Tutorial

Carbides and possible hydrogen irreversible trapping sites in ultrahigh strength round steel

X.Y. Cheng*, H. Li, X.B. Cheng

Institute of Materials, Shanghai University, Shanghai 200072, China

ABSTRACT

The carbides in ultrahigh strength round steel have been investigated by using laser-assisted atom probe tomography (APT) and high resolution transmission electron microscopy (HRTEM) in this paper. Two kinds of carbides are found and one is iron carbide M_6C, where carbide formation elements Cr, Mn and Mo replace partial Fe, while the other is niobium carbide MC, where M includes V and Mo besides Nb. These two carbides, due to their different evaporation field, have various densities in reconstructed image of APT. After correction, the hydrogen content within these two carbides illustrates that M_6C cannot trap hydrogen, while MC can. The different behaviors in trapping hydrogen between these two carbides may result from elements Fe or Cr in M_6C carbide having weaker affinity for hydrogen than Nb and V have in MC.

1. Introduction

Ultrahigh strength round steel is needed as hot-rolled material for mooring chain. As people explore deeper in oceans, longer mooring chains are required, hence the steel used for mooring chains would have considerably higher strength levels through microalloying. As a result, carbide precipitations, as the main reinforcer, can make a difference. Besides new carbides formation, the original carbides, such as cementite or M_7C_3, may evolve. Zhang (2007) has found that element V in steel can promote M_6C precipitation, but impedes the emergence of M_7C_3 precipitation. Wen et al. (2014, 2013) put forward that M_3C and M_7C_3 mainly appear in a Fe-Cr-Ni-Mo high-strength steel when tempering at a rather low temperature (400 °C), while M_2C, M_6C, and MC gradually develop and simultaneously M_3C shrinks and ends in disappearance when tempering at a higher temperature. Mulholland et al. (2011) also think that nucleation and growth of M_2C carbide precipitation are at the expense of the dissolution of cementite Fe_3C in a high-strength low-carbon steel. To design and optimize the steel, a characterization of the precipitation on a nano-scale is required.

It is well known that hydrogen embrittlement (HE) problem becomes more serious as the strength of steel increases. However, some works elucidate that only diffusible hydrogen is directly associated with the degradation, while hydrogen trapping in stronger binding state is innocuous to hydrogen embrittlement (Takai and Watanuki, 2003). Many researchers have found that fine and dispersive metal carbides precipitated in steel may act as useful hydrogen trapping sites and can be expected to mitigate or suppress hydrogen embrittlement. Hence,

the interpretation of HE phenomena needs first a complete knowledge of the different trapping sites of the microstructure (Luppo and Ovejero-Garcia, 1991). However, since hydrogen has some features such as a specific light weight, an extremely low solubility with high diffusivity in bcc-iron, and the ability to remain even in and pervade high-vacuum chamber, still little direct work focuses on differentiating the capability of various carbides to trap hydrogen.

Atom probe tomography (APT) possesses nanometer spatial resolution, excellent chemical mass resolving power ($m/\Delta m$) and prominent signal-to-noise ratio, so it offers a direct three-dimensional reconstruction of all constituent elements, even light elements in alloy, on an atomic scale. Meanwhile, it provides the possibility to analyze quantitatively embedded particles (Kelly and Miller, 2007; Seidman, 2007). Therefore, it is easy for APT to display the morphology, distribution, size, and composition of fine carbides in steel. In detecting hydrogen, APT can resolve hydrogen without any instrumental modification in theory, but unfortunately, hydrogen will be present as a major element in most analyses due to adsorption of residual gas, especially when laser pulsing is employed in APT (Sundell et al., 2013; Cheng et al., 2013). Once the hydrogen adsorbed from the residual gas is distinguished from the hydrogen presented in the precipitation, the hydrogen concentration trapped in the precipitation can be estimated from the APT results. Although hydrogen trapping in bulk samples can be studied by using other methods, such as small-angle neutron scattering (Malard et al., 2012), thermal desorption spectroscopy (Lee et al., 1982; Wei and Tsuzaki, 2006), energy recoil detection (Fukutani, 2002), and secondary ion mass spectroscopy (Nishimoto et al., 2015;

Tarzimoghadam et al., 2016), which can only provide volume-averaged information on microstructural interaction but fail to measure the precise location of hydrogen atoms, APT is relatively superior to other methods in displaying hydrogen distribution on an atomic scale.

In this study, we choose a newly developed ultrahigh strength round steel as our research material and use laser-assisted APT to analyze the composition of fine carbides in it. The types of carbides are determined from their compositions and in the meantime the sizes of carbides can be monitored from three dimensions. In addition, high resolution transmission electron microscopy (HRTEM) is also used to observe the distribution and morphology of these carbides and confirm the types of carbides by analyzing their energy dispersion spectrometry (EDS) and Fast Fourier transform (FFT) pattern. Furthermore, the hydrogen distributions in carbides are measured using APT, and the hydrogen content is determined after deducting the hydrogen in matrix around the carbide, as well as being amended by different evaporation field between carbide and ferrite. The analyzed results about the carbide type and the local hydrogen distribution are used to clarify the possible hydrogen irreversible trapping sites.

2. Material and methods

2.1. Material

The last line in Table 1 lists the chemical composition of the steel investigated in this study. The steel was first melted in a vacuum induction furnace and cast into 90 mm diameter ingot. Then the riser was cut off, we removed the surface oxide of the steel and forged the steel into $42 \times 42 \times 250 \, mm^3$ square billet. Next, the billet was homogenized at 1100 °C for 1 h and then hot-rolled to 17 mm thick plate at a temperature range from 920 to 1050 °C. Later, some sheets for APT or HRTEM analyses were cut from the plate and solution treated at 920 °C for 30 min, quenched in water, and then tempered at 600 °C for 3 h, followed by air cooling.

2.2. Transmission electron microscopy

Samples with < 50 μm in thickness (as thin as possible in order to minimize the effect of magnetism of the sample on the electron beam) were prepared for HRTEM observation from the heat treated sheets. Then these samples were punched to 3 mm wafers in diameter. The wafers were electro-polished to perforation with a twin-jet electropolisher using a solution of 10% perchloric acid in ethanol at 243 K and 45 V. Afterwards, the microstructures of samples were examined by JEM 2010F TEM operated at 200 kV.

2.3. Atom probe tomography

Atom probe tomographic samples were cut from the heat treated sheets as square rods with an approximately dimension of $0.5 \times 0.5 \times 20 \, mm^3$ and then electropolished using the standard two-stage process at room temperature (Miller and Smith, 1989). The first

step utilizes the electrolyte 10% perchloric acid in acetic acid and the second step employs 2% perchloric acid in butoxyethanol.

The APT analyses were completed in a LEAP 4000X HR (Cameca, Madison, WI, USA), which installed femtosecond lasers to successfully assist the field evaporation of materials and hence can reduce the probability of sharp needle sample failure during experimental procedures. The sample chamber was maintained at 50 K and an ultra high vacuum of $\sim 10^{-9}$ Pa. Laser pulsing was done with a laser energy of 60 pJ, with 250 kHz pulse frequency. Data reconstructions were conducted with IVAS™ 3.6.8 software.

3. Results and discussion

3.1. Carbides

3.1.1. APT investigations

Fig. 1 shows the distribution of individual atoms of carbon and carbide formation elements (Cr, Mn, Mo, Nb and V, except Fe) in four samples of this steel. According to the varied clustered positions of different elements, the carbides mainly fall into two categories: one is (Cr, Mn, Mo, V) carbide and the other, (Nb, V, Mo) carbide, though the carbides exhibit differences in morphology and size. Usually, the size of (Cr, Mn, Mo, V) carbide is larger than that of (Nb, V, Mo). Thereinto, some of (Cr, Mn, Mo, V) carbides are lamellar (see Fig. 1a–c) while others are spherular (see Fig. 1d), but all of (Nb, V, Mo) carbides possess an axiolitic shape (see Fig. 1b and d). Of course, there seems to have some very small vanadium carbides which are too small to be identified clearly, but these are neglected for further use.

To better distinguish these carbides, Table 1 lists the composition (excluding the contributions from noise events and hydrogen) estimated from the numbers of different types of atoms within an envelope defining the extent of the typical carbide of each sample. In order to avoid ion trajectory overlaps due to trajectory aberration as narrated later, these selected envelopes also need away from the interface by several nanometers. It can be seen that (Cr, Mn, Mo, V) carbide contains only 10–14 at.% C but (Nb, V, Mo) carbide, about 50 at.% C. Hence, there is no doubt that the former is classified as M_6C and the latter as MC simply according to the atomic ratio, where M denotes the carbide forming elements.

Fig. 2 displays concentration profiles of one typical (Cr, Mn, Mo, V) carbide in sample 1 and one typical (Nb, V, Mo) carbide in sample 2. Note that error bars are omitted here in order to have a clearer observation. First of all, it is noteworthy that after the process of carbide precipitation, the change of atom counts is obviously greater, which is not supposed to happen owing to the uniform cross sections of the selected box. Even considering the ideal carbide and α-Fe densities (103 atoms/nm^3 for Fe_3C, 81 atoms/nm^3 for M_6C, 44 atoms/nm^3 for NbC and 85 atoms/nm^3 for α-Fe), the variation in change is paradoxical, for that indicates the observed maximum density inside (Cr, Mn, Mo, V) carbide is more or less twofold of the expected M_6C density, while the density inside reconstructed (Nb, V, Mo) carbide only approaches to one tenth of the anticipated NbC density (also see column 3 in Table 2).

Table 1
Atomic fractions of selected envelope defining the extent of these two carbides of each sample and steel per se (at%).

Samle No.	Carbide	Fe	Mn	Ni	Cr	C	Si	V	Mo	Nb
1	M_6C	70.37 ± 0.65	3.68 ± 0.12	1.23 ± 0.07	9.05 ± 0.19	14.12 ± 0.24	0.09 ± 0.02	0.25 ± 0.03	1.13 ± 0.06	–
2	M_6C	77.61 ± 0.38	2.71 ± 0.05	1.04 ± 0.03	5.75 ± 0.08	11.49 ± 0.11	0.17 ± 0.01	0.18 ± 0.01	1.02 ± 0.03	–
	MC	1.01 ± 0.10	0.14 ± 0.02	0.55 ± 0.08	1.59 ± 0.15	47.15 ± 0.99	0.19 ± 0.03	12.81 ± 0.46	10.42 ± 0.40	26.08 ± 0.69
3	M_6C	76.60 ± 0.49	2.42 ± 0.07	1.51 ± 0.05	4.54 ± 0.09	13.64 ± 0.16	0.17 ± 0.02	0.14 ± 0.02	0.88 ± 0.04	–
4	M_6C	73.57 ± 0.37	3.37 ± 0.06	1.21 ± 0.04	9.98 ± 0.11	10.19 ± 0.11	0.24 ± 0.02	0.28 ± 0.02	1.09 ± 0.04	–
	MC	0.92 ± 0.39	1.22 ± 0.45	0.92 ± 0.39	2.45 ± 0.64	50.76 ± 3.41	–	9.79 ± 1.32	4.59 ± 0.89	29.05 ± 2.42
steel	–	92.88	0.70	1.39	2.19	1.43	0.55	0.08	0.76	0.02