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X HOT CRACKING IN WELDMENTS OF HAYNES ALLOY NO. 25

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ABSTRACT

Metallographic examination of weldments produced by tungsten inert gas welding of Haynes alloy No. 25 gave evidence of what appeared to be intergranular cracks in the heat-affected zone. This condition was found to result from pull-out of a brittle material during metallographic polishing. When careful metallographic procedures were developed resulting in retention of the intergranular material, it was recognized as the product of a liquation reaction. Segregated carbide precipitates caused melting and hot cracking in the grain boundaries adjacent to the weld pool by means of a multi-component eutectic reaction. Resolidification of the liquid in the grain boundaries formed two distinct phases which were hard and brittle. These were identified by electron microprobe x-ray analysis as a carbide phase and a cored solid

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solution phase. The microstructural characteristics of the base metal indicated that the problem occurred as the result of improper thermal and mechanical treatment of the alloy.

INTRODUCTION

This report involves the metallographic analysis of weldments made during the fabrication of isotopically fueled heat sources for the SNAP-27 program. The cylindrical capsule containing the fuel was enclosed in an outer capsule constructed of Haynes alloy No. 25. The circumferential closure welds of the outer capsule, which served as the strength member of the assembly, were made by tungsten inert gas welding.

A cross-sectional view of the outer capsule is shown in Figure 1 illustrating the weld joint design. The outer and inner portions of the step joint were 0.040" and 0.020" thick respectively, and the entire step joint was 0.060" long. One hundred percent penetration of the weld was required, although it was not required that the weld encompass the entire 0.020" step.

Nondestructive testing¹ was performed on all weldments to detect the presence of defects. Destructive metallographic

analysis was performed on test welds for correlation with NDT results, and example welds made immediately before and after the closure weld of a fueled capsule were examined metallographically to assure that the weld parameters were correct. In general, any well-defined crack was cause for rejection of the weldment. A problem developed in this work involving the interpretation of microstructural detail which neither obviously fit nor misfit the category of well-defined cracks.

The components for the SNAP-27 outer capsule were fabricated from Haynes-25 bar stock which constituted a single heat of material. The wrought bar was solution heat treated in massive form, and the tubular components for the capsule were machined from the bar with no further heat treatment. Characterization of the base metal revealed that the grain size was relatively coarse, carbide particles were distributed in flow lines, within the grains and in grain boundaries, and the machined components exhibited some cold work received from the machining operation.

The nominal composition of Haynes-25 is given by the following specification limits:

Ni	9.00 - 11.00
Cr	19.00 - 21.00
W	14.00 - 16.00
Fe	3.00 Max
C	0.05 - 0.15
Si	1.00 Max
Mn	1.00 - 2.00
P	0.030 Max
S	0.030 Max
Co	Balance

The composition of the material employed in this program was verified by "in house" analyses showing conformance with specification. The silicon content fell on the low side of specification limits at 0.12 percent, and the carbon content fell on the high side of specification limits at 0.13 percent. Phosphorous and sulfur were negligible.

METALLOGRAPHIC EXAMINATIONS

Throughout the metallographic surveillance of weldments in this program, the specimens were examined first in the as-polished condition as this was quite sensitive in revealing defects such as pores or cracks. Examination after etching revealed no "open" defects which were not detectable in the

as-polished condition. "Open" defects were not obscured by smearing as experience showed that smeared metal was not a problem with this alloy.

Three different etchants were employed in studying the weld sections. Figure 2 shows a transverse weld section etched electrolytically in HCl and ethanol. When the specimen is not etched excessively the grain structure in the base metal is not revealed, and the weld is defined in sharp contrast. This is a representative weldment. The large void on the left is a gap at the end of the unmelted portion of the 0.020" step.

Figure 3 shows a transverse weld section etched electrolytically in 10% oxalic acid. The results are essentially the same as the HCl-ethanol etch giving no definition of the grain structure in the base metal. Two weld passes are apparent in this specimen plus the weld overlap area at top left.

Figure 4 shows a transverse weld section etched by immersion in HCl-H₂O₂. This is a much stronger etchant. In addition to the delineation of the weldment, the grain structure in the base metal has been revealed completely showing rather coarse grains.

The heat-affected zone of a weldment is usually described as that portion of the base metal which was not melted, but whose properties or microstructure were altered by the heat of welding. Rather wide heat-affected zones are indicated in Figures 2, 3 and 4 by the presence of microstructural detail extending from the edges of each weldment. Ordinarily the edges of the weldment should be sharp interfaces. None of the detail in the heat-affected zones of these specimens was apparent in the as-polished condition.

The detail in the heat-affected zone revealed by etching in Figure 3 is more prominent near the bottom of the weld, particularly in the unmelted 0.020" step. During welding heat is rapidly conducted away from the weld in both directions, but because of the discontinuity at the end of the step joint, heat builds up excessively in the unmelted step. The effect may vary from essentially no change in a joint with an ideal fit to complete melt-away of the step in a joint with a poor fit. In this case the entire unmelted step must be considered a heat-affected zone.

In some cases the detail in the heat-affected zone appeared even more severe. Two such examples are shown in Figures 5 and 6. Both specimens were slightly overpolished and both

were etched with HCl-H₂O₂. In Figure 5 a crack appears to extend along the left face of the weldment, and in Figure 6 a grain on the left side of the weldment is completely surrounded by what appears to be a crack. When detail such as this was first encountered, its identification as "cracks" was very uncertain as the severity of the detail appeared to vary with the metallographic procedures. When the specimens were etched with HCl-H₂O₂ to reveal the grain structure of the base metal, the detail of concern in the heat-affected zone was consistently observed to be intergranular in nature. A disadvantage of the use of the HCl-H₂O₂ etchant is that it becomes difficult to distinguish ordinary grain boundaries from those revealed due to an unusual grain boundary condition. With the HCl-ethanol and oxalic acid etchants the grain boundaries of concern in the heat-affected zone are revealed sharply without interference.

Figure 7 shows an exceptionally wide weldment in which the entire step joint was consumed. Overpolishing has exposed flow lines revealing the wrought condition of the material. Overpolished specimens consistently appeared worse in the heat-affected zone showing an increased concentration of intergranular voids.

Figures 8 and 9 show enlargements of the detail in the heat-affected zone when severe intergranular voids were present. Often the void sections were discontinuous exhibiting intact segments along the grain boundary between the grain boundary separations.

The unusual grain boundary condition was revealed much more prominently by longitudinal sections. The specimen in Figure 10 was sectioned parallel to the weldment on the side opposite the step joint. The section intersected only the upper portion of the weldment which is revealed at the top. The center portion of the surface represents the heat-affected zone adjacent to the side of the weld. The grain boundary detail shown by the oxalic acid etch is more continuous in this orientation. From the absence of microstructural detail, the lower portion of the surface appears to be outside the heat-affected zone. The distance from the surface to the face of the weldment is greatest at the bottom.

The nature of the unusual grain boundary condition became more obvious with the recognition of brittle pull-out, meaning the dislodgement of a brittle constituent from the grain boundaries during metallographic polishing. Figure 11 shows an unetched specimen sectioned longitudinally in the

heat-affected zone on the step-joint side of the weldment. Severe overpolishing resulted in an excessive amount of brittle pull-out giving the appearance of huge intergranular voids. This is further evidence of a highly unusual condition in the grain boundaries since Haynes-25 is a single phase alloy when completely solution heat treated and contains no brittle intergranular material that is subject to pull-out.

In Figures 12-15 a single transverse weld section is shown in four different conditions to demonstrate the pull-out phenomenon. In Figure 12 the specimen is shown polished and unetched. No detail is apparent. In Figure 13 the specimen is shown etched with oxalic acid. The unusual grain boundaries are well delineated in the heat-affected zone although they do not appear to be void. In Figure 14 the specimen is shown severely overpolished and unetched. The specimen edges are rounded and several "defect" areas are apparent as the result of overpolishing. In Figure 15 the overpolished specimen is shown etched with oxalic acid, and the "defect" areas can be identified as grain boundaries in which brittle pull-out occurred.

The identification of brittle pull-out did not provide an

explanation for all the intergranular voids observed in weldment heat-affected zones as some were recognized to be actual microfissures. These were easily detected when present as they could be recognized at all stages of grinding and polishing. Figure 16 shows a longitudinal section in the heat-affected zone of a specimen known to be severely affected. In spite of the coarse scratches on the as-ground surface, several long, void grain boundaries are quite apparent. When the specimen was polished, as shown in Figure 17, the microfissures were well defined and had essentially the same appearance. Overpolishing undoubtedly would have extended the areas which appear void.

In order to identify the intergranular material which was so highly subject to pull-out, and to define the reactions which occurred during welding, it was necessary to develop an improved metallographic procedure which would result in the retention of the brittle intergranular product. Extensive development work was carried out involving manual, automatic and vibratory polishing techniques and the use of many different polishing cloths, abrasives and lubricants. Of the many procedures attempted, the best results were achieved by a manual technique intended to minimize

polishing time.

Figures 18 and 19 show enlargements of the typical intergranular detail in the heat-affected zone retained by careful polishing procedures. The specimens were wet ground on 180, 320 and 600 grit silicon carbide papers, hand polished at low speed with 3 micron diamond on Texmet polishing paper with heavy pressure for less than one minute employing mineral oil as the lubricant, polished with $\frac{1}{4}$ micron diamond on Microlon D with heavy pressure for less than one minute employing mineral oil, and final polished very briefly with 0.06 micron alumina on Microcloth with light pressure employing water. The large grain boundaries in these specimens can be seen to be filled with solid material. With less than optimum metallographic procedures, pull-out would have occurred and segments of the boundaries would appear to be void.

RESULTS AND DISCUSSION

The study of the retained detail in many areas, such as Figures 18 and 19, gave evidence of the chemical reaction which had occurred. This was identified as grain boundary liquation, defined as melting of material in grain

boundaries at a temperature below the solidus temperature of the alloy. This is a special case of hot shortness.

Ordinarily, hot shortness is the result of trace quantities of impurities which are insoluble in a metal. The segregation of the impurities in grain boundaries results in melting by eutectic reaction at temperatures below the melting point of the metal. During welding severe thermal stresses are present in the heat-affected zone, and the development of a liquid grain boundary film in a local area under tension can produce a physical separation of the grain boundary. Contraction may close the separation, but in some cases resolidification during rapid cooling may result in permanent microfissures - or "hot cracks."

In this case, grain boundary liquation and hot cracking did not result from the presence of insoluble impurities in the Haynes-25, but rather from the presence of carbon which should be present in limited concentration in the alloy in solid solution form. Even though the carbon content is relatively low, second phase carbides will be present if the alloy has been improperly solution heat treated, or if it has been held at temperatures above 1200°F for a significant period of time.

There are a number of types of carbides which occur in super alloys.² MC-type carbides form initially from the melt and exhibit random distribution in the microstructure. $M_{23}C_6$ forms in the solid state as the result of aging at elevated temperature and has a strong predisposition to nucleate at grain boundaries. M_6C may replace $M_{23}C_6$ in alloys rich in molybdenum or tungsten. For Haynes-25 the mechanism of delivery of carbon to the grain boundaries is the precipitation of $(Cr,W)_{23}C_6$ and/or $(Cr,W)_6C$.

If an alloy which contained carbide precipitates in the grain boundaries were slowly heated to elevated temperature ($2150^{\circ}F$ or higher), the carbide precipitates would redissolve in the matrix. However, on rapid heating such as that which occurs in the heat-affected zone during welding, the carbides cannot redissolve as this is a slow diffusion dependent reaction. On arriving at sufficiently high temperature, the carbides interact with the adjacent material forming liquid in the grain boundaries by eutectic reaction.

Figure 20 shows the chromium-rich end of the chromium-carbon binary phase diagram. A eutectic is formed at three weight percent carbon lowering the melting point of chromium approximately $775^{\circ}F$. Similar reactions occur between small

amounts of carbon and every metallic element in Haynes-25 as shown in the following summary.

<u>Element</u>	<u>Approximate Wt. Percent Carbon</u>	<u>Approximate Melting Point Depression</u>
Cobalt ³	2.7	315°F
Chromium ⁴	3.0	775°F
Tungsten ⁵	2.2	1205°F
Nickel ⁶	2.2	255°F
Iron ⁷	4.3	695°F
Manganese ⁸	1.3	27°F

Since the melting temperature of each of the alloying elements is lowered by a small amount of carbon, the reaction which occurs during welding in the heat-affected zone is actually a multi-component eutectic reaction. Resolidification of the liquid film in the grain boundary does not form a solid phase like the adjacent grains of Haynes-25 because the liquid is no longer the same in composition; it is carbon rich. During solidification segregation occurs in the carbon-rich liquid forming more than one phase as dictated by the phase equilibrium relationships.

To illustrate this reaction better, two of the capsule components were intentionally heat treated improperly enhancing carbide precipitation prior to welding. This

provided a specimen for analysis which had experienced severe grain boundary liquation and hot cracking. Figure 21 shows this detail. This is a photograph of a composite illustration made for study at high magnification. Liquation occurred along a continuous grain boundary path extending completely across the 0.020" step.

In the center of the grain boundary liquation area in Figure 21 is a continuous light gray phase with many small fingers protruding to the sides. This represents dendritic growth of the first phase to solidify in the liquid film. The only manner in which this structure can result is by unrestrained growth in liquid. The first phase to solidify is a carbide phase. It is surrounded on both sides by a light colored band, the second phase to solidify, which is much the same in appearance as the adjacent Haynes-25 base metal. This phase is a cored solid solution similar in composition to Haynes-25. The carbide phase is extremely hard and brittle and subject to microcracking. The dark segment in the upper half of the grain boundary liquation area is a void where a small amount of pull-out occurred. With excessive polishing this entire area would have appeared as one continuous fissure. Near the bottom are two large void areas which did

not result from brittle pull-out. These are two microfissures (hot cracks) which resulted from movement of the liquid prior to solidification.

Figures 22 and 23 present further enlargements of the retained detail after severe grain boundary liquation. The many small protrusions from the sides of the carbide phase are particularly apparent in Figure 22, and Figure 23 exhibits similar detail in addition to a wide microfissure at the bottom.

An illustration of exceptionally severe grain boundary liquation is shown in Figure 24. This was the most massive concentration of resolidified liquid in a grain boundary observed in this work and retained during metallographic polishing. The unusual width of the liquid film apparently permitted growth of the carbide phase in a network pattern rather than as the usual platelet at the center of the film. Portions of the fragile carbide network experienced brittle pull-out.

The reaction of carbide precipitates with the metallic constituents of the alloy producing liquation was not restricted to grain boundaries. The individual carbide particles distributed randomly in the microstructure were equally

subject to the same reaction when they occurred in the heat-affected zone. Small, individual, spherical pockets of liquid were formed by this reaction, and resolidification resulted in segregation, just as in the liquid grain boundary films, producing a carbide phase surrounded by a solid-solution alloy phase. Figure 25 shows two small areas which experienced liquation. A star-shaped particle frequently resulted from the rapid nucleation and growth of the carbide phase.

Individual carbide particles distributed in flow lines produced the heat-affected zone detail shown in Figure 26. The interaction of the carbide particles with the base metal formed spherical volumes of liquid of varying size indicative of the thermal gradient across the heat-affected zone during welding. In severe cases a stringer-like effect was created by growth of adjacent liquid pockets which joined together.

In further study of the grain boundary liquation reaction, weldments were examined by sectioning in an additional manner different from the transverse sections and longitudinal sections made vertically at the side of the weldment. Figure 27 is a photograph of a composite illustration made for study at high magnification showing a longitudinal section made

horizontally between the top and bottom of the weldment. The section is near the base of the weldment, but it does not parallel the base due to the curvature of the weld ring. The large voids on the right are the interface of the unmelted step joint, and the segment between the voids is the unmelted 0.020" step.

Numerous grain boundaries which experienced liquation are apparent in Figure 27. They are especially prominent on the right side which is the more extensive heat-affected zone. However, liquation did not occur in all the grain boundaries which touched the weld pool, and those which did experience liquation did not form a continuous network. The orientation of the liquated grain boundaries reflects only the random orientation of the adjacent grains. The relative concentration of microfissures present along with the retained material in liquated grain boundaries can be observed by close examination of this illustration. Seepage of trace quantities of liquid from the voids stained the surface marking the location of each microfissure. These are minute spots, and only a few are present. They appear as very short sections within the liquated grain boundaries.

The phases which resulted from grain boundary liquation were

identified by electron microprobe x-ray analysis. The specimen shown in Figure 21 was employed for this work as it contained the largest examples of the retained reaction products. The determinations were made by scanning slowly across the reaction layer to establish the composition profile for each element of the alloy. The representative results are illustrated by eight curves shown in Figures 28 and 29.

Each of the curves in Figures 28 and 29 is identified with a three line caption which defines the type of x-radiation detected in the analysis, the excitation voltage and beam current, and the counting rate at full scale deflection. The analyses were made under different conditions in order to optimize the qualitative detection of the elements and to illustrate their distribution in the reaction layer more sensitively. The curves made under different conditions cannot be compared quantitatively as their relative positions on the chart are not indicative of the relative concentrations of the elements. The statistical fluctuations in the curves for silicon, carbon and tungsten resulted from the use of lower counting rate scales (higher amplifications) than the scale employed for the other elements.

The tops and bottoms of the curves in Figures 28 and 29 are representative of the concentrations of the elements in the Haynes-25 base metal. The portions of the curves representing the positions of the gray phase in the center of the reaction layer and the surrounding light-colored phase are indicated in the margin. Tungsten, chromium and carbon show sharp enrichments in the gray phase, and the adjacent light-colored phase is slightly enriched in tungsten and chromium. Just outside this phase the Haynes-25 is slightly depleted in these elements. Where tungsten, chromium and carbon are concentrated in the reaction products, cobalt and nickel show corresponding depletions in both phases of the reaction layer. Very small amounts of iron and manganese are present in the alloy, but the curves show definite indication of depletion of these elements in the reaction layer. An insignificant amount of silicon is present in the alloy. The lack of variation in this curve indicates the absence of silicon segregation in the reaction products. Similar analyses were made for phosphorous and sulfur, and the results showed no detectable segregation in the reaction products.

These results indicate that the gray phase in the center of

the reaction layer is a carbide of chromium and tungsten. The ratios of the elements are unknown, although the phase is probably (Cr,W)C as the monocarbides ordinarily form from the melt. The light-colored phase which surrounds the carbide phase does not appear to be significantly different in composition from Haynes-25. However, the portions of the curves which define this phase show considerable slope indicating severe coring. The composition gradients show increased concentrations of chromium and tungsten toward the center of the reaction layer and reversed composition gradients for cobalt and nickel.

Electron microprobe x-ray analyses were also conducted on the reaction products which resulted from the liquation reaction between individual carbide particles and the base metal. The analysis of specimens such as those shown in Figure 25 gave results essentially the same as those described above for the reaction products of grain boundary liquation.

In the metallographic analysis of many weld sections, only occasional evidence was observed of true microfissures. The majority of the intergranular detail which appeared to be void was the result of brittle pull-out. Both conditions

are recognized as being highly undesirable, but it is nonetheless of value to distinguish between them. A series of illustrations is presented in Figures 30-36 to further illustrate grain boundary liquation and the pull-out phenomenon. The specimen is an electron beam weldment of Haynes-25 from the same lot as the material in all the previous illustrations.

Figure 30 shows an unetched transverse weld section prepared by the metallographic procedure described earlier. Some very faint features are apparent in relief on the surface, but the specimen shows no "open" detail.

The identical specimen, still unetched, is shown in Figure 31 after being subjected to additional polishing. Two small voids which were not present in the previous illustration are now present as the result of overpolishing and brittle pull-out.

The overpolished section, etched, is shown in Figure 32, and the two voids in Figure 31 can be recognized as grain boundaries in the weld heat-affected zone. In subsequent illustrations the void grain boundary in the upper right-hand corner is shown in greater detail.

In Figure 33 the specimen is overpolished and unetched, and the void grain boundary has the distinct appearance of a microfissure.

Figure 34 shows the same area of the specimen, etched, before overpolishing, and the grain boundary is shown not to be void, but rather filled with solid material.

Figure 35 shows the same area of the specimen, etched, after overpolishing, and again the grain boundary has the appearance of a microfissure. This illustrates the importance of proper specimen preparation to avoid misinterpretation of the microstructural detail.

Figure 36 is a further enlargement of the same area showing a small segment of the grain boundary material which did not experience brittle pull-out. All grain boundaries which have experienced grain boundary liquation are not equally subject to brittle pull-out. This is probably the result of variations in damage to the brittle constituents by microcracking from thermal stresses which occur on cooling. When pull-out does occur, it originates in the breakup and dislodgement of the first phase to solidify, the carbide phase, followed by the dislodgement of the remainder of the

material in the reaction layer.

The metallurgical factors which promote hot cracking in Haynes-25 appear to be essentially the same as the ordinary causes of embrittlement and cracking. Wlodek⁹ pointed out the probable contribution of $M_{23}C_6$ precipitates to embrittlement and the beneficial effects of fine grain size and low carbon content. Ramsey¹⁰ stated that cold-worked Haynes-25 will crack during welding, and he recommended a limitation of 5% cold reduction and a grain size of ASTM 5 or finer.

The difficulties experienced in this work can be directly attributed to the condition of the base metal. The material was coarse grained exhibiting a variation from $4\frac{1}{2}$ to 1 grain per square inch at 100X. The average grain size was ASTM 3.

The hardness of fully annealed Haynes-25 is Rockwell C 22, and 5% cold reduction increases the hardness to Rockwell C 27. The material employed in this work typically gave a hardness of Rockwell C 30-35, equivalent to approximately 15% cold reduction, and in a few cases the hardness was as high as Rockwell C 42 which is equivalent to approximately 20% cold reduction. The increased hardness of the material was not caused by cold work alone, but was also the result

of carbide precipitates produced by inadequate solution heat treatment and by deformation of the material. Figure 37 illustrates the microstructure of the material near the outer edge of the heat-affected zone where grain boundary liquation is still apparent, and Figure 38 shows the microstructure of the base metal well beyond the heat-affected zone. Both illustrations show gross evidence of stress induced precipitation caused by deformation when the components were machined from bar stock.

The specimens in Figures 39 and 40 were etched electrolytically in 10% sodium cyanide. This etchant is typically employed to reveal the presence of carbides. Figure 39 shows a portion of the base metal containing a high concentration of randomly distributed carbide precipitates in addition to segregated precipitates in grain boundaries. Figure 40 shows a portion of the base metal in which the grain boundaries are well defined by the presence of segregated carbide precipitates.

The specimens in Figures 41 and 42 were also etched electrolytically in 10% sodium cyanide. Figure 41 shows carbide particles distributed in flow lines in stringer-like arrays, and Figure 42 shows the face of a weldment where grain

boundary liquation occurred in the heat-affected zone producing a carbide phase.

The problem of grain boundary liquation and hot cracking experienced in this work was clearly a materials problem. As a result of this experience a new material specification for Haynes-25 was prepared.¹¹ This will serve as the basis for future Mound Laboratory requirements.

The final illustrations, Figures 43-48, show several weldments which illustrate that Haynes-25 is not inherently subject to grain boundary liquation during welding. The weldments were made by tungsten inert gas welding employing material from a source other than that involved in the work described in this report.

The specimen in Figure 43 is a butt weld of sheet material. It was etched electrolytically in oxalic acid and shows a clean interface between weldment and base metal. Figure 44 shows the same specimen etched with HCl-H₂O₂, and a further enlargement of the heat-affected zone is shown in Figure 45. Evidence of grain boundary liquation is not apparent. This material has an average grain size of ASTM 5.

Figure 46 shows the heat-affected zone of a weldment in a

drawn tubular component. The recrystallized base metal has a minute grain size, and the specimen is exceptionally clean and free of grain boundary liquation.

Figure 47 shows a compound weldment in a component made by deep drawing. The specimen was etched electrolytically in oxalic acid and shows a remarkably sharp interface between weldment and base metal. The same specimen is shown in Figure 48 with the grain structure of the recrystallized base metal revealed by the HCl-H₂O₂ etch. Again it illustrates the fine grain size which accompanies a sound weldment free of defects.

SUMMARY

The metallographic analysis of weldments of Haynes alloy No. 25 revealed unusual microstructural detail which appeared to be intergranular cracks in the weld heat-affected zone. The weldments were produced by tungsten inert gas welding at a step joint in tubular components with a wall thickness of 0.060". The identity of the unusual microstructural detail as cracks was uncertain, as the severity of the detail varied with the metallographic procedure. Etching the metallographic specimens with an etchant which did not reveal the microstructure of the base metal showed the presence of an

intergranular material in the weld heat-affected zone. This material was found to experience brittle pull-out during metallographic polishing, and the intergranular voids developed by overpolishing resembled cracks.

An improved metallographic procedure was developed which resulted in the retention of the brittle intergranular material. It was identified as the reaction product resulting from grain boundary liquation - the melting of material in grain boundaries at a temperature below the solidus temperature of the alloy. Segregation occurred during solidification of the liquid films in the grain boundaries resulting in the formation of two discrete phases. These were analyzed by electron microprobe x-ray analysis and found to be a chromium/tungsten carbide phase and a cored solid solution phase similar in composition to the base metal.

The occurrence of grain boundary liquation in the heat-affected zone was attributed to eutectic reaction between carbon and all the constituents of the alloy. Carbon was present in grain boundaries by virtue of carbide precipitates segregated in the grain boundaries. On rapid heating the carbide precipitates were unable to redissolve, and

melting occurred by eutectic reaction. Evidence of similar eutectic reaction was also observed in the heat-affected zone where carbide particles were isolated within grains and distributed in flow lines.

The momentary presence of liquid films in grain boundaries occasionally resulted in intergranular separations due to mechanical factors. These hot cracks were retained when the material experienced rapid cooling. Careful metallographic preparation revealed the hot cracks in the network of liquated grain boundaries, although they were small and few in number in comparison to the intergranular voids observed originally which resulted from brittle pull-out.

Metallographic examination of the base metal revealed the metallurgical characteristics to which the grain boundary liquation and hot cracking were attributed. The material was coarse grained (ASTM 3); carbide precipitates were observed in abundance in grain boundaries, within grains and distributed in flow lines; and the material exhibited some cold work received during machining. Weldments made in material which did not exhibit these characteristics were free of grain boundary liquation and hot cracks.

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FIGURE 1 - Weld joint design.

FIGURE 2 - Transverse weld section,
HCl-ethanol etch (40X).

FIGURE 3 - Transverse weld section, oxalic etch (40X).

FIGURE 4 - Transverse weld section, HCl-H₂O₂ etch (40X).

FIGURE 5 - Transverse weld section showing apparent crack, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 6 - Transverse weld section showing apparent crack, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 7 - Transverse weld section, overpolished, showing flow lines, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 8 - Intergranular void in heat-affected zone, oxalic etch (250X).

FIGURE 9 - Intergranular void in heat-affected zone, $\text{HCl-H}_2\text{O}_2$ etch (250X).

FIGURE 10 - Longitudinal section showing portion of weld above heat-affected zone, oxalic etch (35X).

FIGURE 11 - Intergranular voids resulting from excessive brittle pull-out, longitudinal section in heat-affected zone, overpolished, unetched (45X).

FIGURE 12 - Transverse weld section, as-polished (40X) .

FIGURE 13 - Transverse weld section, oxalic etch (40X) .

FIGURE 14 - Transverse weld section, severely overpolished (40X).

FIGURE 15 - Transverse weld section, severely overpolished, oxalic etch (40X).

FIGURE 16 - Microfissures in heat-affected zone, longitudinal section, as-ground (55X).

FIGURE 17 - Microfissures in heat-affected zone, longitudinal section, as-polished (55X).

FIGURE 18 - Retained intergranular detail in heat-affected zone, HCl-ethanol etch (400X).

FIGURE 19 - Retained intergranular detail in heat-affected zone, HCl-ethanol etch (400X).

FIGURE 20 - The chromium-carbon system.

FIGURE 21 - Severe grain boundary liquation and hot cracking, oxalic etch (475X).

FIGURE 22 - Reaction products of grain boundary liquation, oxalic etch (1200X).

FIGURE 23 - Reaction products of grain boundary liquation, oxalic etch (1200X).

FIGURE 24 - Reaction products of severe grain boundary liquation showing network of carbide phase, oxalic etch (750X).

FIGURE 25 - Reaction products of liquation between carbide particles and base metal, oxalic etch (1500X).

FIGURE 26 - Reaction products of liquation between carbide particles in flow lines and base metal, oxalic etch (1000X).

FIGURE 27 - Horizontal section near base of weld showing frequency and orientation of liquated grain boundaries in severely affected area, HCl-ethanol etch (22X).

FIGURE 28 - Electron microprobe traces for iron, carbon, chromium and tungsten.

FIGURE 29 - Electron microprobe traces for manganese, silicon, nickel and cobalt.

FIGURE 30 - Transverse section, electron beam weld, as-polished (45X) .

FIGURE 31 - Transverse section, electron beam weld, overpolished, showing two areas where pull-out occurred (45X) .

FIGURE 32 - Transverse section, electron beam weld, overpolished, $\text{HCl-H}_2\text{O}_2$ etch (65X).

FIGURE 33 - Intergranular void produced by overpolishing (320X).

FIGURE 34 - Retained solid material in grain boundary where liquation occurred, oxalic etch (320X).

FIGURE 35 - Intergranular void produced by overpolishing, $\text{HCl-H}_2\text{O}_2$ etch (320X).

FIGURE 36 - Intergranular void produced by overpolishing, $\text{HCl-H}_2\text{O}_2$ etch (1500X).

FIGURE 37 - Grain boundary liquation and stress induced precipitation in heat-affected zone, $\text{HCl-H}_2\text{O}_2$ etch (600X).

FIGURE 38 - Stress induced precipitation in base metal, $\text{HCl-H}_2\text{O}_2$ etch (100X).

FIGURE 39 - Randomly distributed carbides and segregated carbides in grain boundaries of base metal, NaCN etch (100X).

FIGURE 40 - Segregated carbides in grain-boundaries of base metal, NaCN etch (1000X).

FIGURE 41 - Carbides in flow lines of base metal, NaCN etch (100X).

FIGURE 42 - Carbides in heat-affected zone, NaCN etch (100X).

FIGURE 43 - Transverse section, butt weld, oxalic etch (40X) .

FIGURE 44 - Transverse section, butt weld, HCl-H₂O₂ etch (40X) .

FIGURE 45. - Heat-affected zone, butt weld, $\text{HCl-H}_2\text{O}_2$ etch (150X).

FIGURE 46 - Weld heat-affected zone in fine grained drawn component, $\text{HCl-H}_2\text{O}_2$ etch (150X).

FIGURE 47 - Transverse weld section, oxalic etch (40X).

FIGURE 48 - Transverse weld section, HCl-H₂O₂ etch (40X).