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## High temperature corrosion behavior of PCGTA weldments of Monel 400 and AISI 304 exposed in the molten salt environment at 600°C

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**Abstract:** This paper investigates the dissimilar joints of Monel 400 and AISI 304 stainless steel obtained by Pulsed Current Gas Tungsten Arc Welding (PCGTAW) process employing ERNiCu-7 filler. Microstructure examination showed the formation of partially liquated zone at the HAZ of Monel 400 and secondary phases at the HAZ of AISI 304. Tensile studies showed that the fracture occurred at the parent metal of AISI 304. Cyclic hot corrosion studies were performed on various coupons of the weldments by exposing them in the molten salt environment containing K<sub>2</sub>SO<sub>4</sub> + 60% NaCl at 600°C. It was inferred from the studies that the parent metals Monel 400 and AISI 304 exhibited higher corrosion resistance compared to the other zones of the weldments.

**Keywords:** Monel 400; AISI 304; PCGTAW; Cyclic hot corrosion.

### 1. Introduction

Joining of dissimilar metals is one of the most essential requirements of many industries today. The dissimilar metal combinations lead to new challenges in research which include utilization of materials in an effective way, weld effectiveness in terms of improved mechanical properties, absence of any negative metallurgical changes etc. Dissimilar metal joints are widely employed in the energy demanding sectors including marine, oil and petroleum, thermal, geothermal and nuclear power plants, where they are prone to high temperature corrosion or hot corrosion and high temperature wear.

The dissimilar combinations of Monel 400 and AISI 304 can be used in moderately high temperature and corrosive environments as in the case of oil gasification plants, chemical processing equipments etc. In addition, a combination of moderate oxidation resistance and creep strength extends their application to steam generator tubing and other components operating at temperatures up to 550° C in conventional fossil-fuel power plants [1, 2].

Pulse current gas tungsten arc welding (PCGTAW) is one of the widely used welding techniques, which has been reported to have numerous advantages over the conventional Gas Tungsten Arc welding (GTAW) or Continuous Current GTA welding process. The beneficial effects most often reported in the literature include claims that the total heat input to the weld is reduced, which results in the reduction of weld bead size, residual stresses by the reduction of heat input, thermal distortion, porosity and micro segregation [3,4].

Current pulsing has been used in the past for obtaining grain refinement in weld fusion zone. Significant refinement of the solidification structure and a transition from columnar to equiaxed growth were reported [5, 6]. These researchers reported about current pulsing to obtain grain refinement in weld fusion zones and improvement in weld mechanical properties.

Hot corrosion can be defined as deposit modified, gas induced degradation of materials at high temperatures. Some of the well known materials employed in high temperature applications include Ni based superalloys, stainless steel and low alloy steels. The operating environments of these dissimilar metal joints involve high temperatures and the presence of various elements which inherently combine to form the molten salts such as  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{V}_2\text{O}_5$  and thus form the eutectic mixtures during cyclic operations. The combinations of these types of molten salt deposits at high temperatures are vulnerable and will fuse on to the dissimilar metal system and thereby accelerating the corrosion attack. Hence characterization of the weldments is must both in the ambient as well as in the high temperature conditions, before putting them in use. Devendranath et al. [7] investigated the performance of bimetallic combinations of Monel 400 and AISI 304 in the aggressive hot corrosion environments.

This paper investigates the characterization of these dissimilar weldments exposed in the molten salt environment containing  $\text{K}_2\text{SO}_4+\text{NaCl}$ . Metallurgical and mechanical characterization was also investigated in the study using the combined techniques of optical and SEM/EDAX analysis to evaluate the structure - property relationships of the weldments.

## 2. Experimental procedure

The chemical composition of the base and filler metals employed in this study is given in Table 1. Before welding, the as-received base plates were cut using wire-cut Electrical Discharge Machining (EDM) process and the dimensions of the samples were 100 mm x 50 mm x 6 mm. The process parameters were established based on the bead on weld studies and also by trial runs. The weld process parameters employed for PCGTA welding of Monel 400 and AISI 304 stainless steel using ERNiCu-7 are shown in Table 2.

Table 1 Chemical Composition of Base and Filler Metals

Base / Filler Metal	Composition, Wt%									
	Ni	Cu	C	Si	Mn	Fe	S	P	Cr	Others
Monel 400	65.38	Bal	0.10	0.40	1.07	2.11	Nil	Nil	Nil	--
AISI 304	8.13	Nil	0.045	0.39	1.64	Bal	0.006	0.022	18.01	--
ENiCu-7	67.6	Bal	0.03	0.9	3.2	0.95	0.006	0.009	---	0.05 (Al) 0.65 (Ti)

Table 2 Process parameters employed

Filler wire	Peak Current ( $I_p$ ) Amps	Base Current ( $I_b$ ) Amps	Frequency (Hz)	Argon Gas Pressure (psi)	Filler wire dia. (mm)
ENiCu-7	215	125	30	10-13	2.5

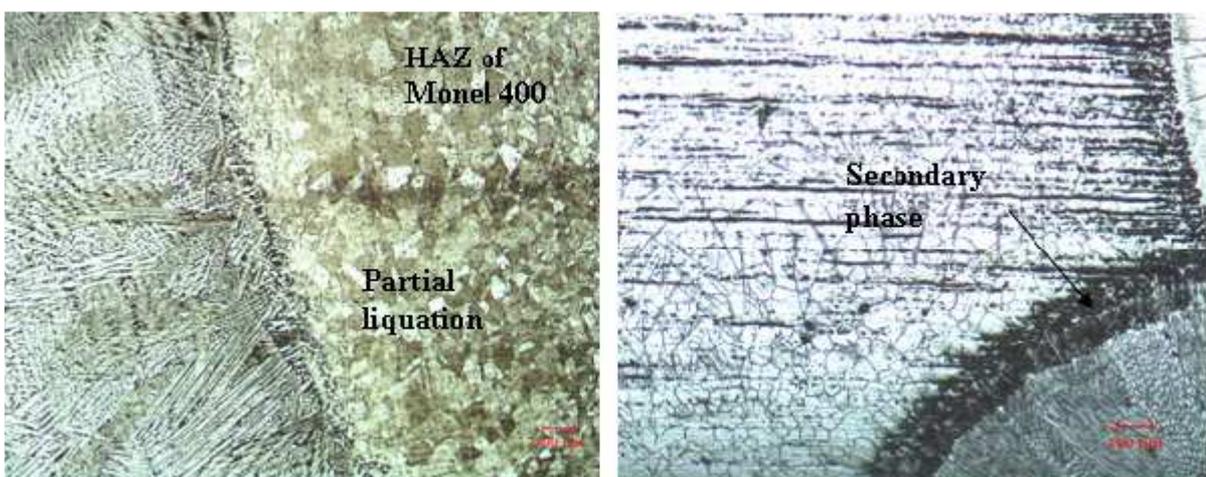
PCGTA welding was carried out on these dissimilar metals using a special welding jig (rigid fixture) with a copper back plate so as to hold the parts in alignment and to ensure for accurate grip without bending. Standard butt joint configuration (single V-groove having a root gap of 2 mm, size land of 1 mm and included angle of  $70^\circ$ ) was chosen for the current study. The weldments obtained by PCGTA welding technique employing different filler wires were assessed for their metallurgical, mechanical properties and hot corrosion behavior and are outlined in the subsequent sections. After welding, the PCGTA weldments were characterized using X-ray radiography NDT technique to determine the weld defects. Ensuing to the NDT results, the welded samples were sliced into coupons of various dimensions to conduct metallurgical, mechanical and hot corrosion tests. Dissimilar weld combinations of AISI 304 and Monel 400 were examined for microstructure at various zones of the weldment using optical microscope. Metallographic examination has been carried out on the region

named as 'composite region' whose dimensions are 30 mm x 10 mm x 6mm which covers all the zones (Parent metals - Heat Affected Zones (HAZs) - Weld Zone) of the weldments. Microstructures of parent metal and HAZ of Monel 400 are characterized using Marble's reagent and for parent metal and HAZ of AISI 304, electrolytic etching (10% Oxalic Acid; 6 V DC supply; current density of 1 A /Cm<sup>2</sup>) was used. Further the weldments were characterized for the mechanical properties. The samples are typically dimensioned as per ASTM E-8 standards and the tensile tests were performed using the Instron Universal testing machine to evaluate the tensile properties of the weldments. Three trials on each weldment were conducted to check the reproducibility of the results. A strain rate of 2 mm/min. was employed in the tensile studies. The fractured samples were characterized to understand the mode of fracture by SEM analysis.

To assess the performance of the weldments in the real time environments, the various zones of the welded coupons were subjected to hot corrosion studies. The coupons used for corrosion studies were mirror polished down to 1  $\mu$  before the corrosion run. Cyclic hot corrosion studies were performed on different zones of the weldments by exposing in the molten salt environment of K<sub>2</sub>SO<sub>4</sub> + NaCl (60%) mixture at 600 °C. Hot corrosion studies were performed on different zones of dissimilar weldments of Monel 400 and AISI 304 each measuring 10 x 10 x 6 mm; also on the composite region measuring 30 x 10 x 6 mm to estimate the corrosion behavior for 50 cycles (each cycle consists of 1 h heating followed by 20 min of cooling to room temperature) at 600 °C. A coating of uniform thickness with 3–5 mg/cm<sup>2</sup> of K<sub>2</sub>SO<sub>4</sub> + NaCl (60%) was applied using a fine camel hair-brush on the samples. The salt coated samples were first heated and dried at 200 °C in the oven. Each cycle consists of 1 hr heating followed by 20 min of cooling to room temperatures. The weight changes have been measured for all regions for each cycle using electronic weighing balance with a sensitivity of 1 mg. The weight gain or loss of the spalled scale was also included at the time of measurement to determine the rate of corrosion. The corroded samples of various regions were characterized for XRD and SEM/EDAX analysis.

### 3. Results and Discussions

Microstructure examination shown in Fig. 3.1 confirmed that the welds produced from PCGTAW process also reveal that the partial liquation zone on the HAZ side of Monel 400. Also there the formation of secondary phases was witnessed in the HAZ of AISI 304 for ENiCu-7 filler wire. The partial liquation zone is also observed adjacent to the HAZ of Monel 400 for ENiCu-7 which may tend to lower the mechanical properties and also the corrosion resistance of this zone. The welding filler wire ENiCu-7 could readily take into the solution of nickel, copper, chromium and iron to the level likely to be encountered in practice by dilution from parent metals. The weld region, therefore, will have the normal dendritic structure of single phase material, for this filler material.



**Fig.3. 1** Interface microstructure showing the PCGTAW weldments (a) Monel 400 side and (b) AISI 304 side

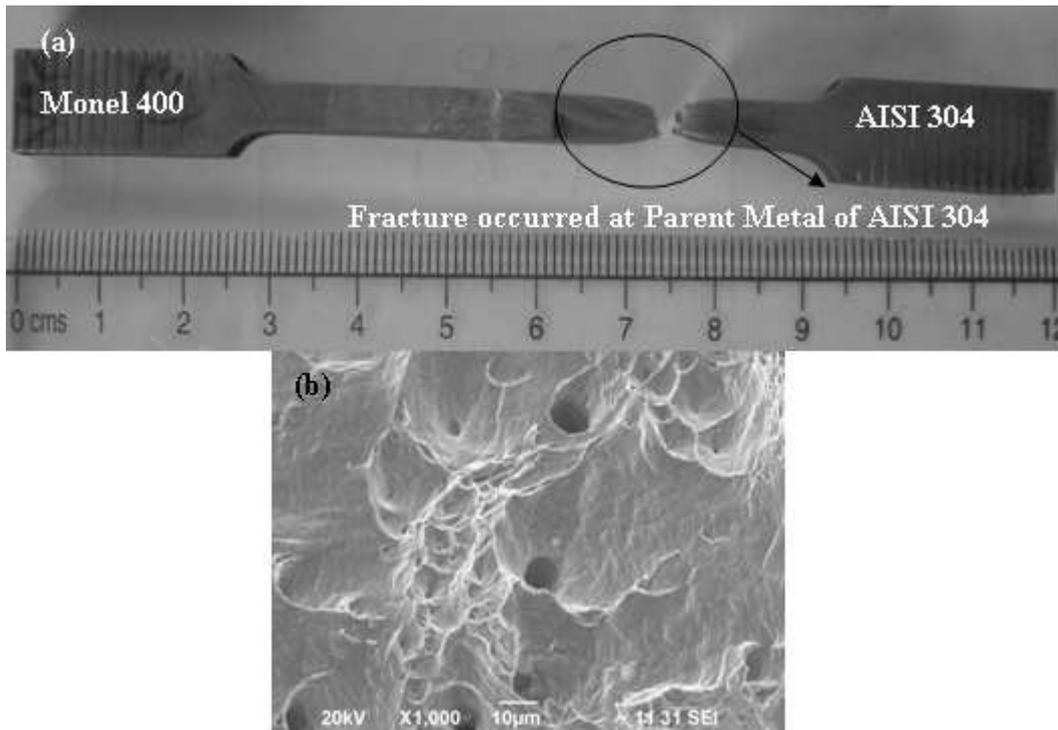


Fig. 3.2 (a) Fractured tensile sample (b) SEM fractograph

Tensile test trails on PC-GTAW samples show that the tensile strength is found to be maximum for ENiCu-7 [551 Mpa] and the tensile fracture has occurred at the parent metal side of AISI 304 for all the coupons. The solidification temperature range has a direct correlation to the solidification cracking susceptibility of a given alloy. Increased levels of Fe, Cr, Cu, and Si in nickel-base weld metal results in increased solidification temperature ranges and ensuring for minimal dilution [7]. This is witnessed on using ENiCu-7 filler while welding the dissimilar AISI 304 and Monel 400. Tensile results showed that the PCGTA weldments offered good tensile strength. It is evident that PCGTA welding normally yields refined grains at the weld region. In this case also, for PCGTA welded dissimilar Monel 400 and AISI 304, the failure occurred at the parent metal of AISI 304. It confirms that the weld strength of the PCGTA.

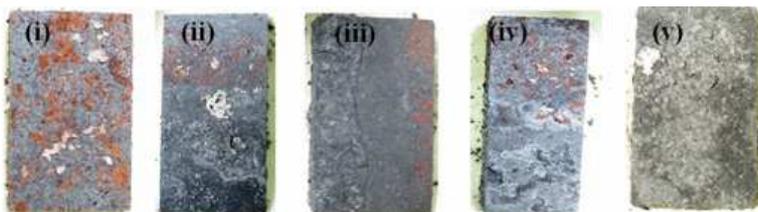


Fig. 3.3 Macrographs of the dissimilar weldments showing i) Parent Metal - AISI 304 (ii) HAZ - AISI 304 (iii) Weld (iv) HAZ - Monel 400 (v) Parent Metal - Monel 400 subjected to the molten salt environment of  $K_2SO_4 + 60\% NaCl$  at  $600^\circ C$ .

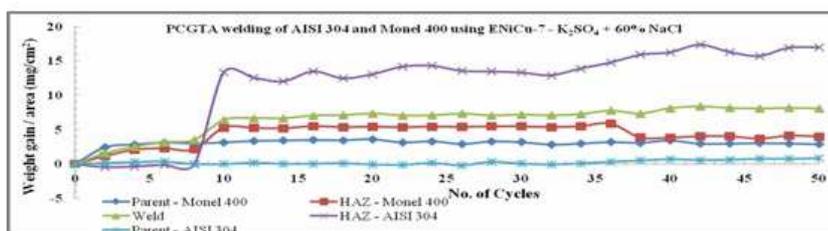
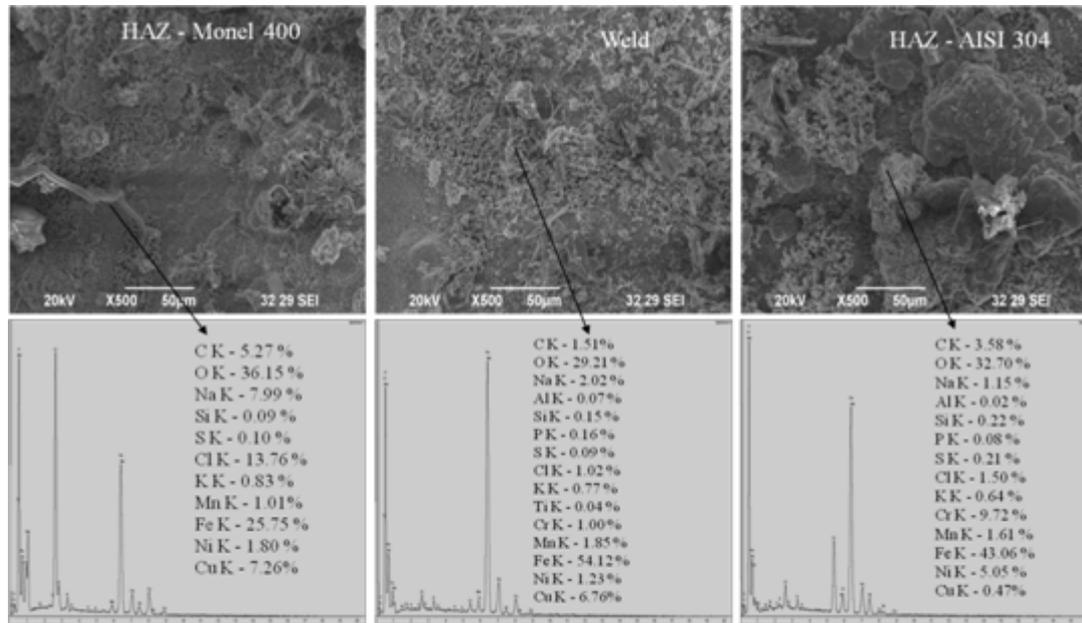


Fig. 3.4 Thermogravimetric plots of the various zones of the PCGTA weldments exposed in the molten salt environment

Weldments is higher or equal to the candidate materials employed. The degree of ductility and strength is found to be more for the weldments utilizing ENiCu-7, which is also evident from the formation of large dimples and micro-voids present in the weldments. Nickel and copper in the ENiCu-7 filler wire are completely soluble in each other thereby forming the iso-morphous system. The presence of copper strengthens the Nickel

to certain limited extent. Because of the high nickel content, a complete FCC structure would be formed in the weld region. The presence of Al and Ti in the ENiCu-7 filler wire also contributes for strength by precipitation hardening. The strengthening precipitates would be the Ni<sub>3</sub>Al and Ni<sub>3</sub>Ti. These precipitates tend to occupy the grain boundaries and exhibited strength.



**Fig. 3.5** SEM/EDAX analysis of hot corroded PCGTA welded dissimilar Monel 400 and AISI 304 (Composite Region) employing ENiCu-7 filler

Visual examination studies showed that in the ENiCu-7 weldments, a rough brown scale is formed on the HAZ of AISI 304; some red spots are formed along with brown scale in the HAZ of Monel 400 and a rough brown scale with white spots are appearing on the weld region. These scales continue to become thicker for every cycle. At the end of 50th cycle, the weld region has tarnished to dark brown color with white patches; the HAZ of Monel 400 has become brown color with accumulated white and red spots. An adhesive, visible white layer is also found in the HAZ side of Monel 400. On the HAZ of AISI 304, the appearance has changed to dark brown color with few white patches of the dried salt. SEM/EDAX analysis on ENiCu-7 weldments showed that the appearance of the oxide scales is found to be mushy shrubs found on the entire zone of HAZ of Monel 400. Furthermore, the weld region has several white oxide scales which are greater in size as compared to other zones. Whereas the scale in the HAZ of AISI 304, it is in the form of splats with cracks.

Hot corrosion behavior studies on PCGTA weldments showed that the corrosion due to this molten salt environment is vigorous on the HAZ of AISI 304 for ENiCu-7 filler wire. This could be due to the grain refinement during the process which is evident from the microstructure examination [Fig. 3.1]. Next to the HAZ of AISI 304, the weld region of ENiCu-7 also undergoes severe corrosion attack [Fig. 3.3]. It is clear from the SEM/EDAX analysis that this could be due to the absence or presence of lesser amounts of NiO. Presence of Cr in the weld and HAZ of AISI 304 might have formed the chromium chlorides, resulted in the high corrosion attack. Mohanty *et al.* [8] reported that the presence of alkali chlorides in the deposit causes much more aggressive hot corrosion attack than a salt deposit containing only alkali sulfates, and the mechanism of attack changes. Active oxidation, involving transport of metal chlorides in the liquid salt phase, destroys the normally protective Cr<sub>2</sub>O<sub>3</sub> scale. In an environment with NaCl deposits, adding aluminum to the subject alloy to generate a protective Al<sub>2</sub>O<sub>3</sub> scale should be able to increase the high-temperature corrosion resistance in a chloride environment [9, 10] Molten salts can penetrate into the alloy substrate via capillary action along voids. Fe and Cr then react with molten salt, where they are depleted in the alloy. Shores *et al.* [11] reported that iron and chromium chlorides, which may form at or below the metal/scale interface, can migrate towards the scale/gas interface as dissolved species in the molten salt phase. The corrosion behavior of PCGTA weldments have shown clearly that the parent metal AISI 304 showed better corrosion resistance towards the hot corrosion.

#### 4. Conclusions

- [1] Sound joints of Monel 400 and AISI 304 could be obtained by PCGTA welding process employing ERNiCu-7 filler

- [2] Formation of partially mixed zone at the HAZ of Monel 400 and the unmixed zone at the HAZ of AISI 304 was observed.
- [3] Hot corrosion studies corroborated the parent metals exhibited better corrosion resistance compared to the other zones of the weldment when exposed in the molten salt environment.

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