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Carbon Diffusion in 304l Austenitic Stainless Steel at 650-750 ^{O}c in Carburizing Environment

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Abstract— ***A 304L austenitic stainless steel is widely used in the petrochemical industry. As it is exposed to carburizing environment, carbon diffuses into metal and form carbides. Effect of the environment on the carbon diffusion is interesting to be known. This study will evaluate the effect of CH_4/H_2 gas concentration and carburizing temperature on carbon diffusion in 304L austenitic stainless steel. Horizontal furnace equipped with a quartz tube and vacuum pump was used to expose the samples to carburizing environment at 650°C - 750°C and 20% - 40% CH_4/H_2 gas composition for 100 hours. Optical microscopy examination of cross-sectioned specimens of 304L stainless steel showed that no carburizing zone formed after the samples subjected to 20% CH_4/H_2 gas composition at 650˚C. It is observed that low carbon deposited on substrates with an average 0.0011g and carbon activity, a_c, equal to 0.31. In comparison, with 40% CH_4/H_2 gas composition at 650˚C, the average carbon deposited on the surface was two times more and carbon activity increased more than one, known as carburizing zone. Carbon diffusion at 750°C was deeper than at 650°C for both CH_4/H_2 gas concentrations 20% - 40%. In conclusion the depth of the carburization zone increases with increasing the temperature from 650˚C to 750˚C and increases with increasing percentage of CH_4/H_2 gas composition.***

Keywords: 304L stainless steel; Carbon activity; CH4/H2; Diffusion; High temperature

1. INTRODUCTION

Diffusion is the transport of atoms from high concentration to low concentration by thermal motion [1]. Carbon diffusion in austenitic stainless steel plays a critical role in phase transformation of steel. Studies of carburization of austenitic stainless steels have been done by many investigators [2-6]. During carburization, high concentration of carbon maintains at a stable constant value at the surface of the steel. At the same time carbon repeatedly diffuses from the surface into the steel which gives a concentration profiles obtained after various times. Carbon activity, ac, is very important for diffusion processes since the larger difference in carbon activities and carbon content in steels, the greater the gradient of carbon activity on the diffusion interface. The carbon diffusion flow across this interface is proportional to this gradient. For instant, carbon always diffuses to a site of lower carbon activity value in steels. It is mentioned in their reports [7-9] that carbon concentration cannot be used instead of carbon activity in steels which may lead to erroneous conclusions. In this paper the effect of CH4/H2 gas concentration and temperature on carbon diffusion in austenitic stainless steel have been studied.

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2. EXPERIMENTS

Samples of austenitic stainless-steel grade 304L with chemical composition [10] as in Table 1, were cut using wire cutting machine with dimensions of 20 mm x 20 mm x 2 mm. All samples were polished up to 1000 SiC paper, and ultrasonically cleaned in acetone for 5 mins before exposing to carburizing atmosphere. Exposure tests were conducted in a vacuumed quartz tube furnace with a diameter of 60 mm. The tests were conducted for a period of 100 hours at temperatures 650°C–750°C, and CH4/H2 gas concentration 20% - 40% with gas-flow rate at a fixed velocity of 100 cc/min during testing. After high temperature exposure tests, the morphology was examined by optical microscopy (OM).

Table 1: Chemical composition in weight percent (wt%) of 304L

C	S	P	Mn	Si	Cr	Ni	N	Fe
0.023	0.003	0.022	1.48	0.44	18.1	8	0.07	Balance

Carburization was occurred when carbon diffused into 304L stainless steel at 650°C - 750°C and 20% - 40% CH_4/H_2 gas concentration. The carbon was formed on 304L stainless steel surface due to the main reaction of CH_4 and H_2

$$CH_4 = C + 2H_2 \quad \Delta H = 75.6\ kJ/mol \tag{1}$$

Carbon activity, ac, was calculated by equation 2 [11].

$$a_c = \left[\frac{P_{CH_4}}{P^2{}_{H_2}}\right] e^{-\Delta G^{\circ}/_{RT}} \tag{2}$$

Since the alloying elements in steel have significant effect on the carbon activity. The carbon activities of 304L stainless steel were calculated by following equation 3 [12], with alloy composition in weight percent.

$$\ln\ a_c^{(F_eCr\ N_i)} = \ln(0.048\ \%C) + \left(0.525 - \frac{300}{T}\right)\%\ C$$

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$$-1.845 + \frac{5100}{T} - \left(0.021 - \frac{72.4}{T}\right)\%\,Ni$$

$$+\left(0.248 - \frac{404}{T}\right)\%\,Cr - \left(0.0102 - \frac{9.422}{T}\right)\%\,Cr^2 \quad (3)$$

According to Fick's second law [13], the equation of carbon diffusion in steel was given as:

$$\left(\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \quad (4)$$

Where C_x is the carbon concentration at distance x from the surface, C_s stands for the carbon concentration at the surface of steel, C_0 is the carbon in the steel and x is the carbon diffusion distance from the surface.

The carbon diffusion coefficient, D, was calculated depend on the 304L stainless steel by the following equation:

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \quad (5)$$

Where D_0 is a temperature-independent preexponential taken as 2.3 x 10^{-5} m^2/s), Q_d is the activation energy for diffusion taken as 148 J/mol for stainless steel, R *is* the gas constant which is 8.31 J/mol K and T is the absolute temperature in Kelvin.

3. RESULTS AND DISCUSSION

Figure 1 depicts the cross-sectional micrographs of the 304L stainless steel after exposure to carburization temperatures 650˚C and 750˚C with difference gas mixture, 20% and 40% CH_4/H_2. Optical microscope result of 304L specimens, Figure 1(a) showed that there is no carburising after the samples subjected to gas composition

20% CH_4/H_2 at 650˚C. Low carbon deposited on substrates with an average 0.0011g is due to carbon activity is equal to 0.31. Compared with Figure 1 (b), carburizing at 650˚C, 40% CH_4/H_2 gas concentration where the average carbon deposited on substrates was 0.0021g and carbon activity 1.107. Figure 1 (c), carburizing at 750˚C and 20% CH_4/H_2 the average carbon deposited and carbon activity are 0.0029g and 0.08075 respectively.

Carbon diffused inward and at first reacts with Cr as main component which form $Cr_{23}C_6$ and Cr_7C_3 carbides. The precipitation of carbides occurred primarily at the grain surfaces which are heterogeneous nucleation sites. The carbides were formed at the grain boundaries as a result from depletion of Cr element. Moreover, the depth of the carburization zone increases with increasing the temperature from 650˚C to 750˚C and the percentage of gas composition was more affected on the carbon concentration.

Figure 2 shows the carbon concentration as a function of distance from surface of austenitic stainless steel carburized at different temperatures 650 ˚C and 750 ˚C with 20% and 40% CH_4/H_2 for 100 hours. At 750˚C - 40% CH_4/H_2, the carbon concentration and number of carbon atoms on the surface were 2.871 wt% and 1.31E20 atoms/cm^2 respectively. This carbon concentration decreased dramatically with increase the distance from the surface. Likewise, at750˚C - 20% CH_4/H_2, with carbon concentration 0.8075 wt% and number of carbon atoms on the surface 1.67E19 atoms/cm^2, but the carbon concentration decreased slightly with increase the distancefrom the surface. Similar trends occurred at lower temperature 650˚C with 20% and 40% CH_4/H_2, with the carbon concentration and the number of carbon atoms on the surface was 0.31 wt%, 6.32E18 atoms/cm^2 and 1.107 wt%, 1.2E19 respectively, but with less depth of carbon diffusion. These results due to the depth of car

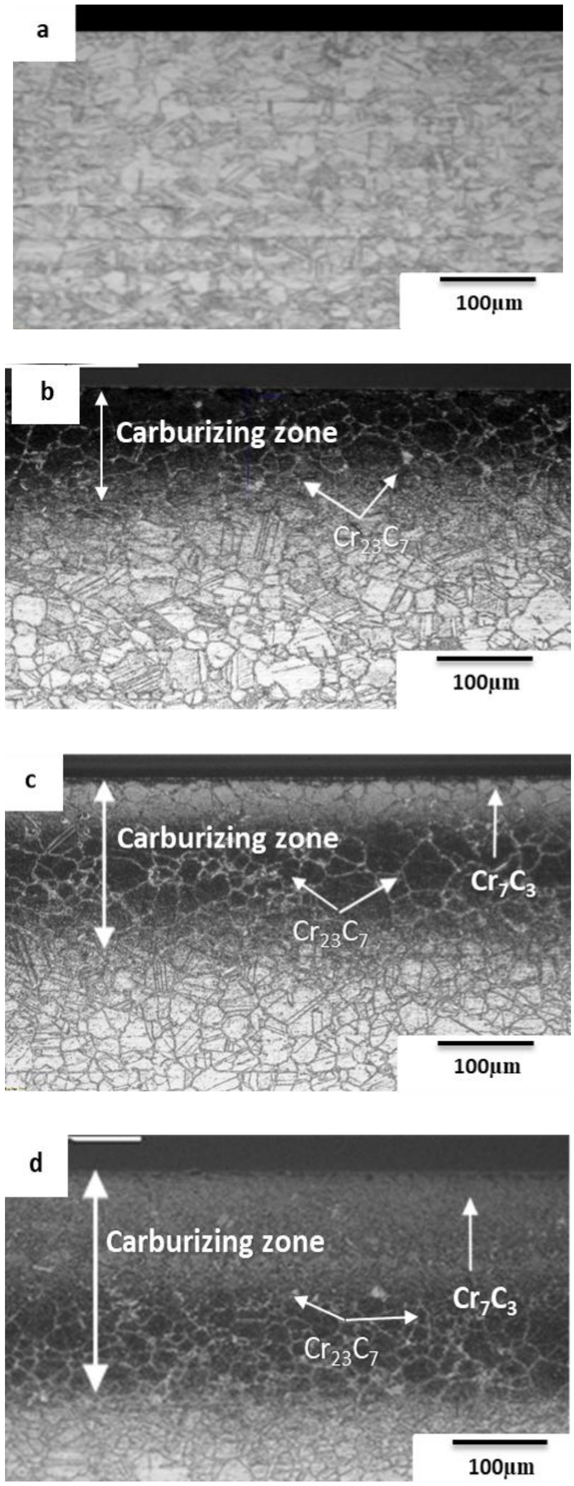

Fig. 1: Cross-sectional images of 304L samples at a) 650˚C – 20% CH_4/H_2, b) 650˚C – 40% CH_4/H_2, c) 750˚C – 20% CH_4/H_2 and d) 750˚C – 40% CH_4/H_2

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bon diffusion depend mainly on the temperature, which increases the diffusion coefficient of the carbon. And the change in carbon concentration depends upon the carbon concentration on the surface and the carbon content within the metal as well as the depth of carbon diffusion.

4. CONCLUSION

The cross-sectional images of optical microscope and carbon concentration as a function of distance from the surface profile encountered in temperature 650 °C - 750°C and 20% - 40% CH_4/H_2 gas concentration carburized 304L stainless steel provide an opportunity to study the diffusion dependence on carbon activity and temperatures. The results show that carbon activity of carburized steel at 650 °C - 40% CH_4/H_2

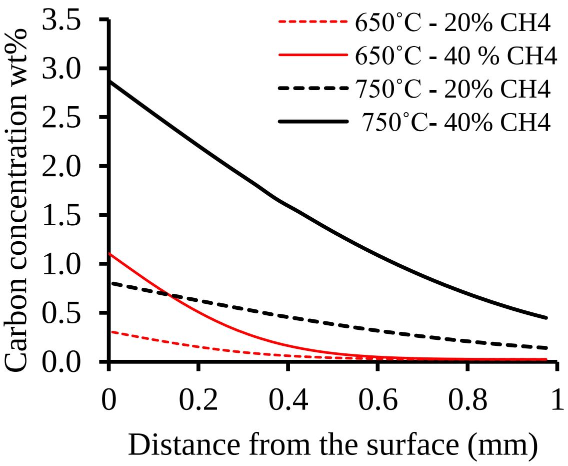

Fig. 2: The carbon concentration vs distance from the surface

gas concentration is higher 1.37 times higher than that of carburized steel at 750 °C - 20% CH4/H2 gas concentration. This carbon concentration decrease closed to zero at depth closed to 0.5mm. The depth of diffusion at 750 °C - 20% CH4/H2 gas concentration is more than at 650 °C - 40% CH4/H2 gas concentration. Depth of carbon diffusion depends mainly on the temperature, which increases the diffusion coefficient of the carbon. Change in carbon concentration depends upon the carbon concentration on the surface and the carbon content within the metal as well as the depth of carbon diffusion.

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