THE DEVELOPMENT OF A NEW WELDING PRODUCT FOR JOINING SILICON-MOLYBDENUM DUCTILE IRON EXHAUST MANIFOLDS TO STAINLESS STEEL CONVERTER HOUSINGS

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Abstract

This paper outlines the development of a new welding product for use in welding silicon-molybdenum ductile iron automotive engine exhaust manifolds to ferritic stainless steel catalyst cans. An existing Ni-Fe-Mn welding product had been previously used with success in this application. More demanding service conditions, however, began to produce cracking in the heat-affected-zone (HAZ) of the ductile iron manifold and limit service life. This phenomenon has been linked to the presence of aligned secondary graphite within the ductile iron HAZ and stress-accelerated oxidation cracking along the aligned graphite particles. Thermo-Calc® software was used to facilitate the development of a Ni-Fe-Mn-Cr-Nb welding product which possesses a more stable microstructure and serves also to enhance the resistance of the ductile iron HAZ to cracking during service.

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Introduction

In the earlier chapters of automotive history, little consideration was given to extension of the lifetime of exhaust components. However, within the past two decades, continually heightening emphasis upon increasing fuel efficiency and emissions control has forced exhaust temperatures upward and placed increased demands upon components. Exhaust temperatures as high as 870°C may be attained in today’s vehicles. One answer to these challenges has been the use of fabricated manifolds, which have performed admirably. More recently, even higher exhaust temperatures have forced a second look at an old design - the cast iron manifold. This old technology has been refurbished with a new material - Si-Mo modified ductile cast iron.

New designs require placement of the catalyst can closer to the engine for faster light off, necessitating placement of a dissimilar weld connecting the Si-Mo ductile cast iron manifold to the ferritic stainless steel catalyst can. Successful fabrication of a durable close-coupled part required development of a new, stabilized, Fe-Ni-Mn-Cr-Nb welding wire called NI-ROD® filler metal 44HT. Durability testing of parts fabricated using the new welding product has shown that the welding material provides the required high-temperature performance, which is superior to that of previously used welding materials.

Past Material Developments

INCO (International Nickel Co.) discovered the beneficial effect of low carbon solubility (0.02% at room temperature) in nickel in the 1940's. Since then, nickel and nickel alloys have been used to arc weld cast iron. Since gray cast iron has nearly no plastic ductility, a weld metal was needed to prevent cracking at the HAZ due to shrinkage stresses imposed by the weld. When gray iron was the material being welded, dilution of the pure nickel weld metal used initially by the cast iron produced graphite in the weld metal upon cooling, causing a volume expansion in the weld and a lowering of shrinkage stress. Graphite inclusions in the nickel weld metal also improved machinability.

As both castings and weld materials advanced in sophistication, ductile cast irons were developed which possessed much better plastic ductility and reduced the need for minimization of weld stress. Other Ni-Fe and Ni-Fe-Mn compositions were developed in order to meet higher strength and ductility requirements. The Ni-Fe-Mn NI-ROD filler metal 44 was the most recent product that continued use of the graphite rejection principle. However, graphite formation in welds proved to compromise performance in some applications, and since manifold welds do not require machining, the focus of alloy design began to shift toward stabilization of the graphite via carbide formation.

Performance of Ni-Fe-Mn Welding Product in Exhaust System Service

Because the Ni-Fe-Mn welding product had performed satisfactorily in previous applications, it was first considered for use in fabricating the close-coupled joint between the Si-Mo ductile cast iron manifold and the 409 stainless steel (see Table 1 for compositions of all alloys discussed in this paper) converter housing, using a pulsed gas metal arc welding process. However, dynamometer testing of the fabricated part resulted in an unexpected failure. The dynamometer test consisted of cycles involving engine operation at full load wide-open throttle for 5 minutes followed by cold motoring of the engine with cold coolant circulated through the cooling passages. Cycling was continued for 150 to 200 hours. The maximum temperature of the weld joint connecting the manifold to the converter housing varied from about 845°C to 870°C. The failure occurred as cracking in the HAZ of the Si-Mo ductile cast iron.
Table I: Chemical Composition of the Alloys of this Study  
(Weight %, Nominal Unless Indicated)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Cb</th>
<th>Ni</th>
<th>Ti</th>
<th>Si</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Mo Ductile Cast Iron</td>
<td>3.45</td>
<td>0.03</td>
<td>Bal.</td>
<td>0.3</td>
<td>---</td>
<td>0.1</td>
<td>---</td>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>409 Stainless Steel</td>
<td>0.08*</td>
<td>11</td>
<td>Bal.</td>
<td>1†</td>
<td>---</td>
<td>---</td>
<td>6XC†</td>
<td>1†</td>
<td>---</td>
</tr>
<tr>
<td>NI-ROD Filler Metal 44</td>
<td>0.30</td>
<td>---</td>
<td>Bal.</td>
<td>11</td>
<td>---</td>
<td>44</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
</tr>
<tr>
<td>NI-ROD Filler Metal 44HT</td>
<td>0.03</td>
<td>7</td>
<td>Bal.</td>
<td>11</td>
<td>0.7</td>
<td>44</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
</tr>
</tbody>
</table>

*Maximum  
†Minimum

In order to characterize the nature of the failure mode, a brief description of the metallurgy of the weld cycle is needed. The as-cast microstructure of the Si-Mo ductile iron is largely ferritic with about 10-20% pearlite. The welding operation is performed at about 250-300 amps and 24-28 volts at travel speeds of about 76 cm per minute. Thus, heat-up, melting and cool-down are all quite rapid. The transformation from ferrite to austenite occurs at approximately 870-900°C (A1 temperature). At and above the A1 temperature, the austenite readily absorbs carbon from both pearlite and graphite nodules. As the welding arc traverses away, the high carbon austenite is quenched, forming principally iron carbides and martensite which dissociate into iron and graphite following successive engine cycles. This secondary graphite formation allows the ductile iron HAZ to be susceptible to stress-accelerated oxidation and subsequent cracking. Figures 1 and 2 show photomicrographs of a NI-ROD filler metal 44/Si-Mo ductile cast iron weld interface in a part which joined a 409 stainless steel catalytic converter housing to a cast iron manifold. The as-received sample was exposed for 15 minutes in air at 870°C and rapidly cooled in ambient air. The observed crack has progressed from the toe of the weld along the HAZ of the ductile iron.

Alloy Development

As a result of discovering this deficiency in the performance of welds fabricated using the Ni-Fe-Mn product, in addition to the realization that the graphite-rejection principle was no longer required for some ductile grades of cast iron, Special Metals Corporation researchers developed a new welding wire. The new material, NI-ROD filler metal 44HT, contained sufficient amounts of carbide-forming elements that would combine with expected amounts of carbon dilution from the ductile iron to form carbides that would be stable at the high temperatures experienced by automotive exhaust systems. The phase stability was ensured through the use of Thermo-Calc software in alloy design. The carbide-forming elements considered for addition included niobium, chromium, and molybdenum. Figure 3 shows a phase stability diagram for the NI-ROD filler metal 44 composition, with 1 wt. % carbon added to simulate dilution from the ductile iron, illustrating the resulting graphite formation. This composition was used as the basis for the developmental product.

The effect of adding niobium to the NI-ROD filler metal 44 upon phase stability at 500°C is illustrated in Figure 4. The target temperature of 500°C was chosen as an acceptable graphite solvus temperature. Adding up to 6 wt. % niobium serves to reduce the expected graphite formation to below one mole percent. However, this amount of niobium was not deemed to be
Figure 1. Photomicrograph showing Si-Mo ductile iron/NI-ROD filler metal 44 weld interface in a part which joined a 409 stainless steel catalytic converter housing directly to a Si-Mo ductile iron exhaust manifold. The sample was exposed for 15-minutes in air at 870°C and rapidly cooled in ambient air. The observed crack has progressed from the toe of the weld along the heat-affected zone of the ductile iron. Figure 2 shows a magnified view at the tip of the crack shown in Figure 1. Samples were not etched.

Figure 2. Photomicrograph showing Si-Mo ductile iron/NI-ROD filler metal 44 weld interface in a part which joined a 409 stainless steel catalytic converter housing directly to a Si-Mo ductile iron exhaust manifold. The sample was exposed for 15-minutes in air at 870°C and rapidly cooled in ambient air. This photo is a magnified view at the tip of the crack shown in Figure 1.
desirable for oxidation resistance. A nominal level of 0.7 wt. % niobium was selected, given this consideration. Given the association of the observed failure mechanism with oxidation, addition of chromium was also considered, in conjunction with the 0.7 wt. % niobium addition. The chromium addition would serve the dual purpose of capturing carbon in the form of carbides in addition to enhancing oxidation resistance. Figure 5 shows the effect of chromium addition upon phase stability of NI-ROD filler metal 44 containing 0.7 wt. % niobium and 1 wt. % carbon, at 500°C. Addition of 6.5 wt. % chromium resulted in a decrease in the graphite solvus temperature below 500°C. An aim level of 7 wt. % was targeted based upon this prediction.

Figure 3. Phase stability diagram for NI-ROD filler metal 44 with 1 wt. % carbon added.

Figure 4. Phase diagram (at 500°C) showing the effect of adding niobium to NI-ROD filler metal 44 with 1 wt. % carbon (all additions replacing iron).
Addition of molybdenum to the new alloy was also considered. Figure 6 shows the effect of adding up to 5 wt. % molybdenum addition upon phase stability of NI-ROD filler metal 44 base composition having 0.7 wt. % niobium and 1 wt. % carbon, at 500°C.

![Figure 5. Phase stability data (at 500°C) generated using Thermo-Calc, illustrating the effect of adding various levels of chromium to the NI-ROD filler metal 44 composition having 0.7% Nb and 1% C (wt. %).](image5.png)

![Figure 6. Phase stability data (at 500°C) generated using Thermo-Calc, illustrating the effect of adding various levels of molybdenum to the NI-ROD filler metal 44 composition having 0.7% Nb and 1% C (wt. %).](image6.png)

Given the quantity of molybdenum required to produce the desired result of minimization of graphite formation, consideration of this element for addition was suspended.

The resulting aim composition is now called NI-ROD filler metal 44HT. Figure 7 shows a phase stability diagram, with carbon elevated at 1 wt. %, indicating no anticipated graphite formation.
While the development phase considered only the addition of 1 wt. % carbon to the weld metal composition, in reality, dilution with ductile iron will result in a decidedly different composition. Uniform dilution of the NI-ROD filler metal 44HT composition with Si-Mo ductile cast iron at the level of 25 wt. % would result in the following weld deposit composition (wt. %): Bal. Fe-33Ni-8.33Mn-5.33Cr-1.08Si-0.89C-0.53Nb-0.28Mo-0.15Ti. Figure 8 shows the phase stability prediction for this composition. For comparison, the 25 wt. % diluted weld deposit fabricated using NI-ROD filler metal 44 would have the following composition: Bal. Fe-33Ni-8.33Mn-1.09C-1.08Si-0.28Mo-0.15Ti. The phase stability prediction for this composition is shown in Figure 9. Again, the propensity for graphite formation in the diluted NI-ROD filler metal 44 weld deposit is evident, while no graphite formation is predicted for the NI-ROD filler metal 44HT deposit.

![Phase stability diagram for NI-ROD filler metal 44HT, with 1 wt. % carbon.](image)

**New Product Characterization**

In order to confirm the predictions that NI-ROD filler metal 44HT would both produce a more stable weld deposit than NI-ROD filler metal 44 (not prone to graphitization), and reduce the incidence of secondary graphite precipitation in the ductile iron HAZ, cyclic exposures of welded samples were conducted in air at 815°C. One cycle consisted of 15 minutes in a vertical electrically heated furnace in an air atmosphere, followed by 5 minutes of cooling in ambient air. The samples were taken from the weld joint connecting a 409 stainless steel catalytic converter housing to a Si-Mo ductile cast iron exhaust manifold. Joints were fabricated with either NI-ROD filler metal 44HT or NI-ROD filler metal 44. Figures 10 and 11 show photomicrographs comparing the weld interface with the ductile iron for each filler metal after each sample had been exposed for 100 cycles. Graphitization of the weld deposit is evident in the case of the NI-ROD filler metal 44 weld, and secondary graphite formation in the
Figure 8. Phase stability diagram for NI-ROD filler metal 44HT diluted 25% with Si-Mo ductile cast iron (weight % composition: Bal. Fe-33Ni-8.33Mn-5.33Cr-1.08Si-0.89C-0.53Nb-0.28Mo-0.15Ti).

Figure 9. Phase stability diagram for NI-ROD filler metal 44 diluted 25% with Si-Mo ductile cast iron (weight % composition: Bal. Fe-33Ni-8.33Mn-1.09C-1.08Si-0.28Mo-0.15Ti).
ductile iron HAZ is more pronounced. A more extended cyclic exposure (566 hours) under the same conditions using 6.4mm diameter wrought wire-rod samples from NI-ROD filler metals 44 and 44HT was also conducted. The enhancement in oxidation resistance provided to the 44HT material via the chromium addition is evidenced by both mass change and depth of oxidation data (Figure 12 and Table II).

The new alloy NI-ROD filler metal 44HT is currently being used to fabricated close-coupled catalytic converter/Si-Mo ductile cast iron manifold assemblies. Parts fabricated using the new filler metal have performed admirably in preliminary dynamometer testing and in actual service as well.

Figure 10. Photomicrographs showing the weld interface between Si-Mo ductile iron (bottom of photo) and NI-ROD filler metal 44 after 100 hours of cyclic exposure in air at 815°C. One cycle consisted of 15 minutes in the furnace followed by 5 minutes in ambient air. Sample was not etched.
Figure 11. Photomicrograph showing the weld interface between Si-Mo ductile iron (bottom of photo) and NI-ROD filler metal 44HT after 100 hours of cyclic exposure in air at 815°C. One cycle consisted of 15 minutes in the furnace followed by 5 minutes in ambient air. Sample was not etched.

Table II. Oxide Penetration Results for NI-ROD filler metals 44 and 44HT after cyclic oxidation testing in air at 816°C (One Cycle = 15 Minutes in Furnace/5 Minutes Cooling in Ambient Air) for 566 Hours

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Oxide Penetration, Microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>693</td>
</tr>
<tr>
<td>44HT</td>
<td>168</td>
</tr>
</tbody>
</table>

Figure 12. Results of cyclic oxidation testing in air at 815°C. Total time per cycle was 20 minutes (15 minutes in furnace/5 minutes cooling in ambient air).
Summary

A new Ni-Fe-Mn-Cr-Nb welding product has been developed which meets the demanding challenges posed by the automotive industry. Thermo-Calc was heavily used in the alloy design phase. The resulting new filler metal is capable of producing welds in Si-Mo ductile cast iron which are of high integrity and offer improved thermodynamic stability and oxidation resistance over the formerly-used Ni-Fe-Mn product.

References