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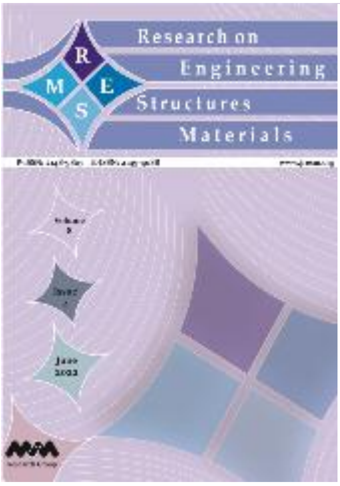

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Technical Note

Corrosion resistant degradation of AISI 304 austenitic stainless steel exposed to simulated carburizing environments

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Abstract

This paper aimed to evaluate the anti-corrosion performance of AISI 304 austenitic stainless steel after exposure to the simulated carburizing environment set up at 600°C, 750°C, and 900°C for 4 hrs. The microstructural alternation was investigated by Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). Electrochemical Potentiokinetic Reactivation (EPR) was employed to study the anti-corrosion performance of AISI 304 austenitic stainless steel after exposure to the simulated carburizing environment. Hardness measurement was also conducted to study the role of carbon atoms released from the simulated environment. The results showed the formation of precipitated chromium carbides along grain boundaries and sensitization degree was found in ascending order: 600°C (Pa =0.23), 750°C (Pa =0.32) and finally 900°C (Pa =0.41). All carburized conditions promote carbon dissociation and diffusion through the substrate of AISI 304 austenitic stainless steel, resulting in the increased hardness and decreased corrosion resistance of AISI 304 austenitic stainless steel after exposure to the simulated carburizing environment.

1. Introduction

Austenitic stainless steels are frequently utilized in industries owing to their acceptable corrosion resistance and mechanical properties. In addition, this material shows good performance in a variety of temperature conditions. For example, it can offer good impact toughness in cryogenic conditions and good oxidation resistance in elevated temperatures up to 1,150°C [1]. Among many, AISI 304 austenitic stainless steel is a widely used material, particularly in petrochemical industries where corrosion and oxidation are a primary concern. As compared to other commercial oxidation and corrosion resistance alloys, AISI 304 austenitic stainless-steel gains the advantages of significantly lower costs with an acceptable oxidation and corrosion resistance [2]. Hence, this alloy is often used in fuel-burning systems, such as exhaust gas pipes in a furnace of petrochemical plants. It is known that fuel-burning systems, i.e., furnaces and related equipment, involve the combustion of fuels releasing not only thermal energy but also various carbonaceous gases, i.e., CO, CO_2, CO/CO_2 mixture and CH_4 [3]. This kind of environment is known as a "carburizing environment" [4], where the long-term anti-corrosion performance of materials used in the fuel-burning systems can be degraded. For instance, this hush environment can facilitate the dissociation of carbon and subsequently promote the diffusion of carbon atoms into the materials, resulting the microstructural degeneration [5]. Besides, the high

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-temperature conditions induced from the combustion can also deteriorate the material, i.e., sensitization of austenitic stainless steel [6]. Both deteriorations potentially lead to the premature failure of the materials in the fuel-burning systems, negatively affecting the overall productivity and reliability of the petrochemical plants. Thus, the anti-corrosion degradation behavior of AISI 304 austenitic stainless steel exposed to such a severe environment is of great interest to study. Basically, the field exposure study of this degradation behavior of AISI 304 austenitic stainless-steel pipe encountered in the actual carburizing environment from a furnace can provide useful information. However, there are several limitations in the field exposure test. For instance, this test would take longer than one year to gain just one time of the investigation. Besides, the parameters of interest may not be precisely controlled. To overcome the drawbacks of the filed investigation, numerous studies have paid their interest in the investigation of metals in the simulated carburizing environment. Carvallho et al. [1] utilized the synthetic environment to investigate the degradation behavior of AISI 304 and AISI 430 stainless steel and they found that hematite was the predominant phase in oxide layers of AISI 304 stainless steel, leading to more oxidation resistance of this alloy. Samaras et al. [7] observed the microstructural alternation of the heat-resistant steel using the simulated carburization environment. Their results showed that $M_{23}C_6$ and M_7C_3 carbides were predominantly found in the carburization layer and the addition of Molybdenum raised the carburization resistance. Haider et al. [8] investigated the carbon diffusion of 304L stainless steel exposed to the simulated carburizing atmosphere and their results indicated that the depth of the carburization zone increased with an increase in the temperature, particularly in the temperature range of 650-750^{o}C. Young at al. [9] found the carburization played a significant role in forming carbide particles in chromium-containing steel. Obviously, the use of the simulated carburizing environment is gaining increased attention from metallurgists. Nevertheless, there has been less work dealing with an investigation on the carburization degradation of AISI 304 austenitic stainless steel, particularly microstructural alternation observation and intergranular corrosion resistance evaluation. In response to the lack of such useful information, this work presented the investigation on the microstructural alternation using the simulated carburizing environment ranging from 600 ^{o}C,750^{o}C, and 900^{o}C. Besides, intergranular resistance evaluation of AISI 304 austenitic stainless steel after exposure to a simulated carburizing atmosphere was also conducted and discussed. The obtained results from this study would provide more comprehension in the carburization degradation of AISI 304 austenitic stainless steel, which can further be the significant information for the materials evaluation under other simulated carburizing conditions.

2. Experimental Procedure

The samples with a dimension of 10 mm X 10 mm X 3 mm were prepared from AISI 304 austenitic stainless steel, the chemical compositions of which were given as follows: C 0.08, Cr 17.80, Ni 8.05, Mn 1.94, and Fe. The simulated carburizing atmosphere was established in the carburized steel container and obtained from the mixture of the activated eucalyptus charcoal and catalysts (Na_2CO_3 and $CaCO_3$) with a ratio of 80:20. This ratio was prepared to ensure the occurrence of carbon dissociation and diffusion in the simulated environment [10,19-20]. The samples were then exposed to the simulated carburizing atmosphere set up at 600 ^{o}C,750^{o}C, and 900^{o}C with the same exposure time of 4 hrs. After exposure to the simulated carburizing atmosphere, samples were naturally cooled and subjected to microstructural observation using SEM-EDS and the hardness measurement. To evaluate the intergranular corrosion resistance, Electrochemical Potentiokinetic Reactivation (EPR) was performed. The specimen after exposure to the simulated carburizing atmosphere test was sectioned to 25 mm X 25 mm X 1 mm coupons and then mounted in cold-curing epoxy. Before the test, each sample was ground with a 120 grit SiC abrasive paper and then polished down to 1 μm finish. The electrochemical test was performed using a three electrodes cell in a standard glass cell (1 liter). The platinum electrode was employed as a counter electrode and Ag/AgCl electrode was utilized as a reference electrode. The solution of the test was a mixed solution of 0.5 M H_2SO_4 + 0.01 M KSCN with a controlled temperature of 30°C. To understand the intergranular resistance alternation, the normalized charge parameter (Pa) of each sample from different exposure conditions was then calculated from the resultant electrochemical curves using the following formula [11].

$$P_a = \frac{Q}{GA_s} \tag{1}$$

Where, Q is total charges consumed during the test which can be obtained by the area under curve calculation (coulomb/cm^2), G is Grain size at 100X, and A_s is Specimen areas.

Pa value can reflect the degree of sensitization of AISI 304 austenitic stainless steel. According to the ASTM G108 standard, when Pa is greater than 0.4, this means that this material is severely sensitized, and precipitation of chromium carbides occurs. Nevertheless, when Pa becomes less than 0.1, this implies that this material is not sensitized. In addition, AISI 304 austenitic stainless steel with the intermediate sensitization degree is noticed when Pa is between 0.1 and 0.4.

3. Results

3.1. Microstructure Examination

Fig.1 illustrates SEM micrographs of the reference specimen and specimens with different carburizing temperature conditions at two magnifications: 1,500X and 5,000X with the aim to differentiate the formation of carbides at grain boundaries.

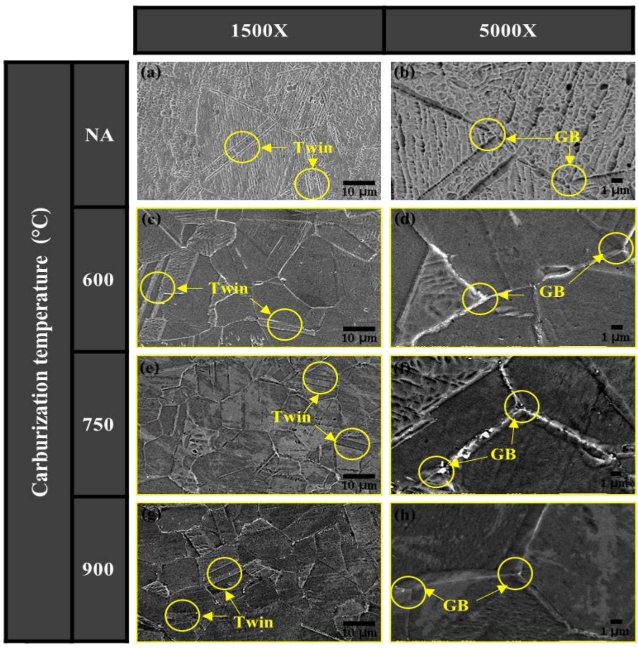

Fig. 1. SEM micrographs: (a)-(b) reference specimens, (c)-(d) 600°C, (e)-(f) 750°C and (g)-(h) 900°C

The reference specimen represents the fresh structure of AISI 304 austenitic stainless steel and its microstructure in lower magnification shows austenite grains and annealing twins as seen in Fig. 1(a). Usually, annealing twins would be formed during the recrystallization [12]. The presence of the austenitic grain boundaries of the fresh structure is clearly shown in Fig. 1(b). Fig. 1(c) reveals the microstructure of specimen exposed to the simulated carburizing atmosphere at the temperature of 600°C and its microstructure comprises of grain boundary and annealing twin. The higher magnification of its microstructure in Fig. 1(d) showed grain boundaries and some precipitated particles. Fig.1(f),(h) showed the precipitation of particles on grain boundaries of the specimens experienced the simulated carburizing atmosphere at the temperature of 750 and 900°C. Basically, the presence of the precipitated particles indicated the microstructural changes of the specimens after exposure to the simulated carburizing environment, which would subsequently affect corrosion-resistant properties. Normally, the thermal energy of this environment can facilitate the formation of particles along grain boundaries [12-13]. In addition, the dissociation of carbon atoms can occur and diffuse into the steel [14]. Thus, the elevated temperature service and the release of carbon atoms from the carburizing environment contribute to the microstructure alternation of specimens. The particles found from SEM micrograph studies were further analyzed using SEM-EDS. The details of the microstructure alternation of the sample exposed to the simulated carburizing environment at 900°C are provided in Fig.2 (a) with the magnification of 1,500X and in Fig. 2(b) with the magnification of 5,000X. The results from EDS analysis are also given. From both results, it is obvious that the particles were formed along grain boundaries, and the results from EDS analysis indicated that the major components of the particle were carbon (C) and chromium (Cr).

SEM mapping was then performed on the specimens subjected to the simulated carburizing atmosphere test set up at 900°C, aiming to obtain significant evidence of the carbide particle formation of AISI 304 austenitic stainless steel after undergoing the simulated carburizing environment. The results are shown in Fig. 3.

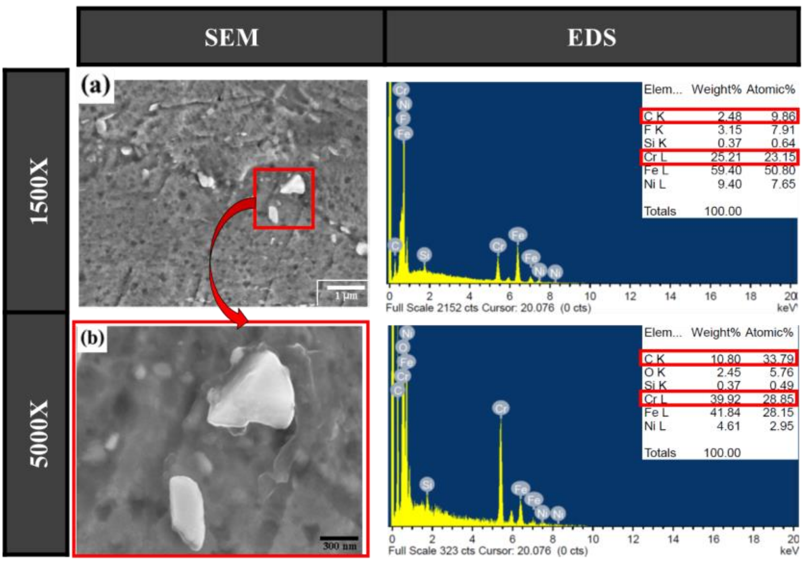

Fig. 2. SEM micrograph together with EDS analysis: (a) 1,500X and (b) 5,000X

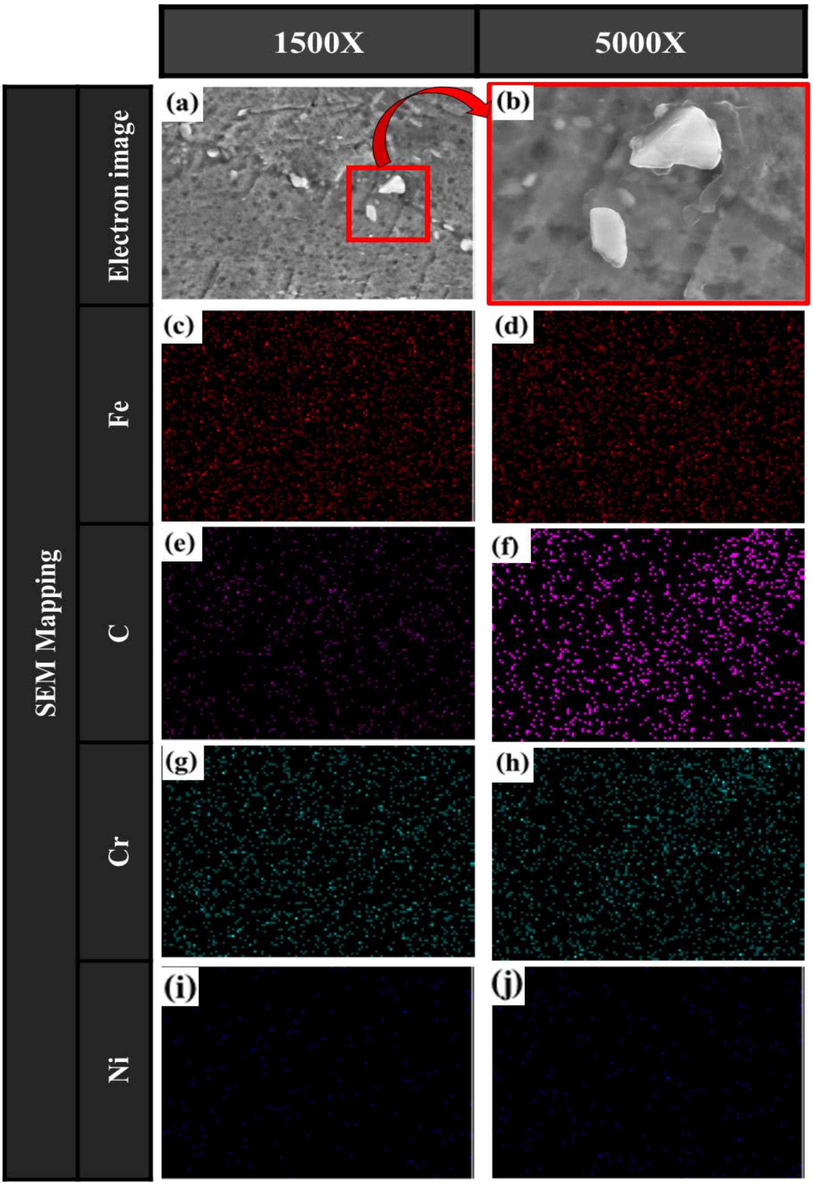

Fig. 3. SEM mapping with the magnification of 1,500X and 5,000X: (a)and(b) electron image, (c)and(d) Fe distribution, (e)and(f) carbon distribution, (g)and(h) chromium distribution and (i)and(j) nickel distribution

From the analysis, it is clear that the major elements were iron, carbon, chromium and nickel dispersed in the matrix. Iron is known as the major element in ferrous-based materials like austenitic stainless steel, but carbon and chromium are alloying elements of the material. Basically, carbon and chromium can react to form the carbide particles in grain boundaries of austenitic stainless steel. Kaewkumsai et al. [15] found the formation of chromium carbide in austenitic steel used in the failed burner pipe which was in a service temperature range of 600-900^{o}C. Kozuh et al. [16] reported the formation of chromium carbides in grain boundaries of austenitic stainless steel after being used in the temperature range of 600-800°C. Thus, the results from SEM micrographs and SEM-EDS analysis point out the particles observed from the test were due to the formation of chromium carbides and this finding corresponds to the works conducted by several scientists.

3.2 Anti-Corrosion Performance Alternation Observation

Electrochemical Potentiokinetic Reactivation (EPR) was performed to obtain insight in the anti-corrosion performance alternation. The resultant electrochemical curves of specimens are given in Fig. 4. There are two types of corrosion behaviors taking place in this electrochemical test. The first corrosion behavior of the reference specimen showed non-sensitization as seen in Fig. 4(a). However, after exposure to the carburizing environment, the electrochemical curves exhibited sensitizing [17] and the maximum current density was found in ascending order: 600 °C, 750 °C and 900°C. Technically, sensitization means the carbide precipitation at grain boundaries in a stainless steel causing it vulnerable to intergranular corrosion. Usually, the ratio between the charge caused by the corrosion at grain boundaries, known as Pa value, can indicate the sensitization degree. Thus, as sensitization occurs, Pa value of each sensitized specimen should be evaluated, and the calculated results are displayed in Fig. 5. As indicated in ASTM G108 standard, Pa value is less than 1, the stainless steel is not sensitized, but the Pa value in the range between 1-4 indicates the intermediate sensitization degree [11]. The Pa value greater than 4 indicated the severely sensitized stainless steel. Clearly, the reference specimen with the fresh surface shows no sign of sensitization. However, Pa values increased with increasing the carburizing temperature and the maximum Pa value was found in specimens with the highest carburizing temperature of 900°C. This result means that increasing carburizing temperature increased the sensitization degree of AISI 304 austenitic stainless steel, especially in the carburizing temperature in 600-900°C. The higher the carburizing temperature, the higher the density of the precipitated chromium carbides. This resulted in increased sensitization and then the decreased anti-corrosion performance of AISI 304 austenitic stainless steel. To understand the role of carbon, the hardness test was conducted on specimens with varying temperatures; the Hardness result and the summarized result are shown in Fig. 6 and Table 1, respectively.

Table 1. The summarized results from the EPR and Hardness test

Carburizing temperature (°C)	NA	600	750	900
Pa (coulomb /cm^2)	0.058	0.231	0.321	0.413
Hardness (HV)	185.0	197.0	203.0	210.0

It is obvious that the higher the carburizing temperature, the higher the hardness of sample is. At the same time, the sensitization degree increased. Technically, the simulated carburizing environment promotes the dissociation of carbon atoms. It is also well known that an increase in temperature enhances the diffusion of atoms into the materials [18]. Wongtimnoi et al. [19] found the carburizing environment can increase the hardness of low carbon steel. Chowwanonthapunya et al. [20] found that carbon atoms can be diffused through the bare surface of alloys and subsequently from carbide particles. Marián Vach et al [21] reported that the second phase particles, such as $M_{23}C_6$, can be found in the austenitic stainless steel and the presence of those particles resulted in increased hardness. Treewiriyakitja et al. [22] found the formation of carbide particles resulted in the degraded corrosion resistance of austenitic stainless steel. In this experiment, microstructural analysis in Fig. 2 shows that the particle is composed of carbon and chromium. SEM-mapping exhibits the distribution of carbon atoms in the austenite matrix of AISI 304 austenitic stainless steel, as shown in Fig.3(c), (h). Thus, carbon atoms released from the combustion in this environment transport through the substrate of samples, resulting in increasing the hardness of samples and promoting the formation of carbide particles [23-24]. As the chromium carbide particles are formed along the grain boundaries, AISI 304 austenitic stainless steel becomes harder and significantly reduces its anti-corrosion performance.

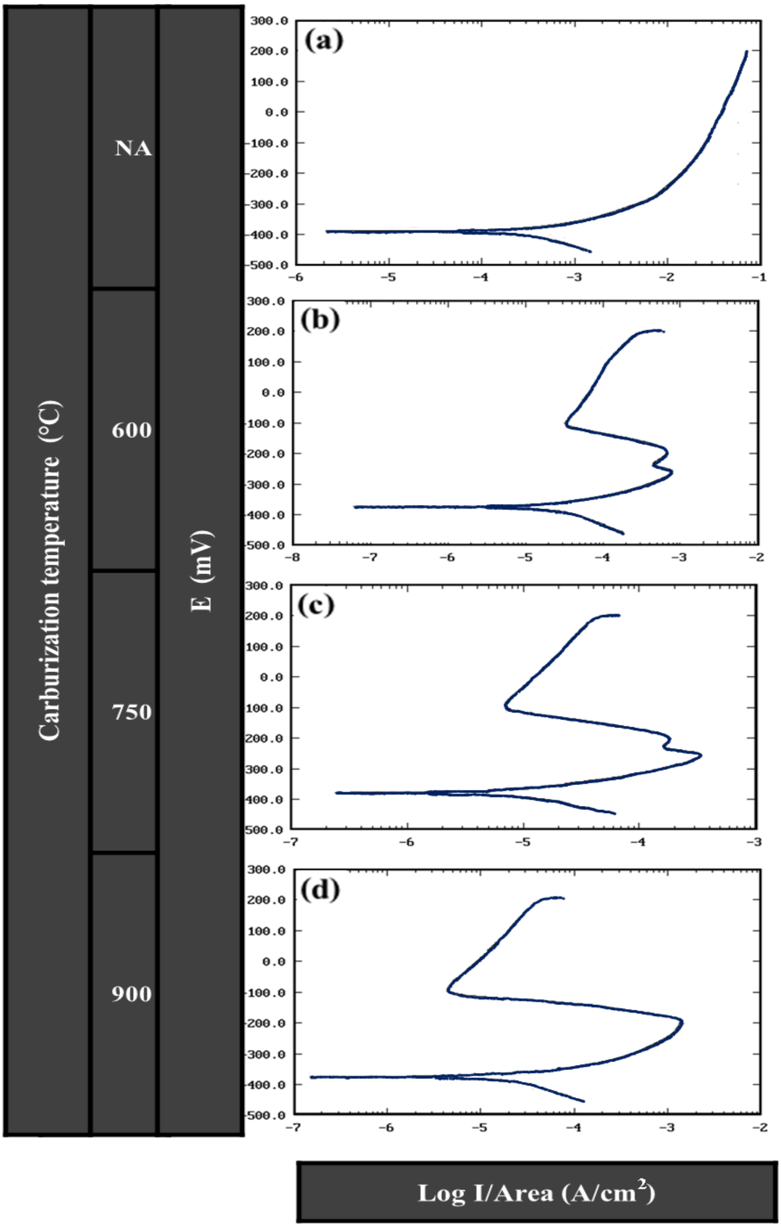

Fig. 4. Electrochemical curves of specimens: (a) reference specimen, (b) 600°C, (c) 750°C, and (d) 900°C

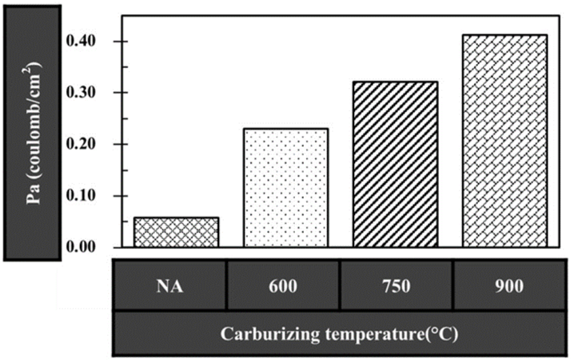

Fig. 5. The Pa value of specimens for varying temperatures.

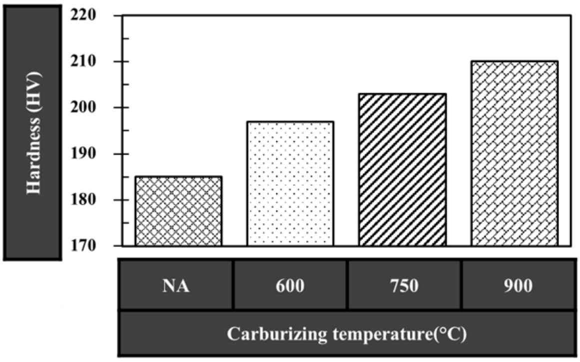

Fig. 6. Hardness of specimens for varying temperatures

4. Conclusions

The anti-corrosion performance of AISI 304 austenitic stainless steel exposed to a simulated carburizing environment set up at 600°C, 750°C, and 900°C was evaluated. In this study, the results revealed the presence of precipitated chromium carbide particles formed along grain boundaries. The formation of these particles resulted in sensitization, resulting in significantly reduced anti-corrosion performance of AISI 304 austenitic stainless steel. Sensitization degree was found in ascending order: 600°C (Pa =0.23), 750°C (Pa =0.32) and finally 900°C (Pa =0.41). Simultaneously, the hardness observation was arranged in ascending order: 600°C (197HV), 750°C (203 HV), and finally 900°C (210HV). All carburized conditions promote carbon dissociation and diffusion through the substrate of AISI 304 austenitic stainless steel, resulting in the increased hardness and decreased corrosion resistance of AISI 304 austenitic stainless steel after exposure to the simulated carburizing environment.

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