Effect of Heat Treatment on Mechanical Properties and Microstructure of L80-13Cr Martensitic Stainless Steel

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Abstract: L80-13Cr martensitic stainless steel (MSS) is a kind of oil casing steel. It has good resistance to carbon dioxide corrosion and seawater corrosion, which makes it common oil casing steel in marine oil and gas exploration. The effect of heat treatment on mechanical properties and microstructure of L80-13Cr MSS has been studied. The specimens were analyzed using the micro-hardness test, optical microscope (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The hardness test showed that the steel was secondarily hardened when tempering at 300 ~ 500°C. But continuous softening occurred when the temperature was above 500°C. The martensite was recovered at temperatures around 300 ~ 500°C, and higher temperature tempering (600°C) caused grain growth and even recrystallization. It has been found that the precipitates in the steels that were tempered at 300°C, 500°C and 700°C, were need-like Fe_3C carbides, coarsed needle-like Fe_3C carbides and rod-like or sphere-like $Cr_{23}C_6$ carbides. Especially when tempered at 700°C, the $Cr_{23}C_6$carbidesprecipitation along the marten site lath was rod-like and precipitation along grain boundaries was sphere-like. Secondary hardening between 300 ~ 500°C tempering of 13Cr is attributed to the precipitation of needle-like Fe_3C. The recovery and recrystallization of the matrix and the coarsening of carbides resulted in the continuous softening of 13Cr MSS during tempering.

1 INTRODUCTION

Oil casing in the process of oil extraction is often directly affected by corrosion, with the depth of the formation of oil mining depth, oil casing to withstand the temperature and pressure is getting higher and higher, more and more harsh environmental environment (Feng Z et al.2016). Ordinary carbon or low alloy steel cannotsatisfy the corrosion resistance requirements, so more and more oil and gas fields began to use the L80-13Cr MSS(Jianqiang Y et al.2015). 13Cr MSS has high thermal strength, oxidation resistance, good impact resistance (Cabello G et al.2013) In the weak corrosive medium has good corrosion resistance, fresh water, sea water, steam, air also has enough corrosion resistance(Sidorin D et al.200).Because of low carbon content in 13Cr MSS, it usually needs to be appropriate heat treatment, in order to obtain a stable small uniform organization (Larsen Jet al.2015). The heat treatment for 13Cr MSS is quenching at a high temperature and followed with tempering. After high temperature quenching, the microstructure of MSS is martensitic with high hardness and low toughness. After tempering，the hardness of the MSS will reduce and the toughness will rise (Isfahany A N et al.2011).However, during tempering, the formation and transformation of second phases may harden the MSS, causing the dramatic reduction of toughness (Chakraborty Get al.2015). At the same time, the complex carbide reactions that occur during tempering may directly determine the corrosion resistance (Pfennig A et al.2013).Therefore, it is necessary to study the impact of tempering temperature on the 13Cr MSS.

The present work is designed to acquire an understanding of the relationship between the microstructure and the mechanical behavior of 13Cr MSS after quenching and tempering. The microstructure and precipitate are characterized using OM, SEM, TEM analysis.

2 MATERIALS AND EXPERIMENTAL

2.1 Material and Heat Treatment

The steel used in this work is the 13Cr martensitic stainless steel, which hasthe chemical composition (in weight percent) of 0.18C, 0.23Si, 0.47Mn, 12.66Cr, 0.15Ni, 0.7Cu and balance Fe. The heat treatment used the SRJX-4-13 chamber electric furnace. Solution treatment was performed at 1050°C for 1 h to allow the complete dissolution of all carbides. After solution treatment, the specimens were water cooled and then tempered at 300°C, 400°C, 500°C, 600°C, 700°C for 2 hrs.

2.2 Microstructure Observation and Precipitation Characterization

The samples were cut by wire cutting machine. All the specimens were ground and mechanically polished, then were etched by a particular etchant comprising 25 ml HNO3, 25 ml HCl, and 50 ml distilled water. The sample prepared for hardness measurements were ground through abrasive papers in turn of 400-, 800-, 1200-, 1500-, 2000-grit.The micro-hardness test was performed with a load of 200 kgf and loading time of 10 s on HVS-1000 type micro-sclerometer. Seven points were tested, take average of five points except the highest and lowest.

The microstructure of each specimen was characterized by OLYMPUS GX71 inverted metallurgic microscope and JSM-6510 SEM. TEM thin foil specimens were prepared by using a Struers TenuPol-5 double-jet electrolytic polisher with a solution of 120 ml HClO4 and 1080 ml CH3COOH. Carbon extraction replication method was used to monitor the precipitation in the heat treated specimens using JEM-2100F TEM.

3 RESULTS AND DISCUSSIONS

3.1 Effect of Heat Treatment on the Hardness of 13Cr MSS Steel

The hardness of the quenched and tempered specimens is shown in Fig. 1. After quenching, the specimen was hardened (~590 HV) by martensitic transformation.The hardness decreased even tempering at a low temperature (<300°C). But whenthe tempering temperaturerose to 300°C (~375 HV), the hardness abruptlybecame harder. It showed the steel was secondarily hardenedafter tempering at 300 ~ 500°C that the hardness abruptly increased. When the steel was tempering ata higher temperature like 600 ~ 700°C, the hardness of steel decreased (~254 HV) at 600°C, and continuous decreased (~225 HV) at 700°C.

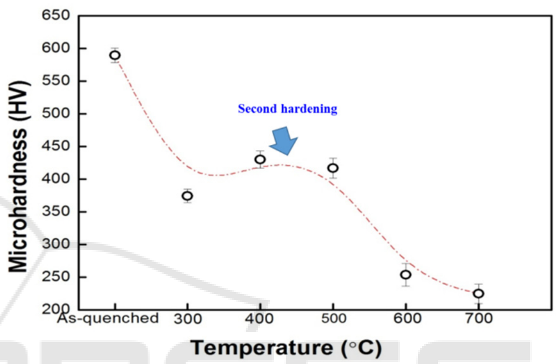


Figure 1:Hardness test results of 13Cr MSS quenched and tempering.

3.2 Effect of Heat Treatment on the Microstructure of 13Cr MSS Steel

The OM microstructure of 13Cr MSS is shown in Fig. 2.The martensitic of 13Cr MSS changes with the tempering temperature rise. In the Martensitic stainless steel after quenching and tempering, the martensite decomposition, through the diffusion of elements, grain boundary migration, the occurrence of organizational changes (Caron R Net al.1972). When the tempering temperature under 600°C, the characteristics of martensite slabs are still evident in Fig.2(a, b, c, d). As the temperature rise to 700°C, the microstructure changes as fine ferrite with carbides in Fig. 2(e).

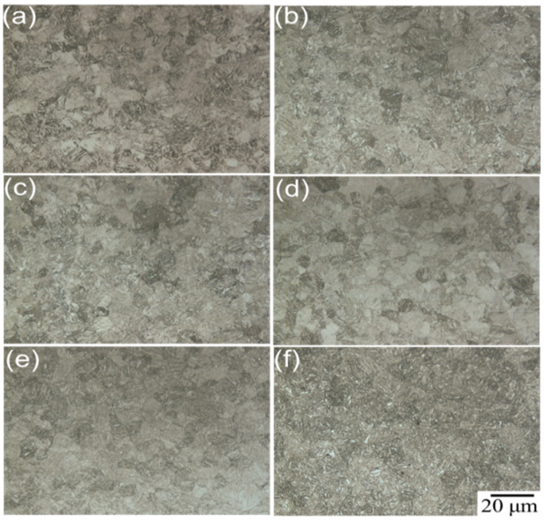


Figure 2：OM microstructures of 13Cr steel (a) quenched at 1050°C tempered at (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 700°C for 2 hrs.

The SEM microstructure of 13Cr MSS is shown in Fig. 3. Carbides are precipitated from the matrix. With the increase of tempering temperature, the matrix, the morphology and distribution of carbides have changed. At a low tempering temperature, the matrix of martensite coarsed in Fig.3(b, c), and at a higher tempering temperature, the martensite matrix began to disappear in Fig.3(d). As shown in Fig.3(e,f),the martensite lath already disappeared, and carbides have gathered to grow into sphere-like .

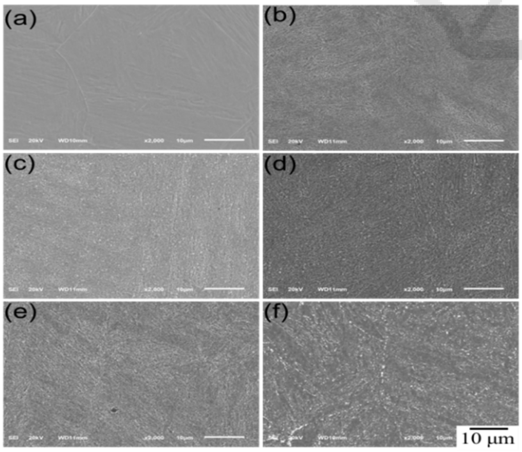
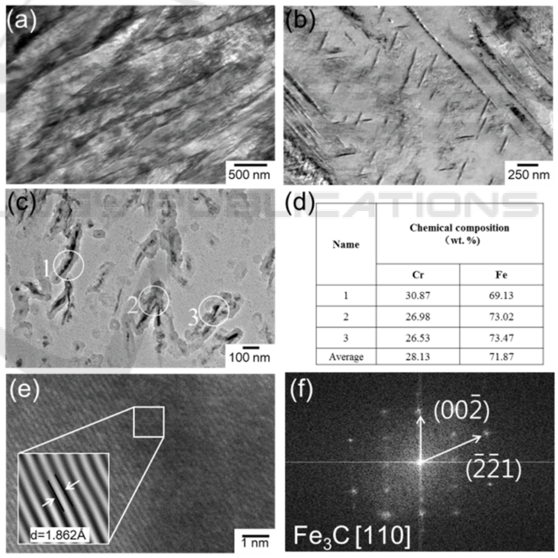


Figure 3：SEM microstructures of 13Cr steel (a) quenched at tempered at 1050°C tempered at (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 700°C for 2 hrs.

In order to judge the different carbides in 13Cr MSS with tempering temperature rising. The TEM samples were prepared with the 300°C, 500°C, 700°C tempering temperature. The TEM analysis indicates that two processes can occur during tempering: recovery and recrystallization of the matrix and the precipitation of various carbides. The TEM micrographs of 13Cr MSS tempered at 300°C is shown in Fig. 4.

As shown in Fig. 4(a), the figure shows a martensite lath area, composed of multiple slabs single crystal, roughly parallel, the slab width, length and length, the thickness of about tens of nanometers to hundreds of nanometers, the existence of slats dislocation substructures. The needle-like carbides is shown in Fig. 4(b). To specifically examine the formation of precipitates, a carbon extraction replica was utilized to precisely identify the carbides formed by tempering in Fig. 4(c).The EDS, high-resolution TEM (HRTEM), fast Fourier transformation (FFT) and the corresponding inverse fast Fourier transformation (IFFT) has been employed to identify the detailed information of these carbides in Fig. 4(d, e, f).The orthorhombic type Fe_3C carbide was found in the specimen tempered at 300°C.



Name	Chemical composition (wt. %)	
	Cr	Fe
1	30.87	69.13
2	26.98	73.02
3	26.53	73.47
Average	28.13	71.87

Figure 4：TEM images of 13Cr steel tempered at 300°C for 2 hrs: (a) matrix, (b) carbides in matrix, (c)carbides analysis by carbon extraction replica technology, (d) EDS results from (c) carbides, (e) HR-TEM images of carbides, (f)The FFT pattern from (e), and inset of (e) shows the IFFT image.

The TEM micrographs of 13Cr MSS tempered at 500°C is shown in Fig. 5. The martensite lath coarsed in Fig. 5(a). The needle-like carbides coarsed in Fig. 5(b,c). The EDS results show the Fe3C carbides increase with the tempering temperature in Fig. 4(d) and Fig. 5(d). The HRTEM, the FFT pattern and the inverse FFT pattern shows that it is also Fe3C carbide when tempering at 500°C in Fig. 5(e, f).

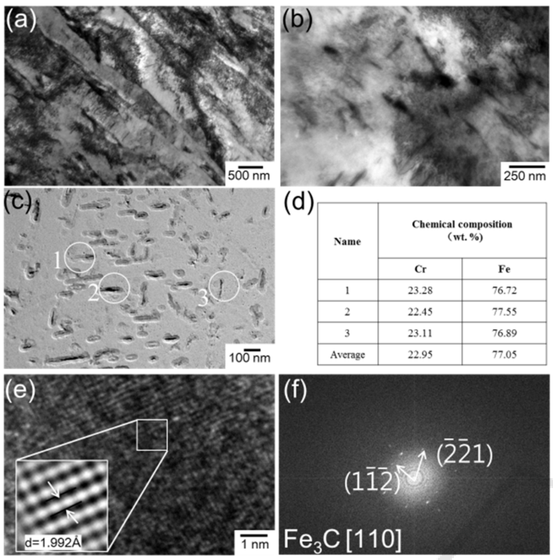


Figure 5： TEM images of 13Cr steel tempered at 500°C for 2 hrs: (a) matrix, (b) carbides in matrix, (c)carbides analysis by carbon extraction replica technology, (d) EDS results from (c) carbides, (e) HR-TEM images of carbides, (f)The FFT pattern from (e), and inset of (e) shows the IFFT image.

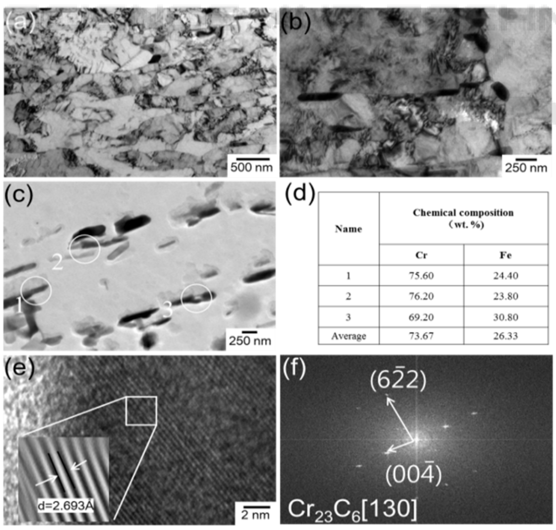


Fig. 6. TEM images of 13Cr steel tempered at 700°C for 2 hrs: (a) matrix, (b) carbides in matrix, (c)carbides analysis by carbon extraction replica technology, (d) EDS results from (c) carbides, (e) HR-TEM images of carbides, (f)The FFT pattern from (e), and inset of (e) shows the IFFT image.

The TEM micrographs of 13Cr MSS tempered at 700°C is shown in Fig. 6. After tempering at 700°C, recovery and recrystallization of the matrix is shown in Fig.6(a). The rod-like Cr-rich carbides was found in original martensite lath and sphere-like Cr-rich carbides was found in original austenite grain boundary in Fig. 6(b, c). The EDS results, HRTEM image analysis, fast Fourier transformation (FFT) and the corresponding inverse fast Fourier transformation (IFFT) indicates that these carbides is $Cr_{23}C_6$carbide in 13Cr MSS when tempering at 700°C in Fig. 6(d, e, f).

4 CONCLUSIONS

During tempering, the matrix recovery by the migration of lath boundaries and annihilation of dislocations to slightly coarsen the lath and decrease the dislocation density at temperatures lower than 500°C, and the formation of fine ferrite grains and subsequent grain growth during tempering at temperatures at 700°C to replace the original lath structure.

Two types of Fe_3C and $Cr_{23}C_6$carbides precipitation are suggested. The needle-like precipitation of Fe_3C in lath martensite occurs at 300 ~ 500°C. As the tempering temperature increased (700°C), the phase transformation of Fe_3C carbides to Cr23C6 carbides occurred. The $Cr_{23}C_6$ carbides precipitation along the martensite lath is rod-like and precipitation along grain boundaries is sphere-like.

Precipitation of Fe3C carbides at low temperature enhances the hardness of the steel upon precipitation hardening. As the tempering temperature increased, the steels were dramatically softened by grain growth and recrystallization.

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