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EVALUATION OF CORROSION RESISTANCE OF A DUPLEX STAINLESS STEEL "FERRALIUM" IN DEAD SEA BRINE

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ABSTRACT

Corrosion behavior of Ferralium Alloy 255 during service in the environment of concentrated Dead Sea brine has been investigated. It was found that, the corrosion attack is intergranular and exists only in the weld heat effected zone (HAZ). It starts at ferrite/austenite grain boundaries and in the ferrite matrix, where chromium nitride precipitates and then propagates with acceleration in the rest of the metal due to the abrasive action of the slurry.

INTRODUCTION

Ferralium Alloy 255, a registered trademark of Bonar-Langey Alloys, Ltd., is a very practical duplex stainless steel consisting of austenite in a ferrite matrix of about equal portions, or vice versa, which enables the alloy to possess a combination of properties that can not be achieved by either fully austenitic or fully ferritic stainless steels. This combination of properties has candidated duplex stainless steels for the sour well applications where moderate agreessive environments exist (1, 2). The excellent resistance to corrosion has resulted in the application of the alloy in a number of processing plants (3, 4). In addition, this alloy has proved to possess good weldability (5).

These properties of the alloy have led the Arab Potash Company (APC) in Jordan to use the Ferralium in some areas of aggressive environment in the processing plant such as the Potassium Chloride production unit. It should be mentioned that the KCl compound is an important element in the fertilizer industry.

However, this alloy-which is now in use is suffering from corrosion and erosion, and any reduction in corrosion rate will be a saving, as the cost of 1 kg of this alloy is approximately $18 (6). The catastrophic attack has been observed in welded parts near the weld joint, as can be seen in Fig. 1. Thus, it was decided to investigate the reasons behind this corrosion.

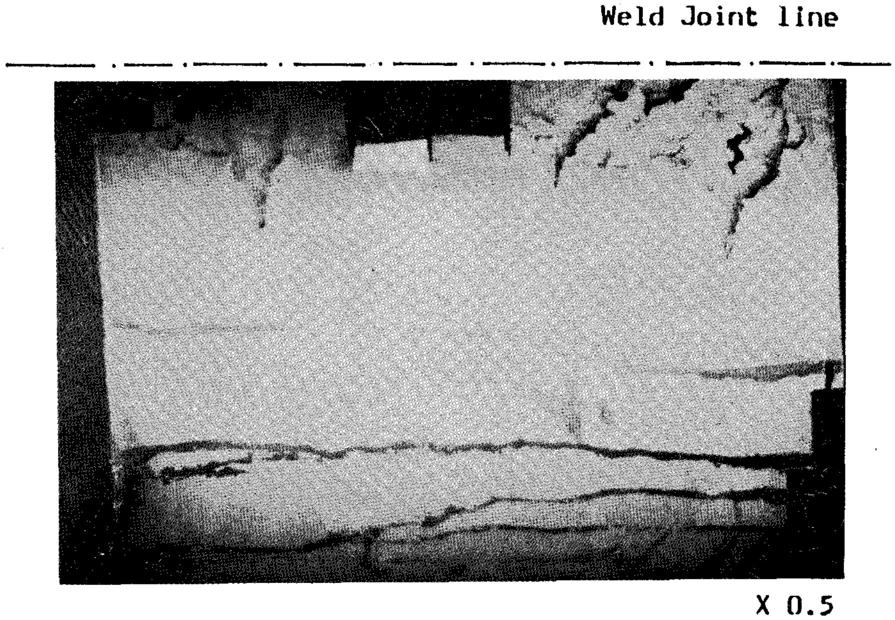


Fig. 1: Part of the corroded spool of Ferralium Alloy 255, which has been drawn from service.
(The stars indicate the areas from which samples have been prepared for metallographic examination)

EXPERIMENTAL

A severely corroded spool of Ferralium Alloy 255 (composition is given in Table 1, has been drawn from service. The spool was fabricated from a 6 mm thick plate through rolling and manual arc welding. The final shape of the spool is shown schematically in Fig. 2. The composition of the welding electrode was similar to that of Ferralium. The spool acts in the process as a diffuser for hot brine (approx. 93°C) inside the cyclones. The composition of the brine is given in Table 2.

Table 1

Compositions of Ferralium Alloy 255 (Wt. %)

C (Max)	Mn	P	S	Si	Cr	Ni	Cu	Mo	N	Fe
0.08	1.5	0.04	0.03	1.0	24-27	4.5-6.5	1.5-2.5	2-4	0.1-0.25	Balance

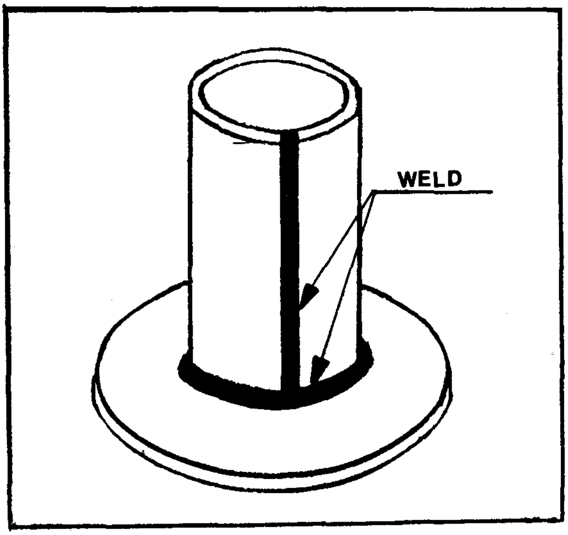


Fig. 2: Schematic diagram showing the final shape of the Ferralium spool.

Table 2

Compositions of the Dead Sea Brine used in process (Wt. %)

KCl	NaCl	$MgCl_2$	$MgBr_2$	CaCl	H_2O
6.3	4.5	25.37	0.68	4.78	58.32

Three transverse samples of the corroded area were cut from the damaged spool, Fig. 3. Sample A, with severe corrosion was the nearest to the weld joint, sample B

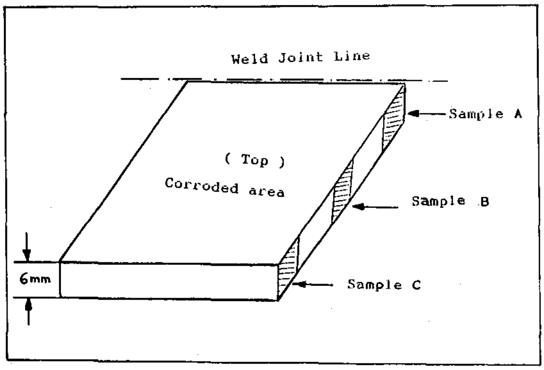
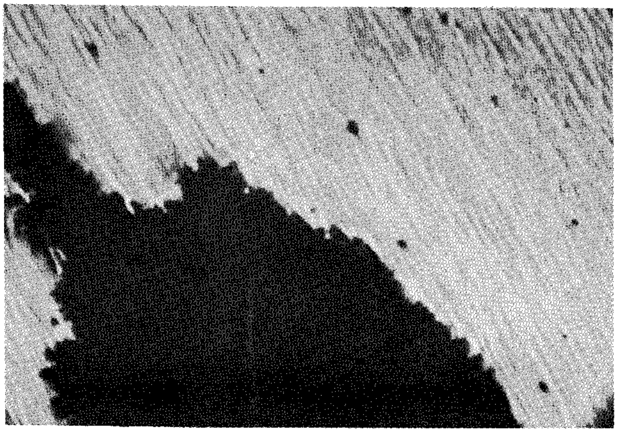


Fig. 3: Schematic diagram showing the locations of metallographic samples.

(moderately attacked) was taken from the heat affected zone (HAZ), and sample C was cut from an area where there was no attack. In addition, sample D was prepared from a new plate of Ferralium not subjected to any corrosive environment for comparison purposes. The four samples were prepared for metallographic examination. The corroded surface of sample A was selected for carbon extraction replicas. The replicas were examined under the Transmission Electron Microscope (Jeol 100 KV TEM).

RESULTS AND DISCUSSION

Examination of the HAZ (samples A and B) under the optical microscope shows intergranular corrosion attack, mostly along the austenite-ferrite boundaries as can be seen in Fig. 4.



A. Low magnification (× 2000)

B. High magnification (× 8000)

Fig. 4: Photomicrographs of sample A, showing intergranular corrosion in Ferralium Alloy 255.

In addition, some pits were observed mostly in the ferrite phase as can be seen in Fig. 5. The attack of corrosion was observed to be more in sample A than B, as sample A was nearer to the weld joint. This type of intergranular corrosion was observed in stainless steel type 304 by many researchers, e.g., Fontana (7), and was also observed in zinc die casts by Askeland (8). Sample C, which was taken away from the HAZ did not show any type of corrosion attack, as can be seen in Fig. 6. Similar results were obtained from sample D which was cut from a new plate. This indicates that sensitization of Ferralium occures in the HAZ as a result of the heat generated during welding process.

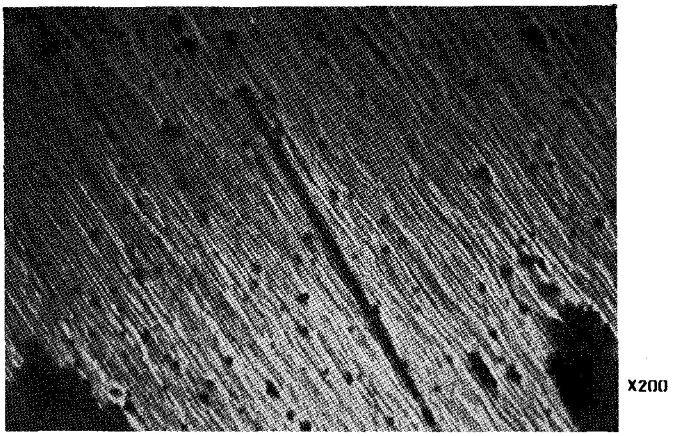


Fig. 5: Photomicrograph of sample A, showing pits mostly in the ferrite phase. (× 200)

Fig. 6: Photomicrograph of sample C, showing the absence of any attack in the structure. (× 800)

Examination of the carbon extraction replicas under the TEM shows precipitation of chromium nitrides (Cr_2N), as identified by spot analysis EDX (Energy Dispersive X-ray), Fig. 7. The precipitates were not uniformly distributed throughout the structure, some were in line, probably situated at the grain boundaries. During cooling from elevated temperatures particles usually prefer to precipitate at the grain boundaries in micro alloyed steels (9) and stainless steels (7).

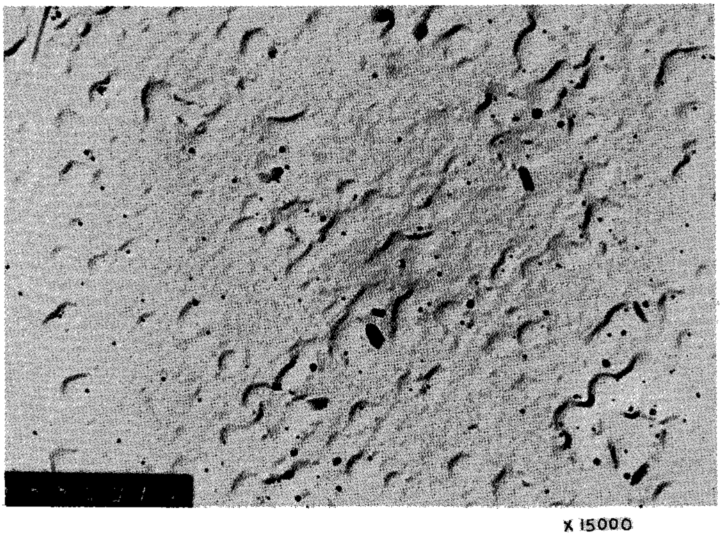


Fig. 7: Cr_2N Precipitation observed in the HAZ of Ferralium. (× 15000)

It is suggested that, precipitation of Cr_2N takes place preferentially at the ferrite-austenite boundaries during cooling from weld temperature. This results in chromium depleted areas adjacent to the grain boundaries; accordingly these areas would be later attacked by the Dead Sea Brine during the process of KCI production. This is not surprising, since these particles can create galvanic cells easily, as the grain boundaries are anodic, compared to the rest of the grains which are cathodic, and the result is intergranular corrosion of the steel.

The slightly preferred attack, and pits initiated in the ferrite phase, suggest that the solute nitrogen formed in this phase as a result of the decrease of the austenite phase during heat input of the welding process, is precipitated as chromium nitride in the ferrite phase, as suggested by Kawasaki *et al,* (10), who examined the corrosion of similar duplex stainless steel. In addition, the solubility of nitrogen in the ferrite phase is lower than that in austenite (11).

The appearance of grooves, valleys, pits, and rounded holes on the corroded surface of the alloy, even by unaided eye, Fig. 1, is due to the abrasive action of the slurry, acting in the direction of the corrosive flow. This permits much easier access of oxygen to the corroded surface, according to Fontana (7) and Smith (12). Such an aggressive flow would accelerate the rate of corrosion in the metal due to the relative motion of the fluid and the metal surface.

Many investigations have reported the precipitation of chromium nitride particles during cooling the duplex steels from high temperature processes, like welding and annealing. Sridhar *et al,* (13), had identified Cr_2N precipitation at the ferrite grain boundaries in the Ferralium 255 Alloy after fast cooling (water quenching) of samples annealed at 1120-1175°C. Kawasaki *et al,* (10), suggested that chromium nitrides will precipitate in the ferrite phase of duplex stainless (ASTM A790) during cooling from welding temperature process, regardless of the cooling rate; however, corrosion was observed only in the rapid cooled samples. They explained their results by the argument that, during rapid cooling, chromium near the Cr_2N precipitates is depleted because the time available for diffusion is insufficient for chromium to heal the chromium depletion. During slow cooling (air cooling), chromium diffusion will heal the depleted areas.

However, the present study shows, Cr_2N precipitates in the HAZ, despite the fact that the corroded spool has been air cooled after the welding process, and it seems that water quenching by Kawasaki *et al,* (10) has resulted in greater chromium depletion in contrary to air cooling in this study, which may have permitted some chromium diffusion, but has not healed the depleted areas completely, in accord with Sridhar *et al,* (13). In addition, there are many other factors which play important role in controlling the Cr_2N precipitation in Ferralium (13), such as annealing time, prior cold work, and section thickness. In these sections (3-10 mm), water quenching resulted in higher corrosion rates than air cooling. However, a slow cooling in insulating K-wool resulted in higher corrosion rates than either air cooling, or water quenching, and it seems that there is an optimum cooling rate for each specific sample condition to obtain best corrosion resistance properties.

It is suggested from this study, that the remainder of the Cr_2N particles after healing process, are still enough to initiate pits at the ferrite-austenite boundaries, and in the ferrite matrix through the attack of the slurry. These pits coalesce at the boundaries and give intergranular appearance. The attack will propagate with acceleration through the metal due to the corrosion process.

CONCLUSIONS

The following conclusions can be drawn as to the corrosion resistance of Ferralium Alloy 255 in Dead Sea brine.

1. The corrosion susceptibility of the steel in Dead Sea brine is greater in the HAZ, with the result of poor corrosion resistance in those areas.

2. The corrosion attack is mostly at ferrite-austenite grain boundaries and inside the ferrite phase, mainly due to the chromium depletion in the areas ajacent to the chromium nitrides precipitated during cooling, from welding temperature.
3. Cooling rate of welded parts is not the only factor controlling the Cr_2N precipitation and the healing process of the depleted areas through chromium diffusion. An optimum cooling rate for each specific condition should be found for best corrosion resistance.

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