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Thermal stability investigation of expanded martensite

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ABSTRACT

The aim of this work is to investigate thermal stability of expanded martensite. For this purpose, two martensitic stainless steels, PH 17-4 and 13-8Mo, were low temperature gas carburized. After heat treatment, it was found out that thermal stability of expanded layer of PH 17-4 is higher than that of PH 13-8Mo. Auger Electron Spectroscopy and microhardness machines were used to investigate carbon concentration and hardness of samples, respectively. X-ray diffraction was done to study crystal structures of samples before and after heat treatment.

1. Introduction

Stainless steels are used in many applications where strength, toughness, and corrosion resistance are required at the same time [1]. Low hardness and weak tribological properties, however, limit their applications [2]. For improving these properties, many methods have been developed most of which are applicable to steels. Such treatment procedures are generally called surface hardening. After all the manufacturing processes such as machining and forming, surface hardening is the last process. The basis of this process is to transform surface of the components into a hard state [3,4].

Surface carburization has different techniques e.g. gas and plasma carburizing and Ion implantation. Corrosion resistance of stainless steels is due to the presence of a passive and adhesive layer of Cr_2O_3 on the surface [1,4]. Hence, appropriate conditions should be employed to prevent free Cr atoms from transforming into Cr carbides during the carburization. In fact, with the formation of carbides, concentration of free chromium atoms in the matrix decreases and subsequently, availability of chromium content to produce the passive layer as well [5]. Conventional methods of carburizing use temperature range between 650 °C and 1100 °C [3,6]. At this temperature range, chromium atoms are enough mobile to diffuse in the lattice and bond with Carbon atoms to form carbides. Therefore, due to carbon affinity of Cr, if time for higher diffusion of carbon at high temperatures in the surface layer last longer carbides are formed, which adversely affects corrosion resistance of the material [7,8]. Consequently, optimized time and temperature for carburization are required in this process [9]. Impressive improvements have been made for this method in recent years. If carburization takes place at a range of temperature that the mobility of chromium atoms is low, carbon content in the surface could be considerably increased [10–13]. Low temperature carburization at temperature range from 300 to 450 °C has been established for this purpose [3]. The upper limit for temperature may vary up to 550 °C [13]. But the important feature of this method is that with carburization at low temperatures, simultaneously the formation of chrome carbides is prevented and the carbon solubility can be considerably increased [14–16]. Many researchers have attributed "S phase" and "M phase" names to this carburized layer on the austenitic stainless steels and on the martensitic stainless steels respectively and have considered it a separate phase apart from the matrix phase [17–20].

Most of the studies about this method have been focused on austenitic stainless steels and only a few investigations is conducted on the stability of carburized layer of non-austenitic stainless steels [3]. For this reason, two martensitic stainless steels, PH 13-8Mo and PH 17-4, were chosen and low temperature gas carburized. After the carburization process, thermal stability of surface phases was investigated.

2. Experimental procedures

The composition of two samples is in Tables 1 and 2. Low temperature gas carburizing was done at 450 °C for 18 h using gas media (38 vol% CO, 2 vol% CO_2 and 60 vol% H_2) on these samples. XRD test was done with the EQuinox 1111 using CuKα tube. Nikon QM microhardness machine with load and loading time of 1N and 15 Sec respectively was used to measure the microhardness of samples. The angle of indenter was 136° and also for the spherical indenter d/D ratio of 0.375 (d = impression diameter, D = ball diameter) was chosen. Microhardness measurement was done in a way that each step was done by going in-plane away from the previous diagonal of indentation as much as

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Table 1
Chemical composition of PH 17-4 stainless steels.

Element	Cr	Ni	Si	C	Cu	P	S	N	O	Mn	Ta
Weight percent	17	4.53	0.83	0.07	3.81	0.05	0.001	0.001	0.002	0.93	0.3

three times the previous size and also 3 μm in-depth. PHI 680 Scanning Auger Microprobe was used for Auger Electron Spectroscopy (AES) to calculate carbon concentration at different depths. To measure the carbon concentration and microhardness at each depth, the samples were exposed to Argon bombardment to remove the carburized layer. After each step of carburized layer movement, microhardness and AES tests were done. Carburized samples at temperatures of 200, 250, 300, 350, 400 and 450 °C with time of 2, 4, and 6 h were heat treated to investigate thermal stability of carburized layers. Microhardness and XRD test were carried out on the surface of carburized layers after each step of heat treatment.

3. Results and discussion

Fig. 1 shows in-depth carbon concentration and hardness of both carburized steels. It is observed that carbon concentration and hardness of carburized layer decreases from the surface of carburized layer through substrate. As it is observed, both concentration of carbon and hardness is constant for both steels which shows these two parameters are correlated. Also, the carbon concentration at the surface of each sample is in Para-equilibrium state.

Fig. 2 shows the results obtained from microhardness measurements of heat treated samples. Regarded to these results, with increasing temperature and time of heat treatment, magnitude of hardness decreases due to relaxation of crystal structure and martensite tempering. For carburized PH 13-8Mo, at 350 °C there was a sudden increase in hardness after being heat treated for of 2, 4, and 6 h, a consequence of martensitic embrittlement. It is reported that this phenomenon occurs in carburized PH 17-4 at 400 °C. Martensitic embrittlement can occur at temperatures between 250 °C and 350 °C, although the presence of such elements like Si and Mn shift the martensitic embrittlement temperature to higher temperatures, as here occurred for PH 17-4 [21,22]. For both PH 13-8Mo and PH 17-4s, with heat treatment at 400 °C and 450 °C for 2 h respectively, hardness decreased steeply. This attributes to the critical time and temperature (CTT), meaning sudden decrease in microhardness for each sample, for the application of these carburized alloys where high hardness is needed.

According to peak broadening and peak shifting observed in XRD data obtained from carburized and non-carburized 13-8Mo samples (Fig. 3), it was recognized that crystal structure is subjected to distortion and expansion after carburization. Furthermore, peaks are less symmetric and appearance of new peaks revealed a new phase, most probably of Fe_3C, was formed during carburization. XRD data obtained from heat treated samples (Fig. 4) shows at 250–350 °C nothing happens to Fe_3C peaks at $2\theta = 39.9°$ and 45.9°. With increasing the heat treatment temperature to 400 °C, however, intensity of this was enhanced and two other peaks at $2\theta = 34.5°$and 36° emerged. The main reflecting plane of martensite is (110) and the angle of main peaks of formed carbide is adjacent to the Bragg's angle of this plane, so the range of 35–55° was selected for 2θ. By heat treatment at upper temperatures for more times, peaks broadening was observed to decrease which is a sign of structure relaxation. There was no any changes in $2\theta = 39.9°$ and 45.9°peaks of Fe_3C. As heat treatment continues at higher temperatures, the amount of crystal expansion decreases until at CTT, deviation from Bragg's angle is almost disappeared (Fig. 4). This is due to the introduction of carbon atoms in carbide structure instead of lying on interstitial sites, causing crystal structure to get closer to the non-carburized form. Hence, it is concluded that CTT means the time and temperature at which carbides appear and hardness decreases suddenly.

XRD data of carburized and non-carburized PH 17-4 samples (Fig. 5) was compared. After carburization martensite is expanded, but not any new phases are formed. After heat treatment at 200 °C and 2 h, however, Fe_3C carbides started to form and persisted up to heating at 450 °C and 2 h (CTT) (Fig. 6). The reason is that carbon was at the threshold for the formation of carbides and needed the lowest activation energy for bonding to M (Fe, Cr …) atoms, so by heating at 200 °C and 2 h carbide are formed. Actually, carbon needed the minimum energy, provided by heating, to get closer to M atoms and bond to them.

It's worth noting that deviations from the Bragg's angle were observed in both heat treated samples up to CTT. Such derivations decrease with increasing temperature and time.

If the strain (ε) is defined as the ratio of Δa to a, it can be seen that strain in [110] direction is larger than that of other directions in both steels (Fig. 7), being associated to the anisotropic poison response because of biaxial compressive stress [23].

The lattice parameter is drawn against Nelson-Riley ($\cos\theta.\cot\theta$) parameter in Fig. 8. It is observed, that distribution of lattice parameter is broadened after carburization and this exist for 13-8Mo compared with 17-4 steel. Magnitude of expansion in [110] direction is higher for 17-4 sample in comparison with the same direction in 13-8Mo sample, showing more elastic strains due to higher content of carbon in this direction. Moreover at CTTs, distribution of lattice parameter is nearly similar to non-carburized state for both steels, meaning that crystal structures are relaxed. Hence, the residual internal strain is nearly zero at CTTs.

4. Conclusions

1- Carbon concentration at the surface is in Para-equilibrium state.
2- Comparing micro hardness data obtained from micro hardness measurements and Auger Electron Spectroscopy shows that carbon content and hardness have similar behaviors.
3- XRD and hardness tests of heat treated carburized PH 17-4 and PH 13-8Mo samples revealed that the thermal stability of carburized layer of 13-8Mo is less than that of 17-4 sample. At the beginning of heat treatment, Fe_3C carbides started to form in the carburized layer of 17-4 sample, showing that a threshold energy is required for carbide formation. With heating at high temperatures and times, no change was seen in the main peak positions of this carbide in both carburized layers. Intensity of the peaks, however, increased in carburized layers up to a critical time and temperature (CTT). At CTTs, other peaks of this carbide were emerged.
4- Deviation from Bragg's angle of expanded martensite reduces with increasing in time and temperature of heat treatment in both steels.

Table 2
Chemical composition of PH 13-8Mo stainless steels.

Element	Cr	Ni	Si	C	Cu	P	S	N	O	Ti	Mo	Al
Weight percent	12.5	8.01	0.06	0.03	0.02	0.003	0.001	0.002	00.02	0.01	2.1	1.05