

IN-SITU OBSERVATION OF CARBIDE PRECIPITATION IN DISSIMILAR JOINING OF CR-MO STEEL

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Abstract

In this study ER90S-B9 welding wire was deposited on 2.25 Cr-1 Mo steel for the joining of dissimilar materials by the gas tungsten arc welding technique. Simulated post weld heat treatment (PWHT) at 700°C was performed under high vacuum in the experimental station BL 3.2 Uv of the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand for low-energy electron microscopy. Microstructural changes at the weld metal side adjacent to the weld interface were observed. There were black triangular flakes present in the microstructure after the PWHT temperature was reached. They grew in epitaxial alignment with the solidification direction of the weld metal. X-ray photoelectron spectroscopy (XPS) was also implemented on the flakes which could possibly be boron nitride (BN). These flakes were not stable as they decomposed during growth leaving the required elements for carbide precipitation. During the decomposition, 3 regions were observed as black (BN), gray, and white contrasts. Beside boron, Cr and Fe were also indicated in the black and gray regions with the XPS technique. After some decomposition, Cr-rich carbide formed and the hard zone became established. A rough mechanism was proposed as the carbide at the heat affected zone dissolved and carbon migrated to the weld metal by the formation of a BN front followed by the decomposition of the BN which provided elements for carbide precipitation and formation of the hard zone.

Keywords: PWHT, carbide formation, LEEM, XPS, in-situ observation

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Introduction

In steam turbine power generation, Cr-Mo steels have been selected for their elevated temperate strength and creep resistance (Gope *et al.*, 1992; Raman and Al-Mazrouee, 2007; Yamamoto, 2008; Anand *et al.*, 2010; Sae-teaw *et al.*, 2010). Dissimilar weldments, especially between low-Cr and high-Cr ferritic steel, are used in a number of steam generator circuits. It is well known that carbon migration occurs across the weld interface from low-alloy ferritic steel to high-alloy ferritic steel during exposure to high temperature. This results in the formation of a hard zone on the high-alloy side of the weld interface.

Many researchers have studied microstructures of the hard zone (Sudha *et al.*, 2002; Sae-teaw *et al.*, 2010; Petchsang and Phung-on, 2013) and have performed mechanical characterization in dissimilar metal weldments (Sudha *et al.*, 2006; Sae-teaw *et al.*, 2010; Petchsang and Phung-on, 2013; Mittal and Sidhu, 2014; Abd elmaoula *et al.*, 2015; Mosa *et al.*, 2016; Mayr *et al.*, 2018). In an as-welded condition, a martensite structure is present in the weld metal side adjacent to the weld interface. On the other hand, the microstructure changes to a formation that is precipitate-rich after post weld heat treatment (PWHT), forming a hard zone. It has been proposed that this behavior is due to the migration of carbon (Race, 1992; Lundin *et al.*, 1996; You *et al.*, 2001; Sudha *et al.*, 2006; Foret *et al.*, 2006; Petchsang and Phung-on, 2013). Hard zones are susceptible to prior cracks and failure during high temperature operation due to the differences in the hardness between T22 steel and the weld metal.

Studies on the precipitation of carbides of the hard zones in dissimilar weldments during PWHT are also essential for the prediction of microstructural instability during prolonged exposure to a high operating temperature which leads to severe degradation in the mechanical properties of the weldments.

While many previous investigations performed in ex-situ conditions and the precipitation behavior of micro-alloying elements in steel is rather complex, there was

still no in-situ investigation which could help provide information for the formation of carbide in the hard zone of dissimilar welding between zones with high and low Cr contents. This study shows the rough mechanism on microscopic precipitation of carbides in the hard zone in real-time using low energy electron microscopy (LEEM) and the microchemistry has been investigated using X-ray photoelectron spectroscopy (XPS). A specimen from T22 welded with ER90S-B9 was heated under the PWHT condition while the microstructures were continuously observed at high temperature at the simulated PWHT condition. The results obtained from both techniques will be helpful as a baseline for further determination of the mechanism of carbide precipitation in Cr-Mo steel dissimilar joints.

Materials and Methods

Materials and Welding Process

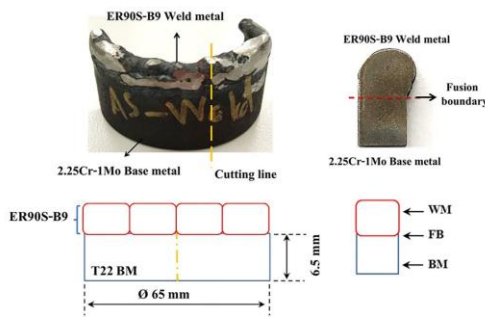
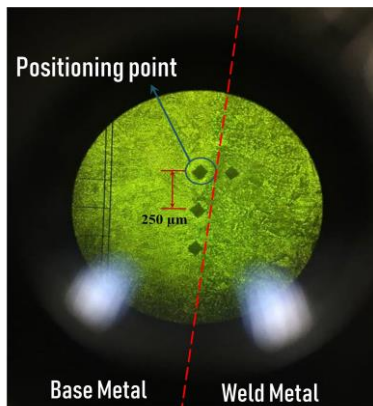
The material used as the base metal for dissimilar welded preparation was a 2.25 Cr-1 Mo steel tube (T22) with dimensions of 65 mm (outside diameter) $\times$ 6.5 mm (thickness). The general chemical composition is shown in Table 1. The specimen was prepared using the gas tungsten arc welding (GTAW) process with ER90S-B9 welding wire. An overlay joint was selected to deposit the weld metal on the wall thickness of the tube, as shown in Figure 1. The welding parameters were 60 A with 11-12 V using direct current electrode negative polarity.

The welded tube was cut in a longitudinal direction to reveal the cross section of deposited weld metal with a size about 5 mm long and 3 mm wide (Figure 1). Surface preparation for microstructural examination was then performed with sandpaper Nos. 100, 320, 400, 600, 800, 1,000, and 1,200, successively. In this case, the specimen was ground to a thickness less than 1 mm in order to reduce the heat mass and to minimize the chance of outgassing and arcing during the

Table 1. Chemical composition of the material and welding wire used

Material	Composition	Element (wt-%)			
		Cr	Mo	Mn	Fe
2.25Cr-1Mo base metal	nominal ⁽¹⁾	1.90-2.60	0.87-1.13	0.30-0.60	95.1-96.8
	measured ⁽³⁾	2.4	1	0.6	96.0
ER90S-B9 weld metal	nominal ⁽²⁾	8.00-9.50	0.80-1.10	1.25	87.3-90.3
	measured ⁽³⁾	4.1	1.1	0.4	94.3

⁽¹⁾ Refer to ASME SA-213/SA-213M, 2015; ⁽²⁾ Refer to ASME SFA-5.28, 2015; ⁽³⁾ Measured in the weldment by SEM/EDS analysis.

**Figure 1. 2.25 Cr-1 Mo steel welds were performed using GTAW process by ER90S-B9****Figure 2. The specimens' positioning with a micro Vickers hardness tester**

LEEM operation. To reveal its microstructure in an as-welded condition and locate the weld interface prior to observation, the specimen was etched using 10 ml HNO₃+20 ml HCl+30

ml water for 60 sec. The weld interface was then marked with a micro Vickers hardness tester using 1 kgf with a spacing of 250 µm (Figure 2). Then, the surface was re-polished again with 1,000 and 1,200 sandpaper followed by a 1 µm diamond. The hardness test was carried out after the PWHT with micro Vickers hardness tester profiles across the weld interface from the weld metal to the 2.25 Cr-1 Mo side at a constant load of 1 kgf with the distance between the points of 250 s (0.25 mm).

Experiment

In this research, the LEEM and XPS characterizations were performed at the experimental station BL 3.2 Ub of the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand as shown in Figure 3. To study the precipitation of carbides in the weld metal side adjacent to the weld interface, the polished specimen was cleaned by ultrasonication in acetone and then ethyl alcohol for 15 min each. Then it was mounted in the sample cartridge (Figure 4) and sputter- cleaned by Ar⁺ ion under vacuum before being loaded into the analysis chamber with the base pressure of 10⁻⁹ torr. An ultrahigh vacuum state was maintained at the level of 10⁻⁹ torr or a higher vacuum condition during the experiment. Heating was introduced both in the radiation mode and by electron bombardment on the back of the specimen. The temperature was measured with a pyrometer with the emissivity of Cr-Mo steel set at 0.28. As shown in Figure 5, the position observed during the experiment was at the weld metal side which was typically 100 microns away from the fusion line.



Figure 3. LEEM system operation

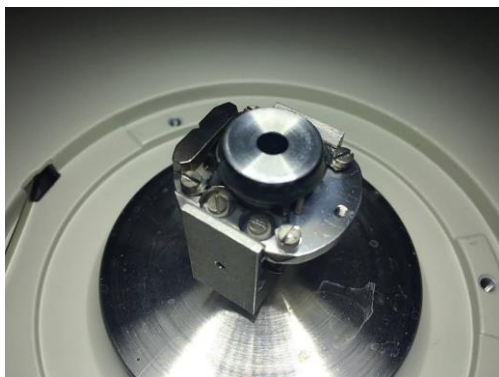


Figure 4. The specimen in the sample holder of the LEEM system

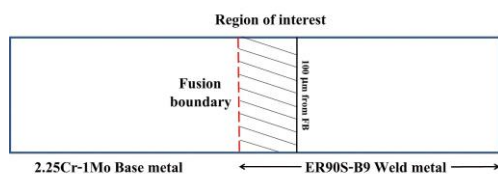


Figure 5. Position of weldment

Figure 6 shows the heating history of the experiment. In order to simulate the condition of the PWHT, the specimen was heated from room temperature to below the Eutectoid temperature (A1) at 700°C as recommended by the American Society of Mechanical Engineers (ASME) Section IX Standard for PHWT. The temperature was held to 700°C for 19 h under

LEEM observation for carbide formation at the weld metal side. During the observation, XPS was also performed to identify the chemical species that were present on the surface. The initial experimental results provided survey scans of the binding energy range that covered chromium, iron, and boron (50-450 eV) with a 0.5 eV scan step as the target for the observed elements.

Results and Discussion

The in-situ recorded micrographs by LEEM are shown in Tables 2 and 3. The results from previous investigations reported that the microstructure of the weld metal close to the interface in an as-welded condition consisted of martensite (Sudha *et al.*, 2006; Sae-teaw *et al.*, 2010; Petchsang and Phung-on, 2013) and a similar microstructure was also observed in this study. The microstructure derived from a mixture between the ER90S-B9 and melted base material which was re-solidified with columnar morphology. Since the specimen was prepared with dissimilar joining, the microstructure should be the composition gradient between the heat affected zone (HAZ) and weld metal at the weld interface. This area could be the area of interest for in-situ observation.

As the simulated PWHT cycle began, there was no significant change in the microstructure under LEEM. Similar results were obtained by Tammasophon *et al.* (2011) and Mosa *et al.* (2016) until finer grains with primary carbides started to be present at a temperature about 630°C on the weld metal side adjacent to the interface as shown in Table 2(a). When the temperature rose to 700°C, the features in the weld metal (Table 2(b)) were also more pronounced with a mix of small sized structures. Then the features started to grow, until they consumed each other.

After further holding of the PWHT temperature for 7 h, small black triangular flakes started to be present on the surface very close to the interface. The triangular flakes grew further as the PWHT time proceeded (Table 2(c-d)). In this case the flake growth

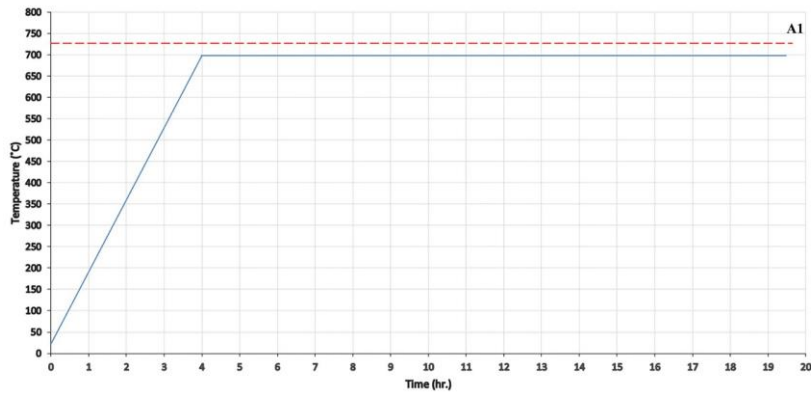
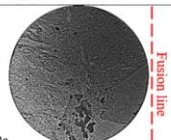
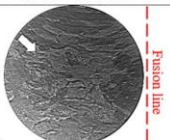
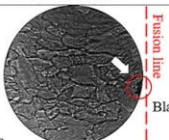
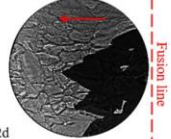
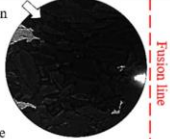


Figure 6. Simulated PWHT history

Table 2. In-situ recorded micrographs by LEEM

LEEM images at weld metal side near the weld interface with start voltage ≈ 0.40 V and 75 μm field-of-view (FOV)		
PWHT 630°C/0 h	PWHT 700°C/0 h	PWHT 700°C/7 h
 2a	 2b -features change to grow until consuming each other	 2c -black of triangular flake started to be present
PWHT 700°C/10 h	PWHT 700°C/13 h	PWHT 700°C/19 h
 2d - epitaxial growth of BN (red arrow)	 2e -surface of triangular flake continued to grow	 2f -dissolution of triangular flake and chromium carboe formed.

was present in the epitaxial type (Table 3(a-f)) along the solidification direction of the weld metal (Nelson *et al.*, 1999; DuPont, 2011). These flakes continued to grow further until the size became larger than 75 microns which exceeded the field of view in the LEEM (Table 2(e)).

As the flakes grew during the increase of the exposure time, there could be instability of the features especially after the growth front had passed. The dark region started to decompose to form gray stripes and white features (Table 2(f)). These phenomena proceeded while the front surface of the black region continued to grow forward from right to left in the field of view.

The instability of the features could be attributed to the gradient in the compositions of the materials in dissimilar welding together with the driving force from the temperature used during the simulation of the PWHT. However, this phenomenon is still not able to be discussed thoroughly as to its mechanism in this study. Still, the steps in the formation of the features could be shown by the results.

Figure 7(a- b) showed the results from XPS spectra measurements of the Cr, Fe, and B obtained from the 3 regions (black, gray, and white in Figure 7(c)) on the surface of the weld metal adjacent to the interface after 19 h of the PWHT. The dark black features firstly occurred on the surface while the gray and

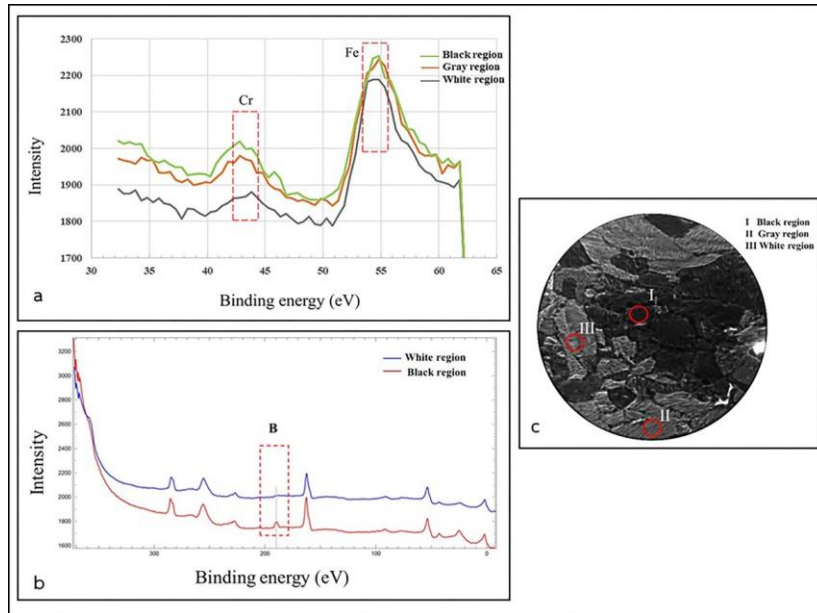


Figure 7. (a-b)The results of XPS spectra of chromium, iron, and boron, respectively; and c) the 3 regions of the HAZ in the weld metal

Table 3. The direction of growth in in-situ recorded micrographs by LEEM

Temp (°C)	LEEM images at weld metal side near the weld interface with start voltage ≈ 0.40 V and $75\ \mu\text{m}$ field-of-view (FOV)					
	40 min after triangular flake started to be present	1.40 h	2.40 h	3.40 h	4.40 h	5.40 h
Heating $T < T_{A1}$ (700°C)	3a	3b	3c	3d	3e	3f
* A Reference point (A) to observe direction of growth with a fixed position						

white appeared later. The gray and white regions had a slightly difference contrast.

The XPS analysis of the black region showed the highest intensity of the boron spectra peak among all regions. The spectra presented the signature of boron nitride (BN)

(Song *et al.*, 2015; Sun *et al.*, 2018). In addition, chromium and iron spectra were also analyzed in all 3 regions (Ilton *et al.*, 2000; Aronniemi *et al.*, 2005; Biesinger *et al.*, 2011). The Cr and Fe spectra in the black and gray regions shifted considerably together and increased to a higher

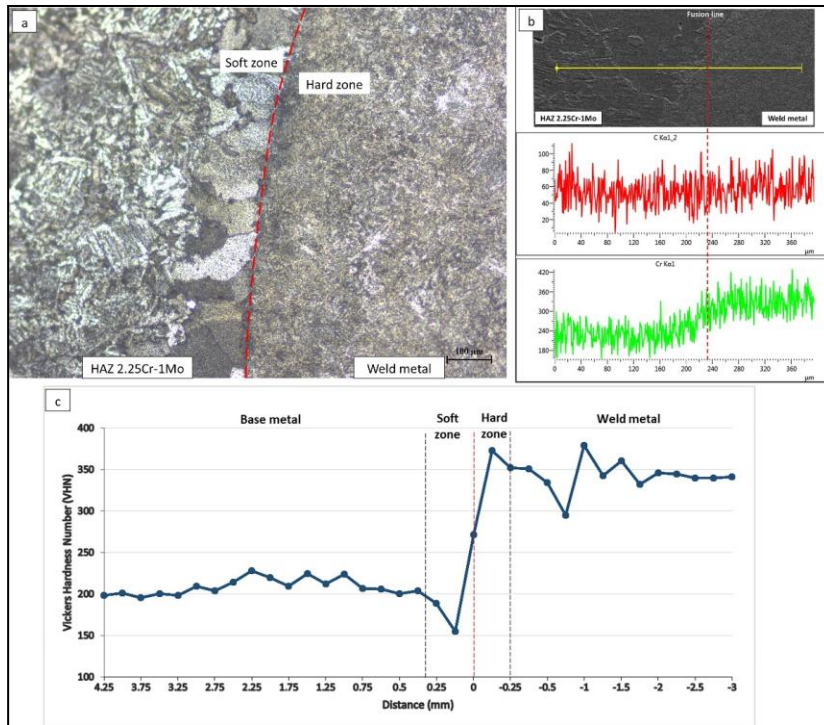


Figure 8. (a) Metallographs of the weld metal and HAZ of 2.25Cr-1Mo after PWHT; (b) SEM/EDS line scans image which shows the redistribution of Cr and C across the weld interface; and (c) Hardness profile across the weld interface

intensity compared to the white region. This could be evidence of higher Cr and Fe contents in these regions which could possible precipitate to form chromium carbides. These could indicate that the dark and gray regions could form either carbides or BN preferably compared to the white region which had possibly only the plain Fe-C matrix. The mixtures of those 3 regions were in the microstructure located adjacent to the weld interface in the weld metal side which was considered as the hard zone. The results corresponded to Sudha *et al.* (2006) in which both the optical and SEM micrographs in the hard zone showed the uniform distribution of high density dispersed fine precipitates.

From the SEM/EDS line scan results, the carbon content was not significantly different between weld metal and HAZ (Figure 8(b)). However, since the Cr content in the weld

metal was higher at 9% due to the filler metal (ER90S-B9) compared to 2.25% in the HAZ, this could provide the affinity to draw the carbon from the HAZ to the weld metal. This mechanism occurred even though the carbon content in the HAZ was slightly higher than the weld metal which was caused by the affinity of Cr as the alloying addition.

During the PWHT, the carbides became thermodynamically unstable from the reason above and dissolved into a matrix which then diffused to form the 2.25 Cr-1 Mo side to the ER90S- B9 side. In addition, since the microstructures of 2.25 Cr-1 Mo were ferrite and martensite, the ferrite matrix has a very low solubility for carbon, and most of the carbon atoms diffused into the high Cr steel form carbides, thus producing a precipitate-rich band (Albert *et al.*, 1997).

Since the carbon had a limited property for diffusion, the formation of carbides was also located at some distance away from the fusion boundary as the cluster of fine precipitates forming the hard zone (Figure 8). This phenomenon proceeded with the aid of BN that formed as the front path dissolving and dragging elements required for carbides to precipitate which could be seen from the XPS results for both the black and gray regions (Figure 7).

The precipitation mechanism of carbides in the hard zone formed on the weld metal side of the weldment were derived based on our observation as follows:

$\alpha' \longrightarrow \text{BN} \longrightarrow \text{carbide formed}$

Conclusions

Both the LEEM and XPS techniques were performed to investigate carbide formation of the hard zone at the weld interface of a Cr-Mo dissimilar joint between T22 steel and ER90S-B9 filler metal using the GTAW process. The results were obtained as follows:

- 1) The formation of hard zones was observed in the ER90S-B9 WM adjacent to the weld interface.
- 2) The triangular BN flakes related to the chromium carbide formation in the hard zone and was shown by XPS measurement.
- 3) The orientation of BN growth was in epitaxial alignment.
- 4) The precipitation of the chromium carbide mechanism in the hard zones has been proposed as a rough mechanism.
- 5) The XPS proves to be an efficient way to characterize the carbide precipitation and dissolution of the micro alloying elements.

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