

Table 1—Compositions for the Alloys Investigated (wt-%)

Materials	Cr	Ni	Si	Mn	Mo	Cu	C	N	S	P
Ferralium Alloy 255	24.9	5.4	0.54	1.1	3.1	1.7	0.027	0.17	0.001	0.023
Uddeholm NU744LN	21.6	4.9	0.44	1.7	2.4	0.2	0.067	0.10	0.001	0.024
Alloy 21-9	20.8	9.0	0.62	1.7	0.07	—	0.024	0.007	0.008	0.025
Alloy 23-7	22.8	7.1	0.54	1.8	0.06	—	0.033	0.006	0.009	0.027
304L (FN 0)	18.3	11.4	0.41	1.7	0.04	—	0.023	0.037	0.002	0.007
304L (FN 4.5)	18.6	10.7	0.54	1.9	0.21	—	0.017	0.040	0.001	0.024

Table 2—Mini-Varestraint Test Parameters

Current	180 ± 10 A
Voltage	17 ± 1 V
Travel speed	152 mm/min (6 ipm)
Electrode-to-work distance	2.38 mm (3/32 in.)
Electrode	W.ThO ₂ , 60-deg included angle
Electrode diameter	2.38 mm (3/32 in.)
Ram velocity	300 mm/s (11.7 in./s)
Shielding gas	Argon
Flow rate (Torch)	0.29 L/s (40 cfh)
Flow rate (Trail)	0.53 L/s (70 cfh)

and the 23-9 alloy all exhibited approximately equal proportions of austenite and ferrite, while the 21-9 alloy contained a greater proportion of austenite. Also evident from Fig. 1 is the elongated morphology of the ferrite. The austenite phase, which formed at ferrite-ferrite grain boundaries, was also elongated, with the exception of the 21-9 alloy, in which an equiaxed austenite grain structure was observed.

A conventional Type 304L stainless steel which contained approximately 5 vol-% (FN 4.5) delta ferrite in the weld fusion zone at room temperature and a Type 304L stainless steel which remained fully austenitic in the weld fusion zone were also tested in order to provide a baseline for comparison of the hot cracking susceptibilities of the duplex stainless steels. Complete compositional analyses for all the alloys tested are shown in Table 1.

Varestraint Testing

The mini-Varestraint test (Ref. 31) was utilized to assess the relative weld hot cracking susceptibility of the duplex and austenitic alloys. As-received 12.8-mm (0.5-in.) thick plates were machined into test specimens with dimensions of 0.64 × 2.54 × 15.24 cm (0.25 × 1.0 × 6.0 in.). The specimens were thoroughly degreased with acetone and wiped dry immediately prior to testing. The GTA welding parameters used in mini-Varestraint testing are listed in Table 2.

The specimens were tested over a range of augmented strains from 0.5 to 5%. The augmented strain, ξ , is given by

the following equation:

$$\xi \approx t/2R$$

where t is the specimen thickness and R is the radius of the die block over which the specimen is deformed.

Following testing, the specimens were chemically cleaned using an alkaline permanganate-citrate acid method (Ref. 32) to remove high-temperature oxides which made observation of hot cracks difficult. The samples were first immersed for 1 h in a boiling solution containing 10% NaOH and 3% KMnO₄ in 1 L of water. After rinsing in water, the samples were immersed for 1 h in a boiling solution containing 12 g ammonium citrate, 100 mg EDTA, and 1 L of water, in which the pH was adjusted to 4-4.5 with citric acid. This cleaning method effectively removed the oxide without attacking the underlying metal. A quantitative measure of the extent of hot cracking in each sample was determined using a binocular microscope equipped with a filar eyepiece. The number and length of all cracks produced along the trailing edge of the weld pool during the mini-Varestraint test were determined at 70× magnification.

Metallography

Selected mini-Varestraint test specimens were sectioned, mounted, and polished with 0.05 micron alumina for metallographic analysis. Sections were made through the cracked regions of the test specimens to reveal the hot crack morphology and in unstrained areas for a more detailed examination of the weld fusion and heat-affected zone structures. Samples were etched using either a mixed acid reagent containing equal amounts of nitric, hydrochloric, and acetic acid or a 10% oxalic acid electrolytic etch at 6 V for 10-20 s.

Fractography

Selected Ferralium Alloy 255 and Uddeholm NU744LN test samples containing hot cracks were carefully sectioned and broken in order to reveal hot crack fracture surfaces. The fracture surfaces were examined using a scanning electron microscope (SEM) equipped

with an energy dispersive spectrometer (EDS) in order to characterize the fracture morphology and identify particles or phases which were associated with the hot crack surface.

Analytical Evaluation

An electron microprobe was used to determine the degree of solute segregation associated with solidification and hot cracking in the commercial duplex alloys. The analyses were performed at an accelerating voltage of 25 kV and a beam current of 10 nA, producing an effective probe size of approximately 1 μ m (0.00004 in.).

Hot crack surface analysis was also performed on the commercial alloys, using a scanning Auger microprobe (SAM). An accelerating voltage of 5 kV and a beam current of 1.85 μ A were used to examine the surface. Composition depth profiles were obtained to a depth of 100 nm by sputtering the surface with a beam of argon ions.

Results

Predicted Solidification and Transformation Behavior

The solidification and solid-state phase transformation behavior of austenitic and duplex stainless steels is a strong function of the composition of the particular steel. Since the duplex stainless steels are basically high-Cr, low-Ni versions of the austenitic stainless steels, the Fe-Cr-Ni ternary system is useful for predicting the solidification and solid-state transformation characteristics of these materials. The pseudo-binary section of the Fe-Cr-Ni ternary system at 60 wt-% iron (Ref. 33), shown in Fig. 2, can be used to describe the behavior of a typical duplex stainless steel upon cooling from the solidification range. A nominal composition, C₀, at 30Cr-10Ni, has been selected as representative, since the majority of commercial alloys contain molybdenum and nitrogen additions which increase their "effective" chromium and nickel contents (Cr and Ni-equivalents), respectively.

Alloys which lie to the right of the triangular, three-phase region at approximately 25Cr-15Ni in Fig. 2 solidify as primary ferrite. Alloys which solidify as ferrite in close proximity to this three-phase region may form some austenite during the final stages of solidification, as a consequence of a peritectic/eutectic reaction (Refs. 21, 23). As the composition is enriched in chromium and depleted in nickel at a constant iron content, this reaction becomes less favorable and solidification is completely ferritic. Thus, Fig. 2 predicts that duplex stainless steels will solidify as primary ferrite with little or no austenite forming as a secondary solidification product.

ized in the ferrite phase. These particles could not be precisely identified, but were found to be enriched in chromium (Ref. 35). A precipitate-free zone corresponds to regions surrounding the austenite, suggesting that austenite may act as a sink for fast-diffusing, interstitial elements, such as carbon and nitrogen, which may be integral in the formation of the precipitate.

The weld microstructure and fusion boundary region of the Uddeholm NU744LN steel are shown in Fig. 3B. The ferrite content of the fusion zone was approximately EFN 70. Similar to the Ferralium Alloy 255, continuous austenite networks existed at the ferrite grain boundaries. A fine distribution of intragranular precipitates was observed within the fusion zone, reminiscent of the HAZ microstructure in the Ferralium Alloy 255 (Fig. 3A).

The weld structure of Alloy 21-9, shown in Fig. 3C, consisted of large ferrite grains with Widmanstatten-type austenite precipitating from the grain boundary austenite. The ferrite content of the Alloy 21-9 fusion zone was on the order of EFN 40, the lowest of the four duplex alloys evaluated. Alloy 23-7 exhibited a highly ferritic fusion zone microstructure with a ferrite content of approximately EFN 80 (Fig. 3D). Austenite in the Alloy 23-7 fusion zone was restricted almost exclusively to the grain boundaries. The fine intragranular precipitation observed in the Uddeholm NU744LN fusion zone was not apparent in Alloy 23-9.

Weld solidification substructure boundaries were not readily apparent in any of the weld microstructures. Closer examination of the Ferralium Alloy 255 microstructure (Fig. 4) did indicate that the intragranular austenite may precipitate along prior substructure (cellular or dendritic) boundaries. As mentioned previously, during solidification as primary ferrite, nickel partitions to the solidification boundaries (Refs. 20, 22, 23). Assuming diffusion is insufficient to eliminate the local nickel enrichment, this boundary will become a preferential site for austenite precipitation during cooling through the austenite plus ferrite phase field (Fig. 2). As the Cr_{eq}/Ni_{eq} increases, diffusion is more pronounced, since the weld cools through a larger temperature range in the ferrite phase field before the austenite transformation begins. As a result, any evidence of prior solidification structure or tendency for intragranular austenite precipitation is severely reduced.

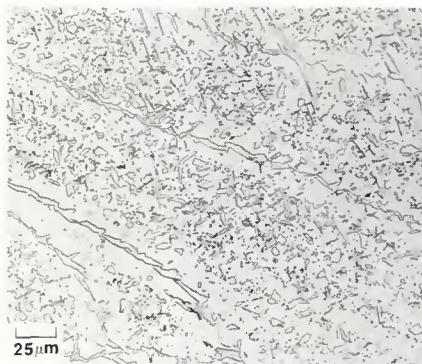


Fig. 4—Ferralium Alloy 255 fusion zone microstructure. Note the alignment of intragranular austenite along the solidification growth direction

cracking susceptibility was provided by plotting the total crack length (TCL) on the specimen surface versus the augmented strain over the range from 1/2 to 5%, as illustrated in Fig. 5. Using this index, the Ferralium Alloy 255 proved to be the most susceptible to hot cracking of the duplex alloys over the entire range of augmented strain. At intermediate strain levels (2 and 3%), the hot cracking susceptibility of Ferralium Alloy 255 and Uddeholm NU744LN were essentially identical, but both exceeded that of the experimental alloys (21-9 and 23-7) and the Type 304L alloy with 4.5 FN. At the lowest levels of augmented strain (below 1.5%), all the alloys tested, with the exception of the fully austenitic Type 304L material, exhibited equivalent crack

Table 3—Summary of Mini-Varestraint Test Results

Material	% Strain	No. Cracks	TCL (mm)
Ferralium Alloy 255	1.0	2	0.41
	1.5	4	0.76
	2.1	13	3.00
	3.1	24	6.24
	5.0	40	10.44
Uddeholm NU744LN	1.0	4	0.34
	1.5	4	0.41
	2.1	16	2.42
	3.1	24	5.57
	5.0	31	6.31
Alloy 21-9	0.5	0	0
	1.0	0	0
	2.1	5	0.72
	3.1	21	3.58
	5.0	43	7.10
Alloy 23-7	0.5	0	0
	1.0	0	0
	2.1	15	1.18
	3.1	12	2.23
	5.0	35	5.98
Type 304L (FN 5)	0.5	0	0
	1.0	0	0
	2.1	5	0.47
	3.1	33	2.65
	5.0	46	5.55
Type 304L (FN 0)	0.5	6	1.73
	1.0	16	6.23
	2.1	21	8.92
	3.1	24	11.86

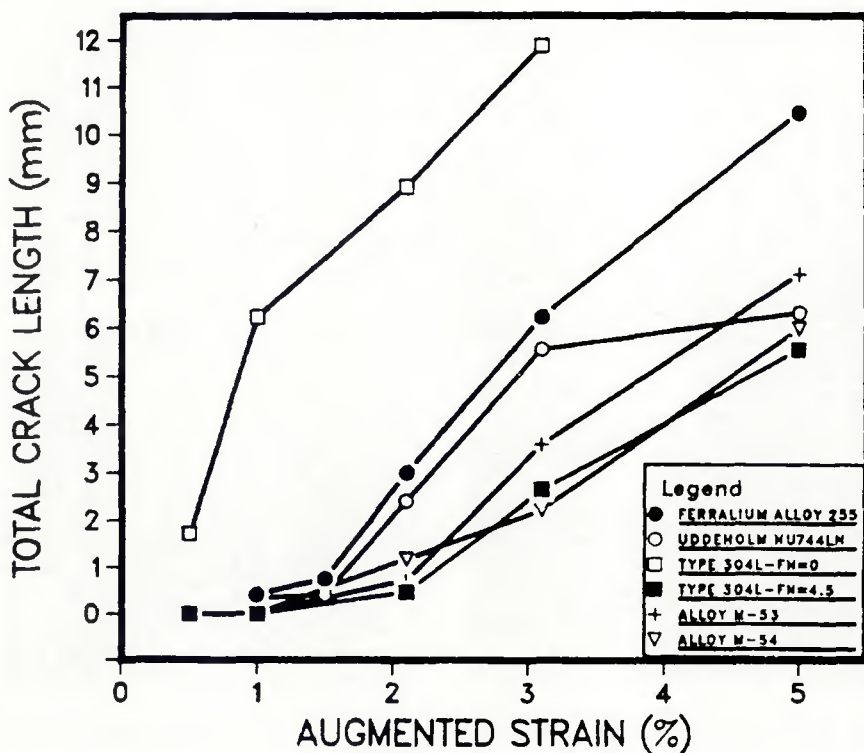


Fig. 5—Results of the mini-Varestraint test in terms of total crack length vs. augmented strain

Varestraint Test Results

The results of mini-Varestraint tests for the four duplex alloys and two Type 304L alloys are summarized in Table 3. The best index of the relative fusion zone hot

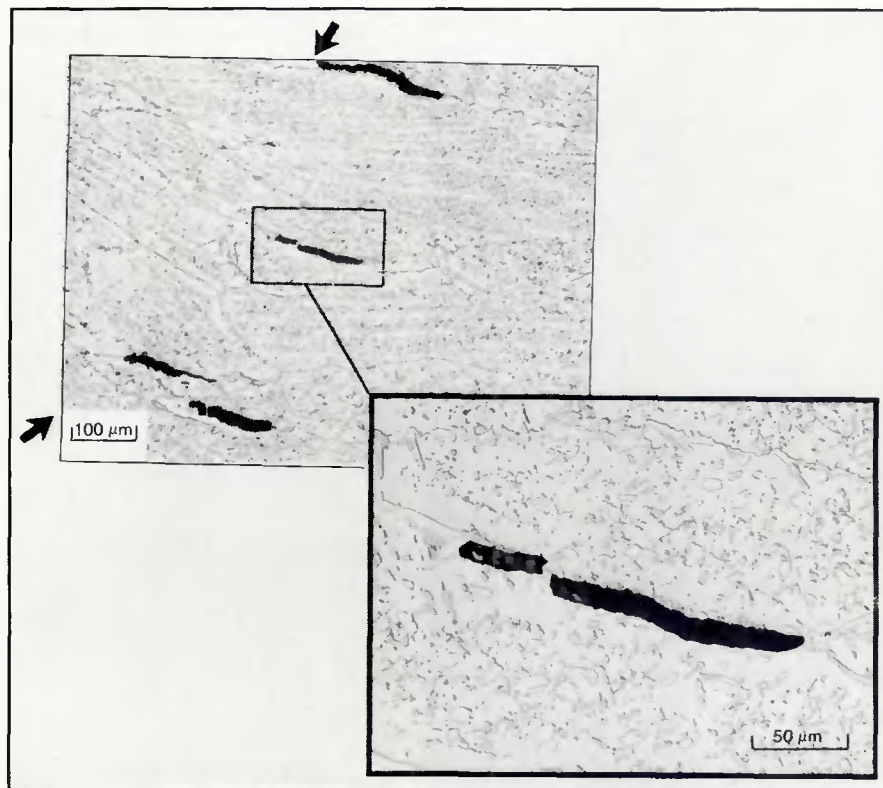


Fig. 6—Fusion zone hot cracking in a Ferralium Alloy 255 Varestraint sample tested at 5% strain (top surface section). Arrows indicate the approximate location of the solid-liquid interface at the instant of testing

susceptibilities. None of the duplex alloys approached the high degree of crack susceptibility found in the fully austenitic Type 304L alloy.

The average length of hot cracks at a particular strain level may also be used as a measure of the degree of susceptibility to cracking and often provides an indication as to the relative magnitude of the

embrittlement temperature range (Ref. 36). The average crack length (ACL) at 3.1% strain for the four duplex materials and the two 304L alloys is presented in Table 4. The ACL for the duplex materials is two to three times greater than that of the Type 304L alloy with FN 4.5, but is only one-third to one-half that of the fully austenitic Type 304L alloy. Assuming that the temperature gradient into the solid is nearly linear at temperatures just below the liquidus and relatively uniform for all the materials (welding parameters were identical), the embrittlement temperature range for fully ferritic or fully austenitic solidification would appear to be signifi-

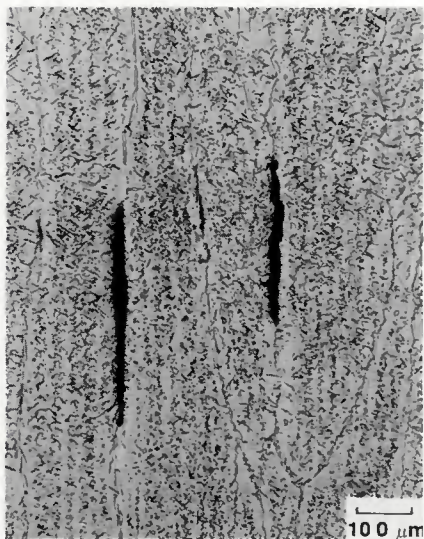


Fig. 7—Transverse section of a Ferralium Alloy 255 Varestraint specimen tested at 3% strain. Note the straight grain boundaries along which cracks propagate

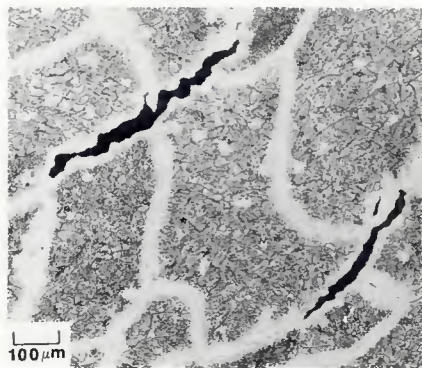


Fig. 8—Fusion zone hot cracking in a Uddeholm NU744LN Varestraint specimen tested at 5% strain

cantly greater than when austenite is a secondary solidification product, i.e., Type 304L, FN 4.5.

Metallographic Analysis of Varestraint Samples

Metallographic examination of the duplex stainless steel Varestraint samples revealed that hot cracking in all four materials was associated with fusion zone grain boundaries. Partitioning of alloy and impurity elements is generally greater along these grain boundaries than at the subgrain boundaries (Refs. 7, 8, 22), and thus weld hot cracking is more prevalent at these sites¹.

The top surface of a Ferralium Alloy 255 Varestraint sample tested at 5% strain is shown in Fig. 6. The hot cracks were distributed around the periphery of the solid-liquid interface at the instant of applied strain. As noted, the cracks shown in Fig. 6 were located at grain boundaries in the Ferralium Alloy 255 microstructure. These boundaries were delineated by the continuous austenite networks.

At higher magnification (inset, Fig. 6), note that austenite side plates emanated from the crack boundaries. Since it is likely that solidification of Ferralium Alloy 255 occurred entirely as ferrite (no eutectic/peritectic reaction), this austenite formed during cooling from the solidification range. Thus, the hot crack shown in Fig. 6 initiated and propagated along ferrite-ferrite grain boundaries.

A transverse metallographic section from a Ferralium Alloy 255 Varestraint sample is shown in Fig. 7. This section was located such that the subsurface hot cracks which formed during the Varestraint test were revealed. The solidification growth direction was nearly vertical in Fig. 7. This growth orientation resulted in relatively straight grain boundaries, which facilitated crack propagation.

A metallographic section representative of the top surface of a Uddeholm NU744LN Varestraint sample is shown in Fig. 8. Again, note that hot cracking was restricted to the prior-ferrite grain boundaries, as delineated by the continuous austenite networks. Similar metallographic sections are presented for Alloy 21-9 and Alloy 23-7 in Fig. 9.

1. Two types of grain boundaries may exist in the weld fusion zone. One type results from the impingement of solidification subgrains of different growth orientation and is delineated by both the growth orientation mismatch and elemental segregation. The other type results from migration of this boundary on cooling from the solidification temperature range. The former is the usual site for weld hot cracking and, unless otherwise specified, will be the type implied in this paper when discussing the weld fusion zone microstructure.

hot cracking than the commercial alloys. Differences in solidification crack susceptibility among similar alloys are often the result of slight variations in chemical composition, particularly with respect to impurity content. Table 1 shows that the level of sulfur and phosphorus in the experimental alloys was higher than that in the commercial alloys. Thus, the increase in cracking susceptibility due to higher impurity levels is not possible.

Note that both copper and molybdenum are present in the Ferralium (1.7Cu, 3.1Mo) and Uddeholm (0.2Cu, 2.4Mo) alloys but absent in the experimental alloys. Electron microprobe and Auger analysis of solidification grain boundaries (Fig. 13) and hot crack fracture surfaces (Fig. 14) of these alloys revealed an increase in both of these elements at these locations. Other elemental segregation (Ni, Mn, Si, P, S) to the solidification grain boundaries was similar among the duplex alloys and thus does not explain the difference in cracking susceptibility.

Copper and molybdenum both depress the melting point of Fe-base alloys (Refs. 37, 38). As a result, significant localized segregation of these elements to solidification grain and subgrain boundaries would likely reduce the solidification temperature relative to the surrounding weld microstructure and expand the effective solidification range of the weld. Unfortunately, it is difficult to predict the effect of individual alloying or impurity elements on hot cracking susceptibility in multicomponent systems from simple equilibrium binary systems. Synergistic interactions with other alloying (Ni, Mn, Cr, Si, C, N) or impurity elements (S and P) may promote the formation of liquid films along fusion zone boundaries, which would not be predicted by consideration of simple binary reactions. These same synergisms may enhance the wetting characteristics of the liquid along ferrite grain boundaries and further increase the cracking susceptibility.

Hot Crack Morphology

Hot crack surfaces generally exhibit fine protuberances associated with primary and secondary cellular-dendrite arms. In the present study, the careful examination of hot crack surfaces for the duplex stainless steels also revealed a columnar, microscopically flat region, and a gradual transition from this flat fracture near the rear portion of the hot crack (that farthest from the solid-liquid interface at the time of straining) to increasingly dendritic fracture near the front of the crack. Similar transitions in hot crack surface topography have been reported previously in stainless steels which solidify to either fully ferritic or fully austenitic structures (Refs. 39-41), and have been

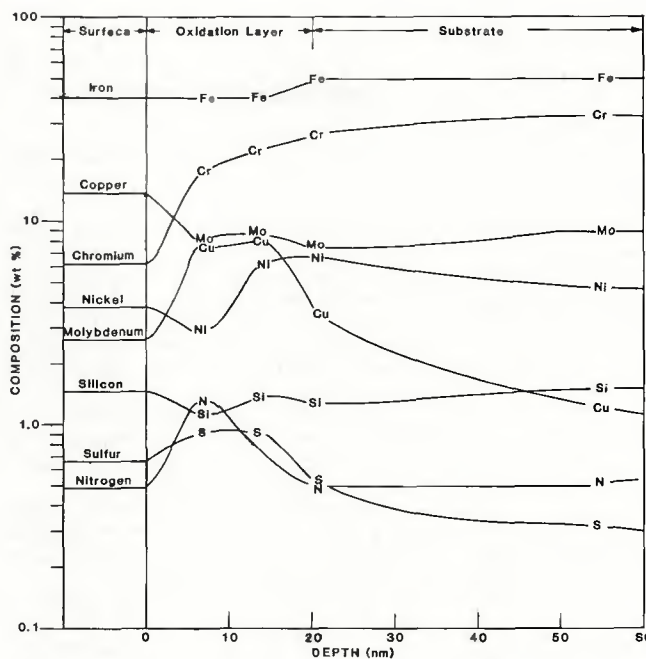


Fig. 14—Auger depth profile showing the concentration of elements on a Ferralium Alloy 255 hot crack surface. Carbon and oxygen were present as a 20-nm-thick contamination layer but have been omitted for clarity

attributed to a decrease in the quantity of residual liquids at interdendritic regions with decreasing temperature. Little tendency for the flat columnar fracture surface has been reported for hot cracks in welds which exhibit coupled ferrite/austenite solidification along fusion zone grain and subgrain boundaries and which contain a small amount of ferrite (FN 3-10) in the room temperature microstructure (Ref. 39). These results are consistent with the fractographic analysis of the FN 4.5 Type 304L alloy evaluated in the present investigation.

In order to understand the origin of the flat fracture on the surface of the weld hot cracks in the duplex alloys, and determine how this morphology relates to cracking susceptibility, it is necessary to define the boundary along which the fracture occurs. The fusion zone grain boundaries along which hot cracking is most prevalent originate by the impingement of cellular dendrites of different growth orientation during the final stages of solidification. Microscopically, this boundary would be expected to be very irregular during the final stages of solidification, and thus would tend to migrate following solidification in an effort to minimize the total grain boundary area. Evidence of such grain boundary migration is often visible in the room temperature microstructure as a difference between the actual grain boundary and the original solidification boundary, as delineated by the presence of residual, segregated alloying elements.

The examination of flat fracture surfaces in the duplex alloys studied in this investigation showed columnar-shaped, smooth fracture surfaces comparable to those commonly observed for intergran-

ular corrosion or mechanical fracture in the weld fusion zone, suggesting that this region is associated with crack propagation along a migrated grain boundary. This possibility is supported by Matsuda and Nakagawa (Ref. 39), who suggest that the flat fracture originates from grain boundary migration among residual liquids in the low-temperature crack region, and by Dixon and Phillips (Ref. 41), who relate flat fracture to the formation of grain boundaries during the final stages of solidification. Unfortunately, details of these grain boundary phenomena during the final stages of solidification have not been reported. Although the present investigation did not identify the specific origin of the flat fracture region, several potential explanations can be offered. These include:

1. Grain boundary migration and straightening while liquid is still present in a continuous or semi-continuous distribution.
2. Liquid penetration under a state of stress of a solidified and migrated grain boundary (analogous to liquid metal embrittlement).
3. The occurrence of solid-state "ductility-dip" cracking.

As noted above, Type 304L stainless steels exhibiting FN 3-15 display an exclusively dendritic crack surface (Ref. 39). Matsuda and Nakagawa (Ref. 39) suggest that this absence of flat fracture is related to the peritectic/eutectic reaction experienced during solidification of most Type 304 stainless steels, which prevents the grain boundary from migrating and straightening at near-solidus temperatures. The concept of such grain boundary irregularity or tortuosity reducing hot cracking in austenitic stainless steels was

