Corrosion Behavior of Martensitic Stainless Steels – Role of Composition and Heat Treatment Procedures

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Abstract: ***Martensitic stainless steels are used in many applications which demand high strength-toughness combination along with good corrosion resistance. Selection of these steels for corrosive environment is generally based on the carbon and chromium content of the steel, and their resistance to corrosion in the heat treated conditions, as the corrosion resistance of these steels depends on carbide volume fraction dissolved in matrix after austenitizing and on the carbide precipitation during tempering. This paper reviews the influence of the composition and the heat treatment procedures which are being followed to get optimum corrosion resistance of these steels.***

Keywords: Corrosion; Martensitic stainless steel; Austenitizing; Tempering;

1. Introduction

Martensitic stainless steel has become increasingly attractive for a number of industry sectors due to their excellent mechanical properties like high strength, adequate ductility and toughness apart from good corrosion resistance. These are used in various industries such as in chemical plants, power generation equipments in gas turbines and compressor blades and discs, aircraft engine components and fittings in marine components [1]. However, the need for superior properties combined with good corrosion resistance in specific applications (e.g. steam generators, mixer blades, etc.) led to wide research on the performance improvement of these steels.

Table 1: The corrosion rate of Cr and Cr-Ni steels during 120 h in 100% H_2S at atmospheric pressure [Naumann, 1938]

Material, Wt.%	Corrosion Rate (mm/yr)	
	344^0C	500^0C
5 Cr	6.10	25.40
9 Cr	5.08	17.78
12 Cr	3.30	10.16
17 Cr	2.29	5.08
25 Cr	-	2.54
18 Cr- 9 Ni	2.03	6.10
26 Cr- 20 Ni	1.50	2.54

Chromium confers the stainless steel it's most important property of being resistant to corrosion. From the point of view of general corrosion, the higher the chromium content of the steel the greater will be its resistance to corrosion. The existence of chromium as chromium carbide particles may be beneficial to stainless steel from the point of view of certain mechanical properties but as far as corrosion resistance is concerned it is beneficial if chromium exists in solid solution [2]. The corrosion resistance of martensitic stainless steels depends on carbide volume fraction dissolved in matrix after austenitizing and on the carbide precipitation during tempering [3-4]. Therefore, for maximum corrosion resistance, the carbon content and heat treatment condition of stainless steel are two important factors to be taken into account while considering martensitic stainless steel for any structural application.

This paper reviews the influence of composition and the heat treatment methods which influence the corrosion resistance of martensitic stainless steels.

2. Effect of Chemical Composition

Increasing chromium in stainless steels increases resistance to atmospheric corrosion in an industrial atmosphere [5]. Data presented in Table 1 [6] indicate that the resistance of stainless steels to corrosion by hydrogen sulphide (H_2S) at elevated temperatures increases with increasing amount of chromium. Chromium increases the resistance of stainless steels to sulphur vapor in flue gases. The protective chromium oxide film imparting resistance to stainless steel from general aqueous corrosion increases with increase in chromium in oxidizing environments. However, the effect is negative in reducing environment.

Increased chromium resists pitting corrosion [2] and stress corrosion cracking in these steels (SCC) [7]. Chromium also increases resistance to oxidation at 1000ºC in the manner as shown in Fig. 1 "A" [8]. For a number of steels maximum temperature without producing excessive scaling is presented in Fig. 1.18 "B" [9] which indicates the beneficial effect of 16% Cr over 12% Cr steel.

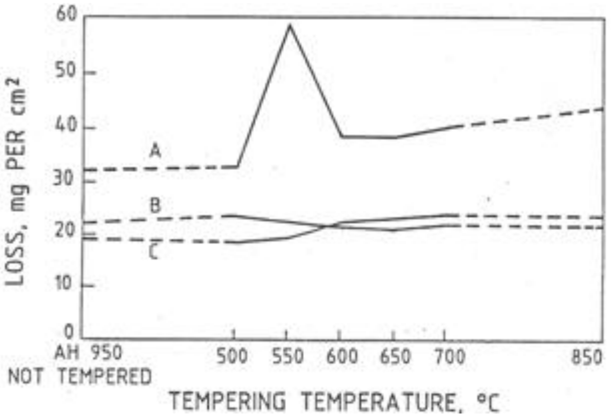


Figure 1: Corrosion resistance of 12% Cr and 17% Cr steels in hardened and tempered conditions [Monypenny, 1951]

Increasing nickel content of 12% Cr steels from 2.5% to 4.5% is found to improve resistance to marine atmosphere corrosion [10]. Brasunas et al. [11] showed that nickel improved scaling resistance in stainless steels with wide range of Cr (11-31%) in air at 532^0C. Nickel in stainless steels is found to improve both general corrosion resistance as well as SCC [10]. It is reported that the small amounts of silicon and manganese (1.0%) in martensitic stainless steels have no noticeable effect on corrosion resistance [2].

C.X. Liʾ and T. Bell [12] have investigated the corrosion properties of plasma nitided AISI 410 martensitic stainless steel and found that the nitrided samples showed higher corrosion potentials and, higher pitting potentials. The improved corrosion resistance was believed to be related to the iron nitride compound layer formed on the martensitic stainless steel surface during plasma nitriding, which protected the underlying metal from corrosive attack under the testing conditions.

3. Influence of Austenitizing and Tempering Temperature on Corrosion Behavior

In 12% chromium steels carbon in the usual limit of 0.2% goes into solution when austenitized at $1000\text{-}1050^0$C. Steel in quenched condition, therefore has all the chromium in solid solution for effective corrosion resistance. On tempering up to 500^0C, the hardness remains more or less the same as that of hardened steel and therefore the steel does not show any change in its corrosion resistance. However, on tempering at 550^0C, the corrosion resistance is found to drop considerably [2]. On tempering at higher temperatures viz., $600\text{-}700^0$C, the corrosion resistance is found to improve again. The explanation given for this behavior of steel by Monypenny is that maximum precipitation of chromium carbide occurs at the tempering temperature of 550^0C. Therefore, with higher tempering temperatures the precipitated carbide particles only grow. As the carbide particles are more electropositive compared to steel matrix, electro-chemical action leading to corrosion can take place on the steel portion [2]. Therefore, the possibility of corrosion is maximum when finer and larger number of carbides are precipitated on tempering at 550^0C, causing a larger surface area of the carbide particles. With higher tempering temperatures growth of carbide particles reduce the surface area of carbides. Moreover, on transformation of carbides from Cr_7C_3 to $M_{23}C_6$ with higher tempering temperature, Cr substitution by Fe in $M_{23}C_6$ is also affected. Thus the effective chromium content of matrix is improved with raise in tempering temperature.

Lim et al.[13] have reported a tempering map for AISI 403 martensitic stainless steel containing 12% Cr and 0.1%C (Fig.2). According to this map for 2 hours tempering between $600\text{-}660^0$C, the steel becomes sensitized and its resistance to inter granular corrosion gets impaired.

The speed of sensitization in martensitic stainless steel is much more rapid as compared to austenitic stainless steel because the carbides form rapidly within the martensitic laths and along the lath boundaries. The resulting corrosion can be intergranular, transgranular or mixed [14-16]. Healing of chromium depleted zone in 12% Cr steel is seen to be occurring only at temperatures above 680^0C, which may recover the microstructure from the effect of sensitization but would also result in considerable loss in strength owing to tempering at very high temperature.

Effects of austenitizing treatment temperatures on aqueous corrosion properties of martensitic stainless steels were investigated by Yoon-Seok Choi, et.al [17] and found that the breakdown potential increased with the increased austenitizing temperature. This indicates the increased relative resistance to initiation of localized corrosion. The samples austenitized at higher temperatures exhibits larger polarization resistance value than samples austenitized at lower temperatures at passive and breakdown states. This was caused by decreasing the amount of Cr-rich $M_{23}C_6$ carbide which acts as preferential sites for pitting corrosion.

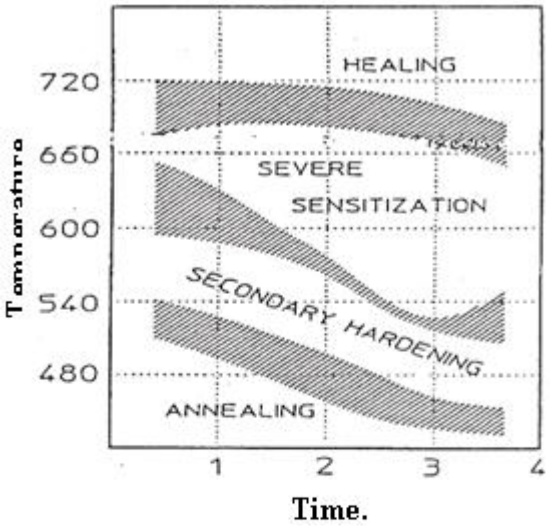
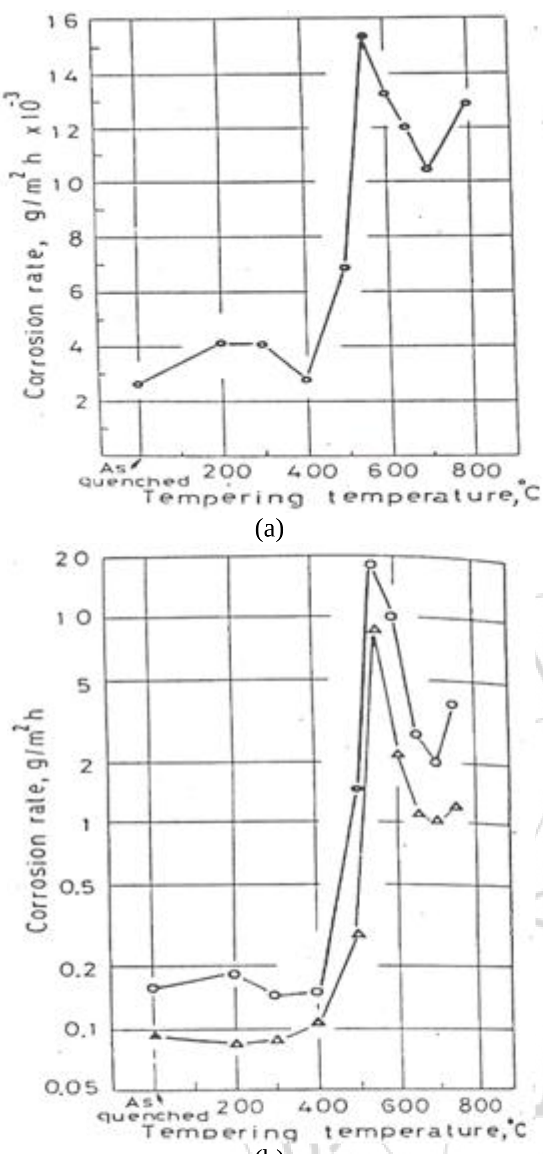


Figure 2: Tempering map of 12Cr-0.1C martensitic stainless steels [Lim et al., 1993]



(a)

(b)

Figure 3: Variation in corrosion rate as a function of tempering temperature for 16Cr-2Ni steel in (a) 3% NaCl solution at 22^0C for 405 hours, and (b) 0.1 N H_2So_4 (o) and 0.1 N HCl ( ) solutions at 22^0C for 24 hours[Ogino, et. al., 1987]

Jee-Yong Park, and Yong-Soo Park [18] have investigated the effects of heat-treatment parameters on corrosion resistance and phase transformation in relation to the dissolution and re-precipitation of carbides in 14Cr–3Mo martensitic stainless steel. It is observed that the corrosion resistance of the experimental alloy was found to be improved at higher austenitizing temperatures. However, it was deteriorated at the specific austenitizing temperatures of 1000 and 1050 °C when the cooling rate was 10 K/s. The deterioration of corrosion resistance was caused by the impaired balance between the matrix and the retained austenite.

Of all the hardenable martensitic stainless steels, 16Cr-2Ni steel is the most resistant to general types of corrosion [19]. 16 Cr-2 Ni steel is slightly superior to the straight chromium alloy of equal chromium content but marginally inferior to the austenitic stainless steels of 18-8 type in most media. However, under certain conditions of tap water, steam, food products and particularly salt spray, the alloy compares very favorably with the 18-8 type stainless steels [19].

Solution and precipitation of carbide is expected to occur in a similar manner in 16Cr-2Ni steel as that of 12% Cr steel. However, since chromium is more in this steel compared to 12%Cr steels, even with all the carbon (up to 0.25%) precipitated as chromium carbide; the steel would be having sufficient chromium to resist corrosion.

The results shown in Fig. 1 illustrate the better corrosion resistance of 16Cr-2Ni steel compared to 12%Cr steel at all heat treated conditions [2]. Thus for applications which are to resist sea water or to be reasonably immune from electrochemical action due to contact with copper alloys, and also nitric acid, 16%Cr steels are preferred to 12%Cr steels [Monypenny, 1951][2].

Tests in acid medium was carried out by Ogino et al [20] on cylindrical specimens of diameter 10 mm and height 15 mm of 16Cr-2Ni steel and the results obtained are shown in Fig.3. It is evident from the data that tempering up to 400^0C (for two hours at each temperature) has negligible effect on the corrosion resistance of the steel. The data also reveal that the highest tempering temperature which provided maximum corrosion resistance in this steel is 400^0C. The reason attributed to this behaviour is that chromium depletion from the matrix is minimal at 400^0C tempering. Between 550-600^0C, where fine carbide precipitation (M_7C_3) in the steel causes substantial chromium depletion, shows minimum corrosion resistance (Fig.3). Tempering beyond 600^0C induces some improvement in corrosion resistance relative to 500-600^0C tempering due to precipitation of equilibrium carbide ($M_{23}C_6$) in which some amount of chromium is replaced by iron i.e., $(Cr, Fe)_{23}C_6$, causing less amount of chromium depletion from the steel. However, tempering beyond 600^0C, shows much lower corrosion resistance as compared to tempering up to 400^0C.

The pitting corrosion resistance of 16Cr-2 Ni steels after austenitizing at various temperatures followed by double tempering was studied by Rajasekhar et.al [21]. The results show that double austenitization followed by double tempering resulted high pitting corrosion resistance as compared to single austenitization temperatures (followed by double tempering). The reason attributed to this behavior is that chromium depletion from the matrix is low in double austenitization treatment that results precipitation of equilibrium carbides $M_{23}C_6$ in which some amount of chromium is replaced by Fe, causing less chromium depletion from the matrix.

4. Conclusions

A review on the present published information on corrosion behavior of martensitic stainless steels indicates that the corrosion resistance depends on carbide volume fraction dissolved in matrix after austenitizing and the carbide precipitation during tempering. Corrosion resistance can be improved by adopting proper heat treatment procedures depending upon the application for which the material is selected.

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