Investigation of Chromium Carbide Precipitation and Corrosion Behavior on Stainless Steel AISI 304 for Welding Process Development

N. Srisuwan[1]*
1) Corrosion technology department, Thai-French Innovation Institute, King Mongkut's University of Technology North Bangkok, Bangkok 10800
**Corresponding Author: Nakarins@kmutnb.ac.th*

Abstract

This research is aimed at investigating the amount of chromium carbide ($Cr_{23}C_6$) in stainless steel AISI 304 by electrochemical technique testing, in calculating the *Pa* values that corresponding to sensitization stage and the corrosion behavior. The results will carry on to developing the welding process. The specimens were produced with Shielded Metal Arc Welding method. Moreover, it was bending at the angle 0, 90 and 180 degree and the process finished on post-heat treatment with different cool down conditions are 800ºC annealed in air cooled, 1100ºC annealed in water cooled and annealed 1100ºC in air cooled respectively. The results show that: first conditional is appeared the maximum amount of *Pa* value (*Pa* > 0.4), indicating that more precipitation of $Cr_{23}C_6$ in heat affected zone (HAZ) of specimen. The second conditional is not found the sensitization stage because when the specimens were annealed at high temperature, the chromium carbide will break up and residual stress in HAZ will decrease. At last conditional is found the less amount of *Pa* value; the reason of using high temperature on annealing process will decrease chromium carbide, but slowly air-induced cooling must pass the critical temperature then some $Cr_{23}C_6$ will appear at grain boundary and cause of high corrosion rate. Concerning to the corrosion behavior, the second conditional present the lowest corrosion rate, corresponding to the better-quality of passive film. Whereas, the first conditional shown the highest corrosion rate and low quality of passive film. Thus, 1100ºC annealed with water cooled is excellent condition for developing the welding process.

Keywords: Stainless Steel, Welding, Chromium Carbide, Corrosion, Passive Film**.**

1. Introduction

Austenitic stainless steels (18% Cr, 8% Ni) are widely used engineering materials in many branches of industry due to their good mechanical properties and corrosion resistance at elevated temperatures. However, the precipitation of intermetallic compounds at grain boundaries affects this resistance [1]. Exposure to a high-temperature range of 480-900 ^{o}C, during welding or service, leads to precipitation of chromium carbides ($Cr_{23}C_6$) at grain boundaries and formation of chromium depletion regions adjacent to these carbides. Corrosion of stainless steel (SS) weldments has been the goal of a wide number of works. Perhaps the most common problem encountered in stainless steel weldments have been associated with sensitization in the heat affected zone (HAZ) leading to intergranular corrosion (IGC), the HAZ of austenitic stainless steel containing more than about 0.05% carbon can be susceptible to form of IGC called "weld decay" [2].

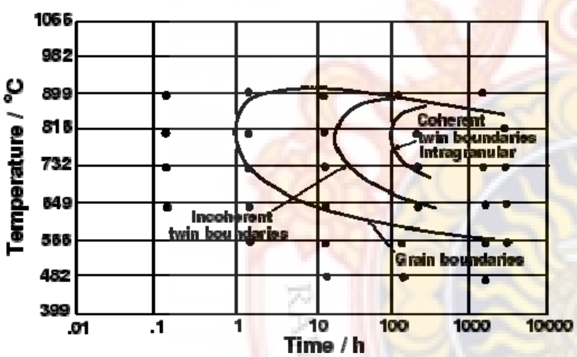


Fig. 1 Isothermal precipitation curve for chromium carbide of stainless steel AISI 304 [3].

The heat-input and cooling rate are two important parameters affecting the corrosion resistance because they could induce segregation of alloying elements and formation of chromium-depleted zones [4,5]. When the cooling rate is high, $Cr_{23}C_6$ may not enough time to precipitate and material can be supersaturated with free carbon (Fig.1). SS with chromium depleted regions at grain boundaries having chromium less than 12-13 wt.% are known to have undergone sensitization [6, 7].

The objective of this paper is to make a contribution on corrosion studies performed on welded stainless steel. To reduce or eliminate IGC problem, the welding process of SS304 are treated with annealing process. The post-heat treatment effect is demonstrated by electrochemical technique testing (ASTM G 108-94 standard test [8]), in calculating the *Pa* value that follow to IGC investigation.

2. Experimental

2.1. Material preparation and welding process

The material used in this work was commercial SS AISI 304, 4.5 mm thick rectangular plate. The chemical compositions obtained by emission spectroscopy were giving in Table 1.

Table 1 Chemical composition for stainless steels AISI 304 (wt. %).

Component	C	Cr	Ni	Mo	Si	Mn	Fe
SS 304	0.05	18.4	8.1	0.16	0.52	0.16	Bal.

The specimens were produced with Shielded Metal Arc Welding method (SMAW): 60 ampere weld current with E308 wire rod. Subsequently, it was bending at the angle 0, 90 and 180 degree and the process finished on post-heat treatment with different cool down conditions: designed for post-heat treatment effect, ***C1***: 800°C annealed in air cooled, ***C2***: 1100°C annealed in water cooled, and ***C3***: 1100°C annealed in air cooled respectively.

2.2 Electrochemical Potentiokinetic Reactivation (EPR) test

The EPR was performed following ASTM G-108. Examined specimens were prepared according to instructions provided by the ASTM G-108: they were wet grinded with the use of abrasive paper (SiC) of increasing fineness (180 to 1200).

The electrolyte was 0.5 M H_2SO_4 + 0.01 M KSCN. An EG&G model 273 potentiostat/galvanostat was used all the electrochemical measurements, test temperature is 30°C $\pm$ 1.

The experimental parameters of the conditioning were the following: a delay of 15 min at open circuit potential (OC), deaerated, an anodic attack -220 mV / Ag/AgCl electrodes. For the EPR results, *Pa* values were calculated using the following formula:

$$Pa = Q / GBA \quad (1)$$

Where *Q* is total charge consumed during EPR experiment, *GBA* is effective grain boundary area = $As \times 5.1 \times 10^{-3} \times exp^{0.3496*G}$ (*As* = specimen area and *G* = ASTM grain size number of the specimen. When *Pa* > 0.4 due to sensitized micro-structure, pitting and attack of entire grain boundaries, if *Pa* < 0.1: un-sensitized microstructure, no pitting. While 0.1 < *P a* < 0.4 due to slightly sensitized micro-structure, pitting and limited IGC attack [7].

2.3 Potentiodynamic polarization scan

The polarization measurements were carried out using EG&G model 273 potentiostat /galvanostat. The specimens are immersed 1hr. in 0.05 M NaCl, using a potentiodynamic sweep from -0.25 V (OCP of Ag/AgCl) to 0.6 V at a sweep of 0.1 V/ min. A platinum rod was used as an auxiliary electrode.

Each polarization plots was analyzed to obtain corrosion current density and corrosion potential. The corrosion rate was determined in millimeter per year (mmpy) using:

$$C.R. = 3.272 \times 10^{-3}\ \mathrm{ai/nD} \quad (2)$$

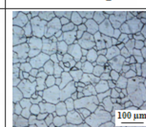
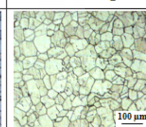
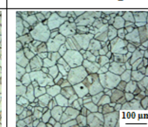
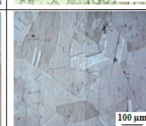
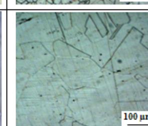
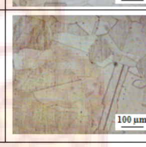
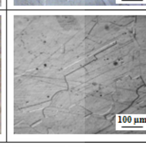
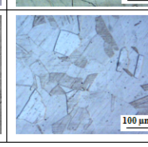
Where, *C.R.* is corrosion rate in mmpy, *a* is atomic weight of the metal, *n* is number of electrons in the reduction of the metal ions, *D* is density of the metal in g/cm^3 and *i* is corrosion current density $\mu A/cm^2$.

3. Results and discussion

3.1 Morphologies image

From table 2, the morphologies image of the specimens which welded and bended at the angle 0, 90 and 180 degree. The specimens were annealed and cooled at the various conditions. It was found that the grain size and the amount of $Cr_{23}C_6$ at grain boundary are different because of the difference annealing conditions which decompose the $Cr_{23}C_6$ and reduce the stress from bending as well as the difference rate of cooling time. However, the grain of SS AISI 304 before welding is fine and does not show $Cr_{23}C_6$ on HAZ.

Table 2. Morphologies image of SS AISI 304 before EPR test.

Conditions	Bend 0 degree	Bend 90 degree	Bend 180 degree
C1 800°C annealed + Air cooled			
C2 1100°C annealed + Water cooled			
C3 1100°C annealed + Air cooled			

3.2 Sensitization of SS AISI 304 and corrosion rate

The results of EPR test, it was found that there are two types of the polarization curves: non-sensitized and sensitized state (Fig.2). When sensitization has occurred, the under peak area of polarization curves must be evaluated in active region range for future *Pa* value calculation.

Fig. 3 shows the *Pa* value obtained at the *Pa* calculation for various post-heat treatment conditions: ***C1*** obtained the high sensitized state (*Pa* > 2.0). Due to the specimen was cooled pass through the critical temperature in range 500-850ºC and the cooling rate of post-heat treatment process is slow then the high amount of $Cr_{23}C_6$ was occurred in HAZ. About the adjustment of bending, *Pa* value is increase when the bending angle increases as a result of the heating temperature is not high enough to reduce the stress in the bended sample. In part of the morphology image of the specimen, it show the small grain size and easily to see the $Cr_{23}C_6$ at grain boundary (Table 2). Moreover, corrosion rate was decreased when the degree of bending is augmenting (see fig. 5).

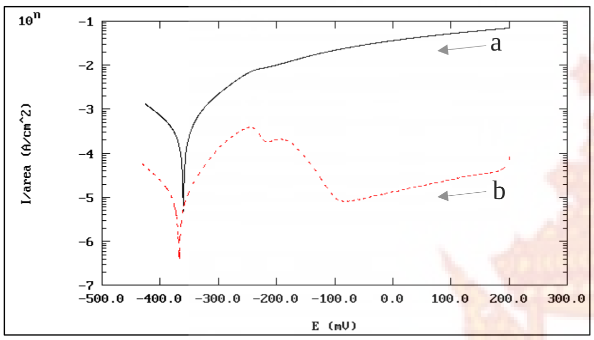


Fig. 2 Polarization curve of SS AISI 304 from EPR test: (a) non-sensitized state and (b) sensitized state for $Cr_{23}C_6$.

C2 does not show sensitization state (*Pa* < 0.1) due to the effect of post-heat treatment that over the critical temperature: any pre-cipitate carbides are redissolved during the anneal and not reform during quenching and the cooling rate of post-heat treatment process is very fast so the separated Cr does not have enough time to combine with carbon at this condition and the adjustment of bending angle not affect to the *Pa* value. However, at 90 and 180degree of bending, corrosion rate were increased as the effect of residual stress, even though the stress was reduced at high temperature which confirm by the large grain size**.**

C3 show evidence of the low sensitized state (Pa < 0.3) as a result of the effect of post-heat treatment that over the critical temperature. However, corrosion rate still higher than ***C2*** and close to ***C1*** because the specimens were cooled pass thorough the critical temperature so the chromium has enough time to $Cr_{23}C_6$ precipitation.

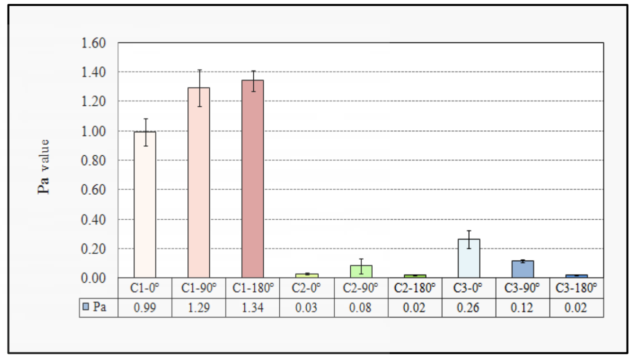
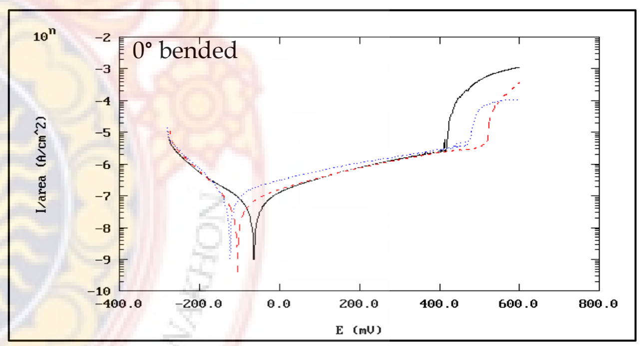


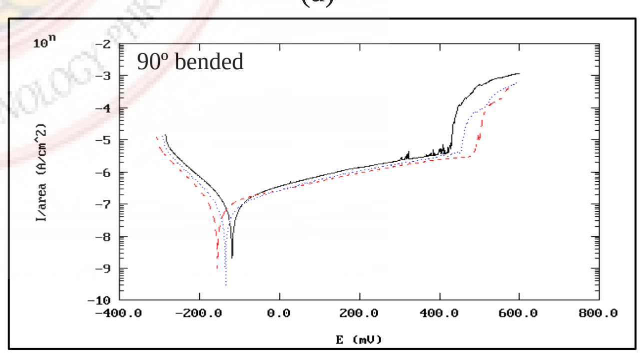
Fig. 3 *Pa* values of SS 304 which welded, bended and annealed at the various conditions.

3.3 Corrosion behavior

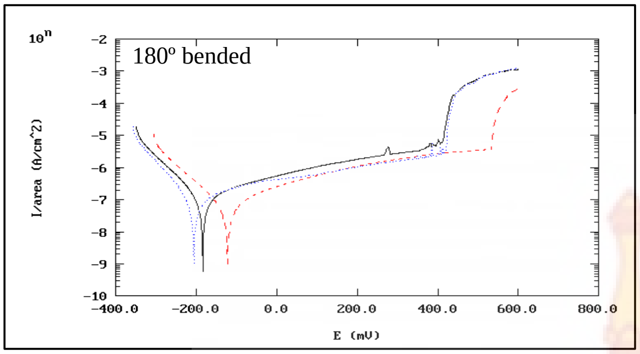
Fig. 4, 5 and 6 presented the information of polarization curve, corrosion rate and passive region respectively, the data was shown that: ***C1*** obtained the lower passive range than ***C2*** and ***C3*** respectively due to the specimens of ***C1*** had more $Cr_{23}C_6$ in HAZ. Therefore the passive film forming among chromium oxide (Cr_2O_3) was reduced and irregular.



(a)



(b)



(c)

Fig. 4 Polarization curve of SS AISI 304 from potentiodynamic polarization scan which welded, bended and annealed at the various conditions: — C1, - - C2 and ...... C3.

About the adjustment of bending, passive range is increase when the bending angle increases as a result of the mechanic force can expand a grain size area, as well as a grain boundary in HAZ is decreased, thus the precipitate of $Cr_{23}C_6$ was diminish. Moreover, ***C2*** shown the better-quality of passive film (more lengthy and low current density at film break down)

4. Conclusion

From the information of $Cr_{23}C_6$ precipitation which analyzed by morphology image, EPR test and corrosion behavior by potentiodynamic polarization scan, it was concluded that: ***C1*** shows the highest *Pa* value more than 0.4 and it was increased while increased the angle of bending. Thus, the specimens have high $Cr_{23}C_6$ occurred at the grain boundaries, the corrosion rate is elevated and the passive film has a low quality. Therefore ***C1*** is not suitable for the weld process development as there is high possibility of IGC attack

About ***C2***, the Pa values obtained were lower than those measured in condition ***C3*** and ***C1*** respectively. The *Pa* values are less than 0.1; it rather suggests that the specimens were non $Cr_{23}C_6$ sensitized and non IGC. Moreover, the corrosion rate of ***C2*** was lowest and its shown the better-quality of protective film. Therefore, this condition is suitable for further work.

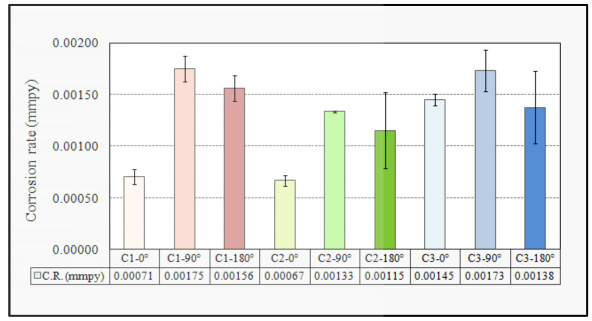


Fig. 5 Corrosion rate of SS 304 which welded, bended and annealed at the various conditions.

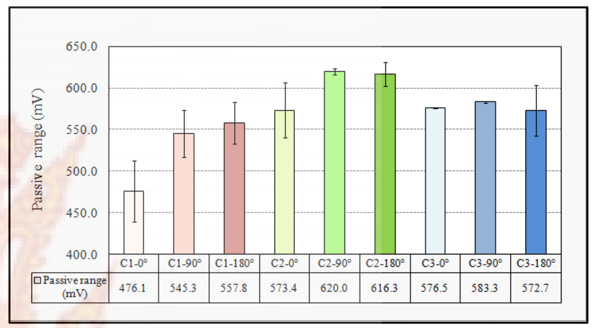


Fig. 6 Passive range of SS 304 which welded, bended and annealed at the various conditions.

Finally, ***C3,*** the *Pa* values was observed when the angle of bending increases from 0 to 180 degree. It obtained between 0.02 and 0.30; it suggests that the specimens were slightly $Cr_{23}C_6$ sensitized and limited IGC attack. However, this condition is not suitable for the weld process development because corrosion rate was higher than ***C2*** and also close to ***C1*** although its had the good quality of protective film.

5. Acknowledgment

The authors acknowledge department of welding engineering technology, College of Industrial Technology for financial support and grateful to staffs in corrosion technology department, TFII. Finally, thanks to all co-workers for operative this research.

6. References

[1] Arutunow A. and Darowicki K., DEIS evaluation of the relative effective surface area of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion. *Electrochim. Acta*., **54**: 1034-1041 (2009).

[2] Kou S., Welding Metallurgy, 2nd edition, New Jersey, U.S.A., 431-446 (2003).

[3] Lewis M.H. and Hattersley B., Precipitation of $M_{23}C_6$ in Austenitic Steels, *Acta Metall.*, **13**: 1159-1168 (1965).

[4] Dadfar M., Fathi M.H., Karimzadeh F., Dadfar M.R. and Saatchi A., Effect of TIG welding on corrosion behavior of 316L stainless steel, *Mater. Lett.*, **61**: 2343-2346 (2007).

[5] Lu B.T., Chen Z.K., Luo J.L., Patchett B.M. and Xu Z.H., Pitting and stress corrosion cracking behavior in welded austenitic stainless steel, *Electrochim. Acta.*, **50**: 1391-1403(2005).

[6] Aydogdu G.H. and Aydinol M.K., Determination of susceptibility to inter-granular corrosion and electrochemical reactivation behavior of AISI 316L type stainless steel, *Corros. Sci.*, **48**: 565-3583 (2006).

[7] Kokawa H., Weld decay-resistant austenitic stainless steel by grain boundary engineering, *J. Mater. Sci.*, **40**: 927-932 (2005).

[8] ASTM Standard G108-94, Standard test method for EPR for detecting sensitization of AISI Type 304 and 304L Stainless Steels, *ASTM*, 457-463 (1994).