decrease the density of the dislocation loop induced during irradiation. The interaction between precipitates and irradiation induced dislocation loops was discussed.

1. Introduction

Reduced activation ferritic/martensitic (RAFM) steel was developed and extensively studied in the world involved the replacement of molybdenum, niobium and nickel in conventional Cr–Mo heat-resistant steels by tungsten, vanadium and/or tantalum based on the consideration of low activation and less swelling [1]. Precipitates play a key role in determining the properties of RAFM steel, which may be induced during the processing, heat treatment and reactor operating. The shape, size and density of precipitate and partitioning of alloying element to precipitates are important in understanding the irradiation resistance and mechanical behaviors. For example, plate-shaped precipitates that form on prismatic planes of the matrix phase are most effective for dispersion strengthening [2]. The partitioning of Cr and Ta element to precipitates may result in the degradation of corrosion-resistant performance and strength of steel. Several microscopic investigations have indentified $M_{23}C_6$ and MC particles as the major precipitates in RAFM steels [3,4]. However, detailed analysis such as the elemental distribution in these precipitates is still needed to be explored further. Furthermore, the presence of precipitates means high interface-to-volume ratio, in which interface can act as a sink for the annihilation of point defects created during irradiation. A critical question has thus arisen: how about the effects of precipitates on the mechanical properties as well as the irradiation behavior of RAFM steels?

A good understanding on the mechanical properties and microstructure evolution of materials under irradiation is of great important for developing structural materials in fusion reactors and for achieving a safe design and operation of innovative nuclear systems. Energetic neutron strikes the target material inducing displacement damage forming interstitial atoms and vacancies and finally resulting in the degeneration of property. All of this microstructural damage and property degeneration of materials irradiated by neutron could be epitomized as neutron-irradiation effects. However, neutron-irradiation programs are extremely costly, lengthy and logistically complicated. The slow attrition in the number of test reactors, the loss of irradiated materials handling capability and the increased difficulty of irradiated materials shipment has exacerbated the cost, extended the duration and compounded the complexity of such studies [5]. Recently, much of the development of charged particle (ion and electron) irradiation for the study of the irradiation effects was driven by the fusion reactor programs. Because the ions have masses comparable to those of the target atoms, they knock the target atoms out of place more than electron beams do. Energetic ion bombards the target material, inducing displacement damage thus forming interstitial atoms and vacancies. Therefore, energetic ion beams can be considered to simulate neutron irradiation to induce displacement damages, thereby allowing the investigation of the irradiation effects on materials without highly activating the specimens, as well as significantly reducing the costs for analysis. A significant

* Corresponding author. Tel.: +86 10 62333580.
E-mail address: qzhan@mater.ustb.edu.cn (Q. Zhan).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.07.085

amount of work has been performed to relate the damages induced by ions and neutron irradiation [6,7]. Displacement cascades induced by ion irradiation were demonstrated to be similar to those induced by neutron irradiation [5,8]. However, the depth of ion penetration is limited (nm to μm) much smaller than that of neutron irradiation (cm). Therefore, nanoscale methods of testing and characterizing on irradiated materials should be taken into consideration. In the present study, we choose China low activation martensitic (CLAM) as the model system. It is one kind of RAFM steels and considered as the primary candidate structural material for the DEMO fusion reactor and the first fusion power plant because of its excellent swelling resistance and thermodynamic properties [9–14]. The microstructure evolution of CLAM steel with and without the addition of Si after the irradiation of hydrogen ions at 773 K was investigated by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Nano-indentation is also a small-scale method that can be applied to investigate the changes in mechanical properties. Here, it was applied to examine the changes in mechanical properties caused by the hydrogen ion irradiation at 773 K. The interaction between precipitates and irradiation induced dislocation loops in the materials was discussed in detail.

2. Experiment

The materials analyzed in this study were CLAM steel with two different compositions: 1# without Si and 2# with 0.2% Si addition. The chemical compositions are listed in Table 1. CLAM steel was melted in a vacuum induction furnace into 5 kg ingots and subsequently hot-forged at 1473 K into 150 mm × 35 mm × 35 mm bars. The surfaces of the samples were mechanically polished. The samples were normalized at 1253 K for 30 min and were fully martensitic after quenching in water at room temperature. Tempering was conducted at 1023 K for 90 min, after which the materials were air-cooled.

Unirradiated specimens suitable for tensile testing were prepared using standard techniques. Tensile tests were conducted at 298 K (room temperature) and 623 K with a gauge section of ∅6 mm × 30 mm in the air, by using MT S809 electro-hydraulic servo controlled materials testing system. The 0.2% proof strength was measured as yield strength (YS).

Given the limitation on ion irradiation depth and sample size, conducting tensile tests was not practical. Instead, nano-indentation experiments were performed to evaluate the mechanical properties of the samples before and after hydrogen ion irradiation. Depth-control mode under ambient atmosphere was used with an MTS Nanoindenter XP system. The indenter tip was a Berkovich-type diamond pyramid, and the tip truncation was calibrated using fused silica as a reference specimen. The allowable thermal drift rate was limited to 0.05 nm/s. Continuous stiffness measurement (CSM) method was applied, and the indentation depth was controlled within 1000 nm to evaluate the effects of irradiation on the mechanical properties better [15]. For each sample, eight measurements were taken to obtain the average values of the hardness.

For the TEM investigation, samples 3 mm in diameter were punched out from strips mechanically grounded to approximately 0.1 mm thick. The TEM samples were polished using a twin-jet electropolisher with a polishing solution of 5%$HClO_4$ + 95%C_2H_5OH compound at 243 K.

Usually, ion accelerator is used to carry out the ion irradiation experiment. Ion irradiation is routinely used to implant ion into materials to modify their properties or to induce displacement damage. This process, generally known as ion implantation, is a very important step in fundamental mechanistic studies on irradiation effects. Hydrogen ion (proton) irradiation was performed at 773 K in an LC-4 ion accelerator. The energy of ion is 58 keV. The damage profile calculated by the SRIM 2008 software is shown in Fig. 1 [16]. The flux of the ions was 1×10^{21} H^+/m^2. The TEM characterization on the microstructure was conducted using an FEI Tecnai F20 microscope equipped with an energy dispersive X-ray spectrum (EDS) analysis system. The accelerator voltage of the microscope was 200 kV.

Table 1
Chemical composition of CLAM steels (wt. %).

CLAM steel	Cr	Mn	C	W	V	Ta	Si	Fe
1#	9.04	0.46	0.099	1.48	0.19	0.07	0	Bal.
2#	8.95	0.45	0.099	1.49	0.21	0.072	0.2	Bal.

3. Results and discussion

3.1. Before irradiation

3.1.1. Tensile test results

Tensile tests were conducted on 1# and 2# specimens at 298 K and 623 K. The results of the tensile tests are shown in Fig. 2a. It is clear that the ultimate tensile strength (UTS) and YS of the two kinds of samples decreased with increasing test temperature. For the 2# specimens, the UTS and YS were 649 and 503 MPa at 298 K and 541 and 433 MPa at 623 K. However, the UTS and YS of the 2# specimens were both higher than those of the 1# specimens at both test temperatures. The differences in UTS and YS for the two CLAM specimens were 43 and 37 MPa at 298 K and 42 and 24 MPa at 623 K. These differences also decreased as the temperature increased. The results suggested that CLAM steel can be strengthened by adding 0.2% Si. Small differences were observed in the total elongation and uniform elongation between the two kinds of specimens at the same temperature, as shown in Fig. 2b.

3.1.2. Microstructure observed by TEM and STEM-EDS

To further understand the reason causing the difference of tensile property between the 1# and 2# specimens, a detailed microstructure analysis was carried out. Fig. 3 shows the low-magnification images of the 1# and 2# specimens before hydrogen ion irradiation. Both types exhibited the lath-martensite characteristic with precipitates present at the lath boundaries or in the martensite grains. The lath widths in both types of specimens were similar. The significant differences between the two CLAM specimens were the size and distribution of precipitates, as listed in Table 2. Dominant larger precipitates with an average length of approximately 120 nm to 130 nm were present at the lath boundaries in the 1# specimens, whereas many fine precipitates of 20 nm to 60 nm in diameter were observed in internal martensite in the 2# specimens. The EDS results indicate that the lath grain boundary phase was Cr-rich $M_{23}C_6$ and the fine intragranular precipitates were Ta-rich MC phase, which are consistent with the majority of reports on RAFM steel [3,4].

It is worth to note that the content of Si was the main distinction between the two CLAM specimens studied. More fine MC particles distributed in the specimens with the addition of 0.2% Si, suggesting that the addition of Si may promote the precipitation of MC phase which result in the precipitation strengthening. On the other hand, silicon is the fundamental and important element in structural steel. It has specific roles in steel such as solid solution strengthening of the ferrite matrix [17,18]. Thus, the tensile strength was increased in 2# specimens with adding Si by solid solution strengthening and precipitation strengthening.

To understand these precipitates more clearly, a composition mapping by STEM-EDS and a corresponding electron diffraction pattern (EDP) were given. Fig. 4a shows a typical low-magnification Z-contrast image of the 1# specimens before ion irradiation. Z-contrast imaging helps eliminate the contrast contributions from coherent strain effects and highlight the mass-thickness differences. The phase containing heavy atoms may exhibit a bright contrast, whereas the one containing relatively light atoms may present a dark contrast. Combined with the EDP (embedded in the figure) of one precipitate marked in Fig. 4a, the dominant precipitate at the lath boundary was determined to be $M_{23}C_6$ which exhibited a bright contrast. The STEM-EDS mapping results of the marked $M_{23}C_6$ precipitate are shown in Fig. 4b. Besides the enrichment on Cr and Mn, a certain amount of W was also found in $M_{23}C_6$ phase. Similar investigation on the fine intragranular MC precipitates in 2# specimens with Si addition was also carried out, as shown in Fig. 5. It was confirmed that these precipitates with