*Sung-Yong Ahn, Myungjin Lee, Kyung-Mox Cho, and Namhyun Kang**
(IIW Doc. IX-C-1058-15)

EFFECTS OF RETAINED δ-FERRITE ON CORROSION PROPERTIES FOR MODIFIED 9CR-1MO STEEL WELDS
EFEKTI ZAOSTALOG δ-FERITA NA KOROZIONE OSOBINE ZAVARENIH SPOJEVA OD MODIFIKOVANOG 9CR-1MO ČELIKA

Originalni naučni rad / Original scientific paper
UDK / UDC: Weld World (2014) 58:491–497;
DOI 10.1007/s40194-014-0132-0
Rad primljen / Paper received:

Jun 2016.
Prevod izvornog rada na srpski jezik: Milica Antić,dipl.ing

Adresa autora / Author's adresse :
**Department of Materials Science & Engineering, Pusan National University, Busan 609-735, Korea*

Mod. 9Cr-1Mo steels have a superior creep strength due to the precipitation of MX (M=V, Nb ; X=N, C) produced from V/Nb soluts and M23C6 induced by Cr/Mo solutes [1]. Low CTE, reasonable ductility and toughness, and a good resistance on hydrogen embrittlement make the alloy attractive to the structural materials for the steam and nuclear power plants [2]. For the welding of Mod. 9Cr-1Mo steels, postweld heat treatment (PWHT) is mostly required to acquire the weld integrity [3]. The study investigated pitting corrosion property with respect to the retained δ- ferrite in Mod. 9Cr-1Mo steel welds produced at various postweld heat treatment (PWHT) time. Base metal was normalized (1080 oC for 1 hr) and tempered (760 oC for 2 hr). Rectangular plates of 6 mm thickness were used for the fabrication of weldments. Bead-on-plate welding was conducted by austogeneous gas tungsten arc welding (GTAW) and welding heat input was 6.4 kJ/mm (150 A, 11.7 V, and 16.5 mm/min). PWHT was carried out at 760 oC as the holding time from 30 minutes to 2 hours. The base metal had a microstructure of tempered martensite (TM) with no retained δ- ferrite. A GTAW process produced the retained δ- ferrite in the martensitic welds. A PWHT process changed the microstructure to the TM with increasing the carbide amount. Potentio-dynamic test was conducted using 3-electrode system in 0.001 mole sodium chloride solution to observe pitting corrosion sites. Increasing the PWHT time, polarization curves shifted to low Ecorr and large Icorr, therefore decreasing the pitting corrosion resistance of the weld. The specimens post to the potentio-dynamic test were observed using optical microscopy (OM). Fig. 1 shows the pits developed in the welds.

Modifikovani 9Cr-1Mo čelici imaju superiornu čvrstoću puzanja zbog taloženja jedinjenja MX (M = V, Nb; X = N, C) nastalih od rastvorenih V / Nb i karbida $M_{23}C_6$ nastalih usled prisustnih rastvorenih Cr / Mo [1]. Niska CTE, razumna duktilnost i žilavost, i dobra otpornost na prsline usled vodonika, čine ove legure privlačnim konstrukcionim materijalom za termo i nuklearne elektrane [2]. Za zavarivanje modifikovanog 9Cr-1Mo čelika, termička obrada (PWHT) je uglavnom potrebna da se obezbedi integritet zavarenog spoja [3]. Studija ispitivanja osobina na tačkastu koroziju u odnosu na zaostali δ- ferit kod zavarenih spojeva od modifikovanog 9Cr-1Mo čelika odnosi se na različita vremena termičke obrade (PWHT). Osnovni materijal je normalizovan (1080 ° C / 1 sat) i žaren (760 ° C / 2 h). Pravougaone ploče debljine 6 mm su korišćene za izradu zavarenih elemenata. Navar na ploči je izveden TIG postupkom sa unetom količinom toplote od 6,4 kJ / mm (150 A, 11,7 V i 16,5 mm / min). PWHT je izvedena na 760 ° C a vreme držanja je od 30 minuta do 2 sata. Osnovni materijal ima mikrostrukturu otpuštenog martenzita (TM) bez zaostalog δ- feriita. TIG postupkom zavarivanja stvara se zaostali δ- ferit u martenzitnim zavarenim spojevima. Postupak PWHT menja mikrostrukturu TM kroz povećanje sadržaja karbida. Potencio-dinamičko ispitivanje je sprovedeno korišćenjem sistema sa 3-elektrode u rastvoru natrijum hlorida da bi se posmatrala mesta sa tačkastom korozijom. Sa porastom vremena PWHT, krive polarizacije su prebačene na mali Ecorr i veliki Icorr, i time na smanjenje otpornosti na rupičastu koroziju zavarenih spojeva. Epruvete podvrgnute potencio-dinamičkom ispitivanju podvrgnute su optičkoj mikroskopiji (OM). Na sl. 1 prikazane su jamice na zavarenim spojevima.

As the PWHT time increased, the coarse pits were nucleated more frequently at the δ/TM interface than at the TM/TM interface.

Kako vreme PWHT raste, grube jamice se stvaraju češće na međupovršinama δ/TM nego na međupovršinama TM/TM.

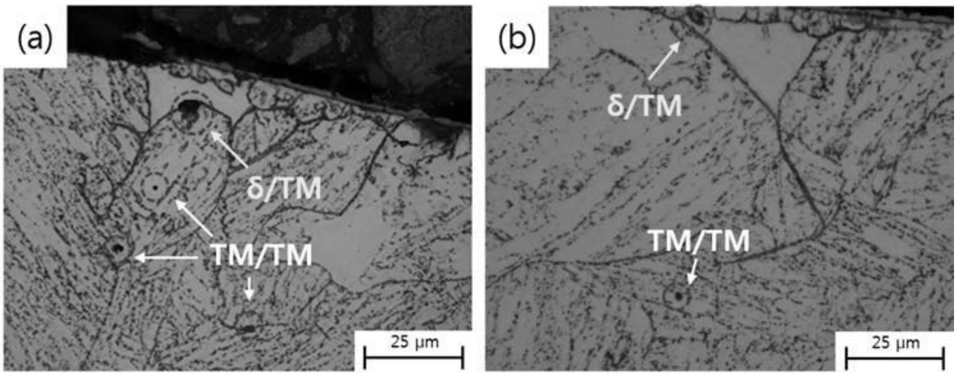

***Fig. 1** Optical micrographs (a) and (b) to indicate pitting position and size, i.e., the coarse pits observed at the δ/TM interface rather than at the TM/TM interface.*

***Sl. 1** Optički mikrografi (a) i (b) koji indikuju položaj i veličinu jamica t.j., grube jamice zapažene na međupovršini δ/TM u većem stepenu nego na međupovršini TM/TM .*

Pitting corrosion in high Cr steels is preferentially generated in the Cr depleted zone adjacent to Cr-rich M23C6 carbides and large M23C6 carbides act as the active sites for the initiation of pitting corrosion [4,5]. On the other hand, MX carbonitrides present in the matrix hinder the precipitation of M23C6 carbides, therefore improving the corrosion resistance of the steel [6]. Therefore, the authors analized the size and distribution of M23C6 existing at TM/TM and δ/TM interfaces to understand the mechanism of pitting corrosion.

Precipitates at TM/TM and δ/TM interfaces were observed using carbon replica method. Transmission electron microscopy (TEM) micrographs is shown in Fig. 2 that two types of spherical partices existed and their size increased with increase of PWHT time. Selected area electron diffraction (SAED) pattern and energy dispersive spectroscopy (EDS) spectrum indicated that the coarse and fine carbides were M23C6 carbides (red dotted line in Fig. 2) and MX carbonitride (blue dotted line in Fig. 2), respectively.

Tačkasta korozija u visoko Cr čeliku se prvenstveno javlja u zoni osiromašenoj na Cr u blizini zone Cr-om bogatih $M_{23}C_6$ karbida i velikih $M_{23}C_6$ karbida koji deluju kao aktivna mesta za pokretanje tačkaste korozije [4,5]. S druge strane, MX karbonitridi prisutni u matrici ometaju taloženje $M_{23}C_6$ karbida, stoga poboljšavaju otpornost čelika prema koroziji [6]. Iz tog razloga, autori analiziraju veličinu i distribuciju $M_{23}C_6$ koji postoje u međuzonama TM / TM i δ / TM da bi se shvatio mehanizam tačkaste korozije.

Talozi na TM / TM i δ / TM međupovršinama su posmatrani metodom ugljeničnih replika. Prenosna elektronska mikroskopija (TEM), odn. mikrografi prikazani na slici. 2 pokazuju da postoje dve vrste sfernih čestica čijaa veličina raste sa povećanjem vremena PWHT. Putanjom izabranog područja difrakcije elektrona (SAED) i spektrom energije disperzivne spektroskopije (EDS) prikazani su grubi i fini karbidi $M_{23}C_6$ karbidi (crvena isprekidana linija na Sl. 2) i MX karbonitridi (plava isprekidana linija na Sl. 2).

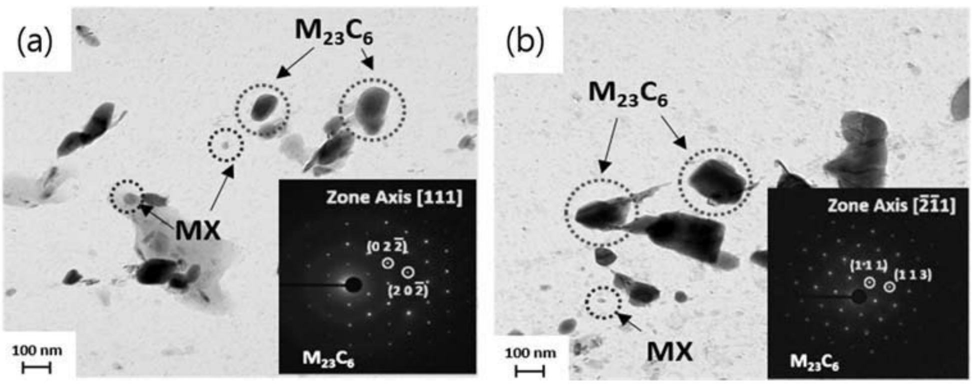

***Fig. 2** Transmission electron micrographs in the weld: (a) PWHT 30 min and (b) PWHT 2 hr*
***Sl. 2.** TEM mikrografi šava: (a) PWHT 30 min i (b) PWHT 2 h*

Focused ion beam (FIB) samples were prepared to analyze the type and size of the carbides at δ/TM interface. Fig. 3 shows the bright field image with SAED pattern and EDS mapping image of Cr. Cr-rich M23C6 carbides were dispersed along the lath boundaries of TM/TM and δ/TM interface. The carbides located at the δ/TM interface were coarser and denser than those at the TM/TM interface

Uzorci za ispitivanje fokusiranim snopom jona (FIB) su pripremljeni za analizu vrste i veličine karbida na δ / TM međupovršinama. Sl. 3 prikazuje svetlo polje slike sa SAED putanje i EDS mapiranje slike Cr. Karbidi $M_{23}C_6$ bogati Cr-om su disprgovani duž granica međupovršina TM / TM i δ / TM . Karbidi koji se nalaze na δ / TM međupovršini su grublji i gušći od onih na TM / TM međupovršini.

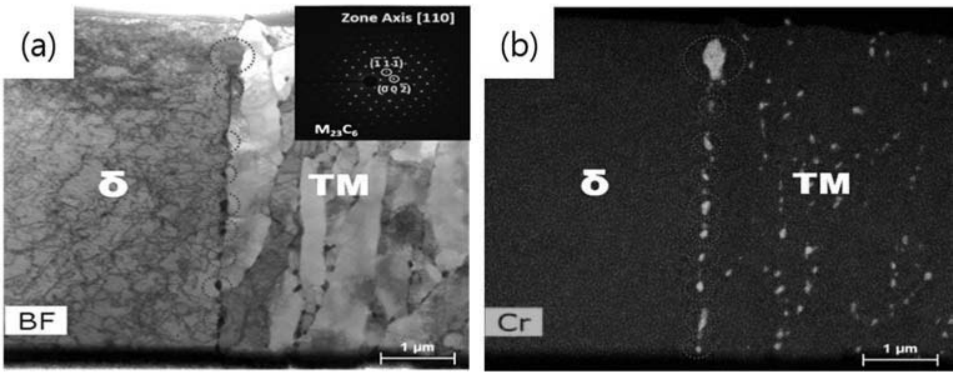

Fig. 3 *Carbide type and size observed for PWHT 2 hr specimens: (a) bright field image of TEM and (b)Cr mapping*
Sl. 3 *Tip i veličina karbida zapažena kod epruveta sa PWHT od 2 h (a) slika svetlih polja pri TEM (b) mapiranje Cr*

Fig. 4 shows the average size of M23C6 carbides as a function of PWHT time. As a PWHT time increased, M23C6 carbides precipitated at TM/TM and δ/TM interfaces increased. The carbides at the δ/TM interface had a size of 90-160 nm and they were coarser than the carbides (70~130 nm) at the TM/TM interface. The δ-ferrite contains more Cr contents that stabilize ferrite phase and martensite has extra C supersaturated [7]. For PWHT, Cr and C diffuse to the interface between δ and TM, resulting in formation of coarser Cr-rich M23C6 than the carbides at TM/TM interface. The coarser carbides are formed, the more Cr diffuse to make it from adjacent area [4,5]. Therefore, the larger carbides of M23C6 caused the severer degradation of pitting corrosion resistance as the PWHT time increased.

Na sl. 4 prikazana je prosečna veličina $M_{23}C_6$ karbida u funkciji vremena PWHT. Kako vreme PWHT raste, $M_{23}C_6$ karbidi se više talože na međupovršinama TM / TM i δ / TM. Karbidi na δ / TM međupovršini imaju veličinu 90-160 nm i oni su grublji od karbida (70 ~ 130 nm) na TM / TM međupovršini. δ-ferit sadrži više Cr koji stabilizuju fazu ferita i martenzita koji je je ekstra zasiđen ugljenikom [7]. Pri PWHT, Cr i C difunduju kroz međupovršinu δ i TM, što dovodfi do formiranja grubljih Cr-om bogatih $M_{23}C_6$ karbida na TM / TM međupovršini.Pri formiranju grubljih karbida, više Cr difunduje iz susednih područja [4,5]. Dakle, veći karbidi $M_{23}C_6$ izazivaju ozbiljniju degradaciju otpornosti na tačkastu koroziju sa povećanjem vremena PWHT.

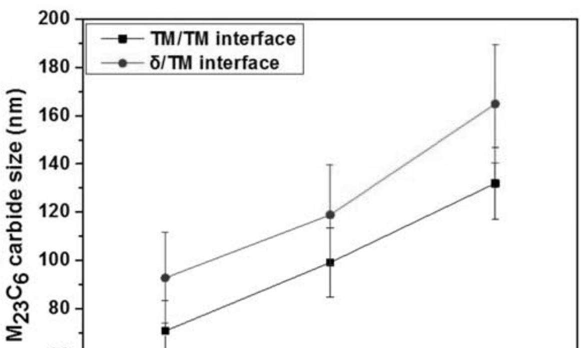

Fig. 4 *Average size of M23C6 located at TM/TM and δ/TM interfaces with respect to PWHT time*
Sl. 4 *Srednja veličina M23C6 lociranih na međupovršinama TM/TM i δ/TM u odnosu na vreme PWHT*

The study investigated the effect of PWHT time on pitting behavior for Mod. 9Cr-1Mo steel welds and the following conclusions are made:

1. The retained δ-ferrite was observed in the weld of Mod. 9Cr-1Mo steels although the base metal consisted of tempered martensite with no δ-ferrite. This is because the welding has non-equilibrium solidification due to the rapid cooling rate. Therefore, the phase transformation from δ-ferrite to austenite was incomplete during the cooling of GTAW.
2. For potentio-dynamic test, Ecorr values decreased and Icorr values increased as the PWHT time increased, therefore decreasing the pitting corrosion resistance of the weld. Pitting was randomly observed at the martensite lath. With increasing the PWHT time, the coarse pitting was found at the δ /TM interface as compared with the pits formed at the TM/TM interface.
3. Coarser and denser Cr-rich M23C6 carbides were formed along the δ /TM interface than at the TM/TM interface with increasing the PWHT holding time. This is caused by diffusion of Cr and C to the interface between the δ-ferrite and TM. The retained δ-ferrite in welds behave as an activation site for pitting corrosion. Therefore, the modified 9Cr-1Mo steel needs a systematic study to optimize PWHT temperature and time after considering the pitting corrosion resistance as well as mechanical properties.

Studija je imala za cilj istraživanje učinka vremena PWHT na ponašanjeu odnosu na tačkastu koroziju zavarenih spojeva od modifikovanog 9Cr-1Mo čelika i mogu se doneti sledeći zaključci:

1. Zaostali δ-ferit je uočen kod šava od modifikovanog 9Cr-1Mo čelika, iako se osnovni materijal sastoji se od otpuštenog martenzita bez δ-ferita. To je zato što zavarivanje izaziva neravnotežno očvršćavanje usled velike brzine hlađenja. Dakle, fazna transformacija iz δ-ferita u austenit je nepotpuna tokom hlađenja posle TIG zavarivanja.
2. Pri potencio-dinamičkom testu, Ecorr (E kor) vrednosti se smanjuju a Icorr (I kor) vrednosti se povećavaju sa vremenom PWHT, čime se smanjuje i otpornost šava na tačkastu koroziju. Tačkasta korozija je nasumično uočena na martenzitnim iglicama. Sa povećanjem vremena PWHT, grube jamice su pronađene na međupovršini δ / TM u poređenju sa jamicama formiranim na međupovršinama TM / TM.
3. Grubljii i gušći Cr-om bogati $M_{23}C_6$ karbidi formiraju se su duž δ / TM međupovršina u odnosu na TM / TM međupovršinu sa povećanjem vremena držanja pri PWHT. To je uzrokovano difuzijom Cr i C kroz međupovršinu između δ-ferita i TM. Zaostali δ-ferit u šavovima se ponaša kao aktiviraciono mesto za tačkastu korziju. Na osnovu toga, modifikovani 9Cr-1Mo čelik zahteva sistematsku studiju sa ciljem optimizacije temperature i vremena PWHT posle razmatranja otpornosti na tačkastu koroziju i mehaničkih osobina.

REFERENCE

R. L. Klueh and D. R. Harries, High-chromium ferritic and martensitic steels for nuclear applications, ASTM monograph 3. American Society for Testing and Materials, West Conshohocken, PA (2001)

M. Sireesha, S. Sundaresan and S. K. Albert, Journal of Materials Engineering and Performance, 10, 320 (2001)

E. Sambamurthy, S. Dutta, A. K. Panda, , A. Mitra and R. K. Roy, International Journal of Pressure Vessels and Piping, 123, 86 (2014)

Y. J. Kim, D. W. Joo, S. H. Park, G. D. Kim and J. H. Sung, J. of the Korean Society or Heat Treatment, 7, 25 (1994)

C. T. Kwok, H. C. Man and F. T. Cheng, Surf. Coat. Technol. 126, 238 (2000)

Q. Lu, W. Xu and S. van der Zwaag, , TMS 2013 Annual Meeting Supplemental Proceedings, TMS, (2013)

F. Abe, T. Noda, H. Araki and S. Nakazawa, J. Nucl. Mater. 179, 663 (1991)