REPAIR WELDING AND METALLURGY OF HP-MODIFIED ALLOY AFTER LONG TERM OPERATION

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Abstract
This study aimed to improve the weldability of HP-modified cast alloy, Fe-35%Ni-25%Cr-Nb, Mo, W, which had been in service for several years, relating the repair weldability to the steel metallurgy.

From a programme of weldability tests, low-ductility secondary phases, $M_23C_6$ and Nb-Ni-Si intermetallic compound, which precipitate during high temperature operation, had a strong influence on the weldability. Solution-annealing prior to repair welding is considered to be an important issue to recover the ductility of parent metal. However, if the annealing temperature is too high, this may not be acceptable from the viewpoint of high temperature strength.

Some welding parameter variables such as heat-input, preheat and interpass temperature controls were also investigated, however, these were not found to exert a significant effect relative to the solution-annealing. Solidification cracking in the weld metal may be a problem even when welding solution-annealed specimens, although solution-annealing may reduce the cracking susceptibility of the parent metal.

1. INTRODUCTION
High alloy austenitic steels have been widely used in petrochemical plants for ethylene pyrolysis furnace tubes. They are exposed to extremely high temperatures of approximately 800-1100ºC during operation. By virtue of this high temperature operation, damage mechanisms such as carburisation, oxidation and creep can be operative, requiring the tubes to be replaced at intervals of approximately five or six years. Even though HP grade (Fe-35%Ni-25%Cr) alloys have relatively good resistance to the damage mechanisms mentioned, the materials may still become sufficiently embrittled that the weldability is deteriorated after operation and then the repair welding is difficult.

Damage mechanisms and welding problems associated with high alloy steels have been studied for over three decades, and there have been a number of suggestions [1-8] concerning the weld cracking mechanism in the parent metal and repair welding procedure. However, a systematic study to improve repair weldability of HP grade alloys, looking in particular at the welding metallurgy, has not been carried out in sufficient depth to be of assistance to actual field repairs. The practices adopted for field repairs are, therefore, still dictated by previous practical experience. The present study aimed to investigate the relationship between repair welding and the steel metallurgy in order to try to improve the weldability of HP-modified cast alloy, Fe-35%Ni-25%Cr-Nb, W, Mo (hereafter referred to as HP-Nb, Mo, W), which had been in service for several years in an actual plant.

The microstructure of Nb-containing HP alloys comprises three phases in the as-cast condition, namely an austenite matrix with niobium carbide (NbC) and chromium carbide ($M_7C_3$) precipitates. During high temperature operation, NbC is transformed to a Nb-Ni-Si intermetallic compound by the diffusion of nickel and silicon to the niobium carbide boundary, and the $M_7C_3$ on dendrite boundaries is transformed to $M_{23}C_6$, or $M_{23}C_6$ itself precipitates in the austenite matrix as a result of the ingress of carbon from the process flow via carburisation [4][5]. These secondary phases severely reduce the weldability of service-aged material because of their brittle nature [5] or through the liquation caused by the lower melting point of the Nb-Ni-Si intermetallic phase [4]. It is therefore apparent that the control of these secondary phases, for example by heat treatment, must be an important factor for the improvement of weldability, although the metallurgical effect of heat treatment has yet to be satisfactorily explored. In addition, there has only been limited study to determine the effectiveness of welding
parameter control in improving repair welding [1][2]. The present study, reported in this paper, has mainly focused on these two matters.

2. EXPERIMENTAL DETAILS

2.1 Material
The HP-Nb,Mo,W tubes removed from an ethylene pyrolysis furnace after several years of operation were used for this study. The diameter and thickness of the tubes were approximately 108mm and 10mm respectively. The chemical composition of as-cast HP-Nb,Mo,W alloy as detained on the mill certificate is shown in Table.1. The service-aged tube specimen contained 0.6-0.8 mass% carbon close to the inner wall as a result of carburisation. The tubes were measured to have been carburised to half of the thickness using by a ferrite meter, LST-11 of Kett Science Research Co. Ltd.

Two welding electrodes for Gas Tungsten Arc (GTA) welding were used for the weldability test; one was essentially a matching filler (MF) and the other was AWS A5.14 ER NiCrMo-3. The compositional information as detained on the mill certificate of the tube, the consumable certificate of MF, and the typical specification of ER NiCrMo-3 defined in AWS A5.14 are shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Chemical compositions of alloy tube and welding electrodes</th>
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<tr>
<td>C  Si  Mn  P  S  Ni  Cr  Mo  Nb  W</td>
</tr>
<tr>
<td>HP-Nb, Mo,W tube</td>
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<tr>
<td>MF (matching filler)</td>
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<tr>
<td>ER NiCrMo-3</td>
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2.2 Heat treatment
The details of the solution-annealing heat treatments carried out on parent material samples to investigate the effect on the improvement of mechanical properties, ductility in particular, are detailed in Table 2. The heating rate was 250ºC/hr and the samples were air-cooled.

<table>
<thead>
<tr>
<th>Table 2 Heat treatment conditions</th>
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<tr>
<td>Temperature(ºC)</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>1100</td>
</tr>
<tr>
<td>1200</td>
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<tr>
<td>1250</td>
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2.3 Microstructural examination
The microstructures of the as-cast sample, service-aged sample, and samples after solution-annealing and welding were examined by light microscopy. A sample from each heat treatment condition was prepared to a 1µm diamond finish using standard metallographic preparation techniques. The samples were electrolytically etched using 10% oxalic acid with 3V for 20sec. A Scanning Electron Microscope (SEM) was also used to examine the surface of a fusion line crack.

2.4 Phase analysis
In addition to the microstructural examination, Back Scattered Electron image (BSE) and X-Ray Diffraction (XRD) analyses were carried out to check the composition and area fraction of secondary phases precipitated in the samples.
2.5 Tensile testing
Ambient temperature tensile testing was carried out to confirm the effect of solution-annealing on the recovery ductility and strength. The tensile test specimens were extracted from the inner and outer sides of the tube; it was expected that the inner side would be less ductile than the outer side due to the difference of carbon content. Figure 1 shows the configuration of the tensile test specimen.

2.6 Weldability testing
Two types of weldability test were performed; one was a ‘bead-on-plate’ test and the other was a self-restraining test. The configuration of the self-restraining test specimen for the tube sample was based on the Slotted Plate Weld Evaluation Test specimen described by Alloy Casting Institute and Welding Research Council [9], and a specimen used in the experiment by Shinozaki et al [5]. Figure 2 shows the configuration of test specimen. The welding was carried out using the manual GTA process. The welding current was varied between 70 and 170A to control the heat-input. The standard joint design was a V-groove with a 3mm root-gap; a narrower root gap of 1.5mm, in combination with a U-groove, was also used to check the effect of joint design. In addition to the welding current and joint design variables, the effect of preheat and interpass temperature (using levels of 200 and 400°C respectively) and the use of ER NiCrMo-3 filler wire were also examined. After welding, four transverse sections of each weldment were prepared and examined using a light microscope to check for the presence of cracking.

3. RESULTS

3.1 Microstructural transformation by solution annealing
The microstructures of the as-cast, service-aged and solution-annealed samples are shown in Fig 3. From the BSE and XRD analyses, NbC and M₇C₃ precipitates were identified on the initial dendrite boundaries in the as-cast sample (Fig 3a). After high temperature operation, it was confirmed that each phase had been transformed to Nb₃Ni₂Si (γ-phase) and M₂₃C₆ along the former dendrite boundaries (Fig 3b) as suggested in a previous study by Shinozaki et al[5]. Small M₂₃C₆ particles had also precipitated in the austenite matrix. It was suggested that some high alloys precipitate G-phase (Nb₆Ni₁₁₆Si₇) [4][10], however, this was not detected in the present HP-Nb,Mo,W alloy.

Figures 3c-3f show the microstructures after solution-annealing at 1000°C, 1100°C, 1200°C and 1250°C for 1 hour. Annealing at a temperature of 1000°C (Fig 3c) did not give rise to a particularly marked microstructural transformation from the service-aged condition. There were some indications that annealing at 1100°C did cause...
dendrite boundaries and some precipitates remained within the matrix phase. Most of the secondary phases precipitated in the matrix dissolved during annealing at 1200°C (Fig 3e), and some segregation to the former dendrite boundaries could be observed. After annealing at 1250°C, there are very few small precipitates remaining in the matrix (Fig 3f) and the segregation to the former dendrite boundaries had progressed compared with Fig 3e. There is also some coarsening of the second phase particles at 1250°C (Fig 3f).

Fig.3 Light photomicrographs of HP-Nb,Mo,W (a) as-cast (b) service-aged and, (d-f) after solution-annealed with one hour at (c) 1000°C (d) 1100°C (e) 1200°C (f) 1250°C

The change in area fraction of each of the secondary phases, measured by BSE, is shown in Fig 4 and 5. Figure 4 shows the effect of solution-annealing temperature while Fig 5 shows that of annealing time. In the service-aged sample, there was around 10% M$_{23}$C$_6$ and 4% Nb$_3$Ni$_2$Si. From Fig 4, it is evident that the area fraction of M$_{23}$C$_6$ gradually decreased with increased the solution-annealing temperature between 1000°C and 1200°C, however, it was increased at a temperature of 1250°C. The intermetallic ç-phase, Nb$_3$Ni$_2$Si, was not dissolved even at 1200°C but was completely dissolved at 1250°C. NbC which was lost during operation began to reform during annealing. As shown in Fig 5, the area fraction of M$_{23}$C$_6$ decreased with increased annealing time, however, Nb$_3$Ni$_2$Si appeared less sensitive to annealing time at a temperature of 1100°C.
Figures 6 and 7 show the relationship between solution-annealing temperature and elongation and tensile strength. Both the ductility and tensile strength were recovered by solution-annealing, with the extent of recovery increasing with increased annealing temperature. The effectiveness of annealing time was also investigated at a temperature of 1100°C between 30min and 2 hours, however, the degree of improvement in ductility and strength was small.

3.3 Weldability testing

3.3.1 Bead-on-plate test
The inner surface of the service-aged tube was shaved by 1mm, 4mm and 7mm in order to check the effect of carbon content on weldability. After welding, the weld was inspected using dye penetrant testing and a number of transverse sections prepared for examination. No cracking was detected in any of the samples.

3.3.2 Self-restraining weldability test
Table 3 summarises the results of self-restraining weldability tests.

All service-aged samples exhibited through-thickness cracking in the parent metal, originating from the fusion boundary area. Many small cracks were also observed in the base metal. The service-aged sample had through-thickness cracking even with careful control of the welding parameters.

The sample which had been solution-annealed at 1100°C still exhibited cracking although some improvement was gained from adjustment of preheat at 400°C and joint design with a narrower V-groove or a U-groove.

In the case of the sample solution-annealed at 1200°C, no cracking was observed in the parent metal. However, solidification cracking was evident in the weld metal when 200°C preheat and the ER NiCrMo-3 filler wire were employed. A higher solution-annealing temperature is effective towards the avoidance of cracking in parent metal, but the risk of hot cracking in weld metal still remains.
3.4 Crack observation

Figure 8 shows a region on a transverse section of the service-aged sample after welding using the matching filler wire. A large crack is evident, propagating approximately coincident with the fusion boundary; some smaller cracks can also be seen in the base metal. Figure 9 shows the weld made using the ER NiCrMo-3 filler wire. The extent of cracking was considerably reduced by the use of the more ductile ER NiCrMo-3 electrode which seemed to absorb the contractional strains.

Figure 10 is a SEM image of a fusion boundary crack. The phases present on the crack surface were analysed, and showed that $M_{23}C_6$ exhibited fully brittle fracture, while the cracking surface of $Nb_3Ni_2Si$ was more ductile in appearance. No liquation cracking was observed. Figure 11 shows a BSE image of a region of cracking in the service-aged sample. It can be seen that the cracks propagated along the interface between the secondary phases (both $Nb_3Ni_2Si$ and $M_{23}C_6$) and the matrix, or within the secondary phases. Cracking associated with $M_{23}C_6$ seemed to be the preferred crack propagation route compared to $Nb_3Ni_2Si$.

![Fig 8](image1.jpg)

**Fig 8** Light photomicrograph of weld cracking in service-aged sample (electrode; Matching Filler)

![Fig 9](image2.jpg)

**Fig 9** Light photomacrograph of weld cracking in service-aged sample (electrode; ER NiCrMo-3)
4. DISCUSSION

4.1 Effectiveness of heat treatment
Solution-annealing is effective in recovering the ductility and weldability of service-aged material through the dissolution of brittle secondary phases. Higher solution-annealing temperatures than 1200°C might be expected to be better, however, judging from the microstructure observed after 1250°C solution-annealing, the secondary phases existed as discrete particles on the austenite grain boundaries and they were coarser than the microstructures generated by solution-annealing below 1200°C. At the lower annealing temperatures, the grain boundary decoration was more continuous, with second phase particles forming a ‘necklace’ effect on the austenite grain boundaries. The discontinuous coarse array of secondary phases observed at 1250°C may lead to a reduction in the high temperature creep strength[11] since the movement of dislocations at high temperatures cannot be blocked at the grain boundary. From the results of the weldability tests, 1100°C annealing did not give adequate improvement to the weldability. Thus, a heat treatment temperature around 1200°C would be preferable from a viewpoint of the improvement of the weldability and also to ensure high temperature strength for subsequent operation.

4.2 Weld cracking mechanism
A previous study [5] suggested that Nb$_3$Ni$_2$Si phase would be more detrimental to crack initiation than M$_{23}$C$_6$. According to this report [5], the network of secondary phases covering the former dendrite boundaries restricts the deformation and then increases the stress concentration on these brittle phases resulting in cracking; Nb$_3$Ni$_2$Si would be expected to play the most significant role because it is inherently more brittle than M$_{23}$C$_6$. However, the results presented in this paper suggest that this phase does not have a significant effect on the weldability. It is concluded from the experimental results presented that the Nb$_3$Ni$_2$Si phase would provide a lesser contribution towards cracking than M$_{23}$C$_6$. Firstly, Nb$_3$Ni$_2$Si phase tends to form small eutectic lamellar-type structure with ductile austenite as shown in Fig 11 and the austenite would be able to absorb more of the contractional stress. Secondly, the grain boundary area occupied by M$_{23}$C$_6$ is greater than that of Nb$_3$Ni$_2$Si, so the M$_{23}$C$_6$ provides a preferential crack propagation path. In fact, it appears that most of the cracks observed in this study had propagated along the M$_{23}$C$_6$, as shown in Fig 11. This evidence suggests that control of the M$_{23}$C$_6$ phase may be more important than that of Nb$_3$Ni$_2$Si phase in controlling weldability.

4.3 Welding parameters
There have been various suggestions from previous studies relating to weld parameter control[1][2]. According to the present study, the key factor to improve the weldability is the reduction of the restraint because the parent metal has low ductility even after solution-annealing. The cracking in the parent metal is the main concern, however, the solidification cracking in the weld metal must also be concerned. The restraint and some impurities segregated during the welding may increase the risk of solidification cracking. Especially, when the parent metal
has poor ductility and is unable to absorb significant contractional strain, and thus the weld metal has to absorb greater strain than when welding new material.

The following suggestions can be made based on the results of the present study, from the viewpoint of reducing restraint and the prevention of solidification cracking:

1. Preheat may be beneficial in reducing the risk of cracking in the parent metal. Even the use of relatively high preheat temperatures would be acceptable because HP alloys do not usually precipitate ω-phase which is harmful to other austenitic steels. However, a risk of solidification cracking was also found when preheat was employed.

2. Although the effect of heat input was not clear from this study, the use of lower heat input may be favourable because of the avoidance of solidification cracking and of less restraint caused by the thermal expansion and reduced dilution.

3. The use of a narrower root-gap appeared beneficial, but care is required to ensure adequate back-shielding.

4. The use of a more ductile filler metal is beneficial as it is able to absorb more of the contractional strains. ER NiCrMo-3 filler metal has lower high temperature properties than HP-Nb, Mo,W, however, it is expected to be better than Alloy 800.

5. The sensitivity to solidification cracking in repair welding seemed higher than in original welding so that the general requirements when welding austenitic steels such as lower heat input, lower preheat and interpass temperature and good joint cleanliness should be adhered to.

5. CONCLUSIONS
From the programme of mechanical testing, microstructural examination, heat treatment and weldability evaluation carried out, the following conclusions can be drawn with respect to improving the weldability of the HP-Nb,Mo,W casting alloy:

1. The weldability tests clearly demonstrated a beneficial effect of solution-annealing in improving the weldability. A minimum annealing temperature of 1100ºC should be adopted, although 1200ºC gave improved weldability. A temperature of 1250ºC gave improved ambient temperature strength, elongation and weldability, however, it may reduce the high temperature strength in the subsequent operation.

2. The effect of welding parameter control on weldability is limited compared to that of solution-annealing, however, the use of lower heat input and a narrower root-gap appear to be beneficial.

3. In order to reduce the risk of cracking in the parent metal caused by the contractional strains, the use of a more ductile filler metal, for example AWS A5.14 ER NiCrMo-3, would be beneficial provided the high temperature strength is adequate for the required service.

4. The risk of cracking in the parent metal can be reduced by solution-annealing, however, there is still a risk of solidification cracking in the weld metal. From a viewpoint of the avoidance of solidification cracking, lower heat input, preheat and interpass temperature may be beneficial.
REFERENCES


