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Heat Treatment of Duplex Stainless Steel Weld Metals

High-temperature annealing prevented sigma embrittlement in Ni-enriched welds, but contributed to reduced yield strength

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ABSTRACT. Weld metals for duplex stainless steel Alloys 2205 and Ferralium® 255(1) were investigated for their response to annealing heat treatments. Those weld metals enriched in nickel for good as-welded properties were found to be embrittled by formation of sigma phase when annealed at 1900°F (1038°C). There was evidence that the sigma forms during heating to 1900°F and some of it dissolves only very slowly at 1900°F. Extended anneals of these weld metals at 1900°F appear to reach an equilibrium in which nearly half of the original ferrite becomes sigma. Annealing at temperatures of 2000°F (1093°C) or higher dissolved the sigma without difficulty. These weld metals could also be annealed above 2000°F, furnace cooled to 1900°F and held for a time, then quenched. Either the higher temperature anneal or the step-anneal resulted in high ductility and toughness but reduced yield strength. The weld metals with nickel matching the base metals could be annealed at 1900°F without producing sigma, and had adequate ductility but low toughness. In all cases, the annealed yield strength was considerably less than the as-welded yield strength. Higher nitrogen, up to 0.29%, tended to raise the annealed yield strength, but the 80 ksi (550 MPa) requirement for wrought Ferralium 255 could not be consistently achieved.

Introduction

Duplex austenitic-ferritic stainless steel base metals consist normally of approximately equal percentages of austenite and ferrite. In addition to general corrosion resistance at least equal to common austenitic stainless, duplex stainless steels have far superior stress corrosion cracking resistance and on the order of double the yield strength as compared to common austenitic stainless. Both the high strength and the stress corrosion cracking resistance of duplex stainless steels are attributable to the mixed microstructure, with usually an assist from alloying with nitrogen (often 0.10 to 0.30% N).

Wrought and cast duplex stainless steels solidify in ingot or casting form as essentially 100% ferrite. Some of that ferrite transforms to austenite during cooling from solidification. Further formation of austenite is achieved by annealing heat treatment, with or without hot working, to produce the final, approximately equal amounts of austenite and ferrite desired for best properties.

Welding of duplex stainless steels presents certain special problems. For weldments to be used in the as-welded condition, filler metal that matches the base metal, because of rapid cooling rates associated with welding, produces a microstructure that is predominantly ferrite. The resulting weldment has poor ductility, poor toughness and relatively poor corrosion resistance. Blumfield, Clark and Guha (Ref. 1), Bryan and Poznanski (Ref. 2), and Kotecki (Ref. 3) have clearly dem-

KEY WORDS

Duplex Stainless
Stainless Alloy 2205
Ferralium 255
Sigma Embrittlement
Heat Treatment
Annealing Treatment
Sigma Stability
Flux Cored Weld Wire
Ni-Enriched Weld Metal
Step-Annealing

(1) *Ferralium 255 is a registered trademark of Haynes International, Kokomo, Ind.*

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Table 1—Composition and Mechanical Property Requirements for Duplex Stainless Steel Base Metals

ASTM Specification	A240	A240	A743 or A744
Type	Alloy 2205	Ferralium 255	CD-4MCu
UNS Designation	S31803	S32550	—
C	0.030 max	0.04 max	0.04 max
Mn	2.00 max	1.5 max	1.0 max
P	0.030 max	0.040 max	0.04 max
S	0.020 max	0.030 max	0.04 max
Si	1.00 max	1.0 max.	1.00 max
Cr	21.0-23.0	24.0–27.0	24.5–26.5
Ni	4.50-6.50	4.5–6.5	4.75–6.00
Mo	2.50-3.50	2.0–4.0	1.75–2.25
N	0.08–0.20	0.10–0.25	not specified
Cu	not specified	1.5–2.5	2.75–3.25
Tensile, ksi (MPa)(a)	90 (620)	110 (760)	100 (690)
Yield, ksi (MPa)(a)	65 (450)	80 (550)	70 (485)
% Elongation(a)	25	15.0	16
Charpy V-notch	not specified	not specified	not specified

(a) Annealed at 1900°F (1040°C) minimum and water-quenched.

onstrated the desirability of filler metals enriched in nickel, but otherwise matching the base metal, for producing as-welded weld metals with reduced ferrite and improved mechanical properties. Biehl (Ref. 4) showed that the pitting resistance and stress corrosion cracking resistance of such enriched nickel weld metals are equivalent to that of the base metal. Filler metals resulting from these studies are in general commercial use at present.

However, not all duplex stainless steel weldments are intended for use in the as-welded condition. Cast pump shells, for example, may require weld repair of casting defects followed by annealing heat treatment. Pipe fittings may be fabricated by welding, hot formed, and subsequently annealed. Forgings may be repaired by welding and subsequently annealed. It is important, then, to examine the response of duplex stainless steel weld metals to annealing heat treatments.

Heat Treatment of Duplex Stainless Steel Base Metals

Duplex stainless, by virtue of its high ferrite content and the high chromium (and usually molybdenum) in that ferrite, is sensitive to two serious forms of embrittlement due to exposure to elevated temperatures. Solomon (Ref. 5) describes these in detail. Briefly, at temperatures centered around 885°F (475°C), a chromium-rich BCC phase, known as "alpha prime," precipitates in the BCC iron-rich ferrite, causing marked hardening and embrittlement. And at temperatures centered around 1300°F (700°C), a complex intermetallic compound that is approximately 50% iron-50% chromium, known as "sigma phase," forms from ferrite, causing marked embrittlement. Molybdenum tends to accelerate formation of both alpha prime and sigma phases, while nitrogen seems to have some beneficial effect in slowing formation of these phases. As a result of these two embrittlement mechanisms, heat treatment (and service) temperatures of 600°-1700°F (315°-925°C) are avoided. Moreover, annealing of duplex stainless steel is almost always followed by water quenching to avoid sigma and alpha prime during cooling.

For the present study, weld metals for two rather common duplex stainless steels were considered. These are Alloy 2205 (UNS designation S31803) and Ferralium 255 (UNS designation S32550). Ferralium 255 is compositionally similar to the cast alloy CD-4MCu so that the same filler metal can be suitable for both. The ASTM standards (Refs. 6–8) covering all of these alloys require a minimum annealing temperature of 1900°F, followed by water quench or other rapid cool.

Table 1 lists the composition and mechanical property requirements for base metals of the types for which filler metals were being evaluated in this study. Although a toughness criterion is not specified for these base metals, use in arctic service often imposes a supplementary 20 ft-lb (27 J) at −50°F (−46°C) Charpy V-notch requirement.

Reasons for the Present Study

As part of a development program for self-shielded flux cored duplex stainless steel wires for Alloy 2205 and Ferralium 255 to be used in the as-welded condition, a couple of 1900°F annealing experiments were carried out. Unexpectedly, the all-weld-metal tensile specimens exhibited extremely low ductility, and Charpy V-notch impact specimens tested at −50°F showed very low absorbed fracture energy. Furthermore, metallographic examination revealed extensive sigma phase in the metal. The accuracy of the furnace control for the annealing was checked with independent thermocouples and found to be adequate.

A literature search uncovered a study by Grobner (Ref. 9) of cast stainless steels, including duplex alloys, in which it was observed that increasing nickel from 5 to 20% in a 25% Cr-3.5% Mo iron-base alloy increased the maximum temperature at which sigma phase remained stable from less than 950°C (1740°F) to more than 1100°C (1980°F). And Howell, *et al.* (Ref. 14), observed sigma after a 1922°F (1050°C) anneal of a 20% Cr, 8.5% Ni, 3.2% Mo weld of unknown, but presumably low, nitrogen level.

In view of Grobner's work, that of Howell, *et al.*, and the early observation of sigma phase embrittlement in enriched nickel duplex weld metals, it was considered important to examine in more detail the annealing behavior of weld metals for duplex stainless steels.

Experimental Procedure

All weld metals examined herein were produced with self-shielded flux cored wires, mainly in 1/16-in. (1.6-mm) diameter, although the lowest nickel welding wires were produced in 3/32-in. (2.4-mm) diameter. The objective in designing these wires was to try to match the required base metal properties in annealed all-weld-metal test specimens, and to try to meet a Charpy V-notch minimum of 20 ft-lb (27 J) at −50°F (−46°C).

For each experimental welding wire, all-weld-metal test plates were prepared in 3/4-in. (19-mm) thick mild steel plates as given in AWS A5.22 (Ref. 10). The joint faces were buttered with two layers of weld metal, leaving a groove with a 45-deg included angle and 1/2-in. (12.5-mm) root opening. This groove was then filled in about six layers of two passes per layer. For 1/16-in. wires, welding conditions were 220–240 A, 28–30 V DCEP, 1-in. (25-mm) electrode extension. For 3/32-in. wires, welding conditions were 275–300 A, 28–30 V DCEP, 1 1/4-in. (31-mm) electrode extension.

Several test plates were prepared with each electrode to allow testing of several heat treatment conditions. After a weldment was completed, the base metal was cut away by oxyacetylene about 1-in. (25-mm) from the buttering. For annealing, the remaining weldment, about 4 1/2 in. (115 mm) wide and 14 in. (355 mm) long, was placed in a furnace initially above 1000°F (540°C), and the controller of the furnace was then set to the desired annealing temperature. From four to five hours were required to reach the annealing temperature, and holding time at temperature was not considered to begin until preset temperature was reached. A few test plates were step-annealed, first at a higher temperature and then furnace cooled to 1900°F (1038°C) and held. When heat treatment was completed, the test plate was withdrawn from the furnace and dropped immediately into a barrel of cold water for quenching.

After heat treatment, a standard all-weld-metal, ½-in. (12.5-mm) diameter tensile specimen (Ref. 10) and five Charpy V-notch specimens were machined. The Charpy specimens were oriented transverse to the weld centerline and notched perpendicular to the original plate surface. The tensile specimen was broken at room temperature, and the five Charpy V-notch specimens were broken at −50°F. Charpy results were then averaged for reporting purposes.

After each tensile specimen was fractured, a flat area was ground—finishing with 600-grit abrasive—on one shoulder outside the reduced section parallel to the original plate surface. Five ferrite measurements were taken in this area using a Magne Gage and the procedure given in Ref. 11. The average ferrite number was then calculated.

In addition to the all-weld-metal test plates, an eight-layer all-weld-metal pad for chemical analysis was produced with each experimental wire using the same welding conditions. A complete analysis, including nitrogen, was run on each pad. Since nitrogen can depend to a certain extent on welding conditions with self-shielded flux cored wires (Ref. 12), a second nitrogen check was made on broken tensile specimens, which confirmed the nitrogen analysis of the matching eight-layer pad. Nitrogen results reported herein are those obtained from annealed sigma-free tensile specimens.

When sigma phase was observed in the first welds annealed at 1900°F, it was considered that there could be two possible explanations. The more obvious was that sigma in these weld metals is stable at 1900°F. The second possibility is that sigma was forming during heating to 1900°F and slow to dissolve at 1900°F. When a test plate was placed in the furnace, it brought the furnace temperature down quickly and, as noted earlier, four to five hours was needed to reach 1900°F. So the test plate had to spend considerable time at temperatures where sigma forms rapidly. To test which was really the case, a piece about ½ in. long was cut from the shoulder of one tensile specimen that had been annealed at 1900°F (embrittled by sigma), and one that had been annealed at 2000°F (1093°C) or higher (no sigma). This was done with samples from Alloy 2205 weld metal and from Ferralium 255 weld metal. These small samples could be placed directly in the 1900°F furnace and reach temperature very quickly, so they saw very little additional time in the sigma temperature range. Then by withdrawing the samples and quenching after various holding times, one could follow the progress of sigma formation or dissolution by measuring ferrite on the samples. After ferrite measurement, the samples were returned to the 1900°F furnace for further holding at temperature. This was repeated until no further ferrite change occurred. Finally, to be sure that interrupting the anneal at various times was not influencing the results, a second sample from each tensile specimen was annealed at 1900°F for 96 h continuously before quenching.

The manufacturers of Ferralium 255 strongly recommend annealing of this alloy at 1900°F to optimize the partitioning of nitrogen between ferrite and austenite (Ref. 13). This is claimed to optimize corrosion resistance. When sigma was observed in welds annealed 2 to 4 h at 1900°F, longer anneals (up to 16 h) and step-anneals (holding first at 2100°F / 1149°C to be certain that all sigma was dissolved, furnace cooling to 1900°F, and then holding at 1900°F before quench) were considered as alternatives to comply with this recommendation.

Experimental Results—Alloy 2205 Type Weld Metals

Only two compositions of Alloy 2205-type weld metal were considered. One contained about 8.3% Ni and the other was a matching composition, 6.1% Ni. Table 2 details the test results obtained, both as-welded and heat treated. The 8.3% Ni composition is the same as was developed in the as-welded study (Ref. 3) and shows excellent as-welded properties. The 6.1% Ni weld has surprisingly good ductility in the as-welded condition, in view of the findings of the as-welded study. However, the as-welded toughness of the 6.1% Ni weld would not be acceptable for a 20 ft-lb at −50°F (27J at −46°C) requirement.

The properties of the 8.3% Ni weld annealed at 1900°F (1038°C), as noted in "Reasons for the Present Study" above, were a surprise—very low ductility and toughness. A ferrite measurement on the shoulder of the broken tensile specimen suggested extensive sigma phase, since ferrite transforms to sigma, as noted earlier. Metallographic examination confirmed the presence of extensive sigma, which was not present in the as-welded condition—Fig. 1. In contrast, the 8.3% Ni weld annealed at 2000°F (1093°C) was free of any traces of sigma—Fig. 2. The etchant, Kalling's reagent, darkens ferrite rapidly, attacks sigma more slowly, and

Table 2—Alloy 2205-Type Weld Metal Results

Experimental Wire			9292-109				9292-204	
Deposit C			0.028				0.027	
Mn			1.77				0.67	
P			0.025				0.007	
S			0.006				0.011	
Si			0.46				0.26	
Cr			21.60				22.61	
Ni			8.32				6.11	
Mo			3.15				3.10	
N			0.12				0.193	
Anneal, h	As-	2	4	4	4	As-	4	4 + 2
@ Temp., F°(C°)	Welded	1900 (1038)	1950 (1066)	2000 (1093)	2050 (1121)	Welded	1900 (1038)	2100 (1149) 1900 (1038)
Tensile, ksi	117.0	109.4	106.0	103.0	105.0	108.4	108.0	104.0
(MPa)	(807)	(754)	(731)	(710)	(724)	(747)	(745)	(717)
Yield, ksi	86.0	72.5	65.0	66.0	66.2	85.3	66.8	64.9
(MPa)	(593)	(500)	(448)	(455)	(456)	(588)	(461)	(447)
% Elongation	30.5	4.5	28	36	36.0	28	33.5	39.0
Charpy V@ −50°F/−46°C, ft-lb (J)	38.0 (51.5)	2.3 (3.1)	49 (66.4)	52 (70.5)	53.6 (72.7)	18.5 (25.1)	17.1 (23.2)	16.2 (22.0)
Ferrite of Tensile Specimen, FN	46	4	20	43	42	88	61	58

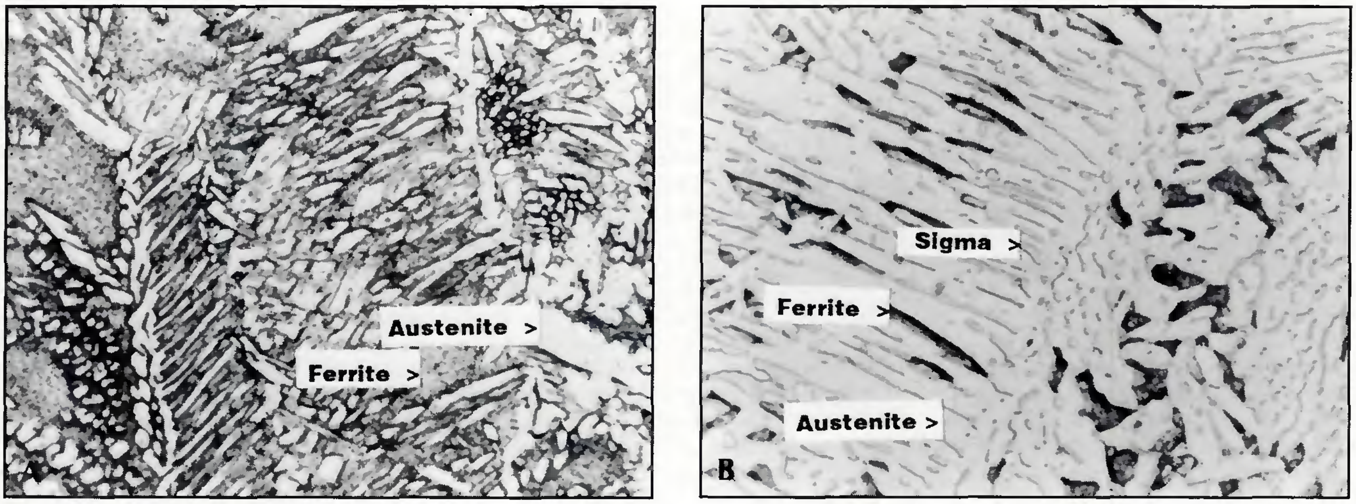


Fig. 1—Microstructures of welds from Experiment 9292-109 (8.3% Ni Alloy 2205). A—As-Welded; B—annealed at 1900°F (1038°C) for 2 h

leaves austenite unattacked. Some coarsening of the microstructure is observable after annealing, especially at higher temperature.

To examine if the sigma formed at 1900°F, or if it formed during heating and was slow to dissolve, small pieces were cut from the shoulder of the tensile specimen annealed at 1900°F with sigma already in it, and from the shoulder of the tensile specimen annealed at 2000°F, as described earlier. Ferrite numbers measured on these samples after various times at 1900°F are shown in Fig. 3. It can clearly be seen that, with the sigma-embrittled material, ferrite content rises with time at 1900°F as some of the sigma dissolves and reverts back to ferrite. On the other hand, for the sample annealed at 2000°F, ferrite drops from the initially high value as some sigma forms and the equilibrium ferrite plus sigma content at 1900°F is approached. With long-enough annealing, both samples reach the same ferrite content, which is considerably less than that of the as-welded condition for the same wire. Considerable sigma is present along with the ferrite and austenite—Fig. 4.

The sample of 8.3% Ni weld metal annealed at 1950°F (1066°C) for four hours showed some evidence of sigma also (Fig. 5) but considerably less than after 1900°F anneal.

The 8.3% Ni samples annealed at 2000°F and 2050°F (1121°C) showed no sigma. Their mechanical properties are very good, exceeding the base metal requirements (Table 1) for Alloy 2205, although their yield strengths barely exceed the minimum requirement. The anneals at these two temperatures markedly lowered the yield strength compared to the as-welded condition, while significantly improving upon the already adequate toughness.

On the other hand, the 6.1% Ni weld metal annealed at 1900°F or step-annealed at 2100°F (1149°C), and then 1900°F, showed similar loss of yield strength but no improvement in toughness. Neither annealed weld of this composition met the 20 ft-lb at −50°F toughness criterion. There was no evidence of sigma in these weld metals.

Since both the 2000°F and 2050°F anneals resulted in 8.3% Ni weld metal that met base metal requirements for Alloy 2205, it did not appear of interest to explore additional compositions. The 8.3% Ni filler metal could be recommended for both the as-welded and annealed conditions, although it required more than the minimum annealing temperature specified by ASTM A240.

Experimental Results—Ferralium 255 Type Weld Metals

In all, twelve wire compositions of Ferralium 255-type weld metal were produced and evaluated. The compositions were chosen in an iterative fashion over a period of about three years, seeking an optimum composition for the annealed condition. These are listed in Table 3. Some additional annealing conditions were tried also, with some weld metals, but they added nothing to understanding

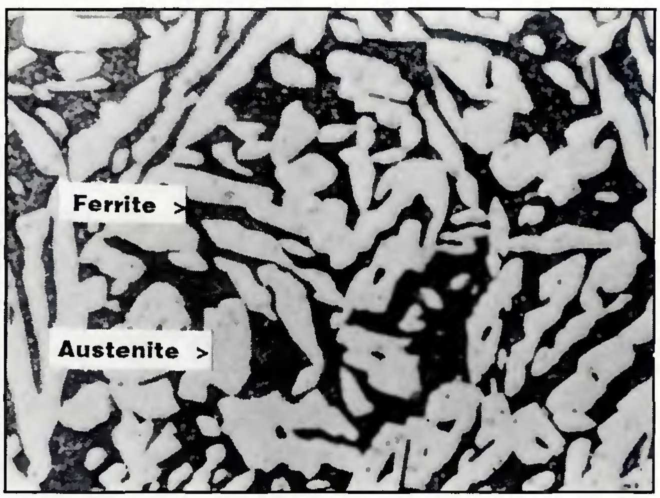


Fig. 2—Microstructure of weld from Experiment 9292-109 (8.3% Ni Alloy 2205). Annealed at 2000°F (1093°C) for 4 h

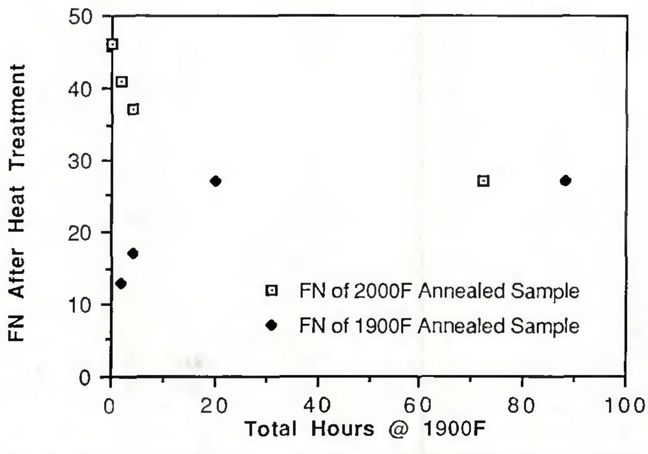


Fig. 3—Effect of extended heat treatment at 1900°F on ferrite content of weld 9292-109

Table 3—Ferralium 255 Type Weld Metal

Experiment	9292-112	9292-136	9292-137	9292-161	9292-174	9292-202	9292-203	9292-231	9292-358	9292-622	9292-650	9292-678
C	0.014	0.019	0.020	0.022	0.025	0.024	0.023	0.018	0.019	0.023	0.019	0.018
Mn	1.06	1.11	1.08	0.94	0.97	0.59	0.92	0.95	1.39	1.38	1.36	1.33
P	0.026	0.033	0.028	0.029	0.028	0.004	0.030	0.033	0.029	0.025	0.033	0.026
S	0.005	0.010	0.009	0.005	0.005	0.011	0.007	0.004	0.006	0.015	0.008	0.009
Si	0.36	0.61	0.78	0.33	0.25	0.03	0.20	0.37	0.17	0.22	0.37	0.16
Cr	24.51	23.41	23.31	24.26	24.34	25.20	25.08	25.12	26.26	25.31	25.39	26.29
Ni	10.17	7.31	7.18	8.96	8.46	5.85	9.04	9.55	9.20	9.35	9.42	9.52
Mo	3.18	3.29	3.77	2.93	2.74	2.99	3.01	3.41	3.40	3.30	2.93	3.40
Cu	2.14	2.00	2.06	1.70	1.93	2.04	1.97	2.00	1.90	2.14	2.09	2.13
N	0.100	0.203	0.217	0.154	0.194	0.173	0.152	0.134	0.249	0.256	0.266	0.289
As-Welded Properties												
Tensile, ksi (MPa)	121.8 (840)	127.6 (880)	131.8 (909)	120.1 (828)	123.2 (849)	120.8 (833)	125.2 (863)	126.8 (874)	131.3 (905)	120.2 (829)	123.5 (852)	132.3 (912)
Yield, ksi (MPa)	89.6 (618)	98.9 (682)	105.0 (724)	93.1 (642)	89.9 (620)	98.6 (680)	98.0 (676)	100.1 (690)	98.9 (682)	89.4 (616)	94.2 (650)	99.8 (688)
% Elong. in 2 in.	24.5	21.5	18.0	28.0	31.0	22.5	26.0	13.0	27.5	30.0	33.0	30.5
ft-lb (J) @ −50°F	26.3 (35.7)	13.3 (18.0)	13.2 (17.9)	30.4 (41.2)	22.1 (30.0)	10.6 (14.4)	24.1 (32.7)	23.6 (32.0)	18.2 (24.7)	18.0 (24.4)	15.1 (20.5)	15.1 (20.5)
Ferrite, FN	45	42	53	64	50	100	54	58	53	34	42	36
Properties After Anneal With at Least Some Embrittlement												
h @ °F	2 @ 1900	—	—	4 @ 1900	4 @ 1900	—	4 @ 1900	2 @ 1900	4 @ 1900	4 @ 1900	4 @ 1900	4 @ 1900
Tensile, ksi (MPa)	106.1 (732)	—	—	110.5 (762)	116.2 (801)	—	114.7 (791)	101.1 (697)	122.0 (841)	123.2 (849)	114.1 (787)	110.2 (760)
Yield, ksi (MPa)	79.1 (545)	—	—	65.7 (453)	73.4 (506)	—	69.3 (478)	85.1 (587)	92.9 (641)	76.4 (527)	81.5 (562)	92.6 (638)
% Elong. in 2 in.	1.0	—	—	37.0	34.0	—	7.0	1.5	2.0	10.0	2.0	1.0
ft-lb (J) @ −50°F	2.6 (3.5)	—	—	49.5 (67.1)	10.3 (14.0)	—	2.3 (3.1)	2.2 (3.0)	1.4 (1.9)	2.2 (3.0)	1.9 (2.6)	1.4 (1.9)
Ferrite, FN	2	—	—	40	39	—	28	1	5	16	4	3
Properties After Anneal With No Embrittlement												
hr @ °F	2 @ 2050	4 @ 2000	4 @ 2000	4 @ 2100	4 @ 2050	4 @ 1900	—	2 @ 2100	4 @ 2100	4 @ 2100	4 @ 2100	4 @ 2100
Tensile ksi (MPa)	106.2 (732)	118.5 (817)	120.7 (832)	109.8 (757)	114.4 (789)	114.7 (791)	—	117.1 (807)	125.7 (867)	117.6 (811)	117.1 (807)	124.3 (857)
Yield, ksi (MPa)	65.7 (453)	73.0 (503)	73.6 (507)	67.0 (462)	72.2 (498)	71.4 (492)	—	73.8 (509)	80.0 (552)	72.3 (499)	73.8 (509)	79.2 (546)
% Elong. in 2 in.	33.0	32.0	33.5	33.5	36.0	30.0	—	32.0	30.0	35.5	39.5	38.0
ft-lb (J) @ −50°F	52.1 (70.6)	21.4 (29.0)	23.9 (32.4)	53.5 (72.5)	32.7 (44.3)	12.0 (16.3)	—	52.6 (71.3)	26.6 (36.1)	32.8 (44.5)	30.2 (41.0)	25.0 (33.9)
Ferrite, FN	45	44	48	43	39	66	—	52	44	30	28	41
Properties After Step Anneal With No Embrittlement												
h @ 2100 °F	2	—	—	2	2	4	4	—	—	—	—	4
h @ 1900 °F	2	—	—	2	2	2	2	—	—	—	—	2
Tensile, ksi (MPa)	107.3 (740)	—	—	108.8 (750)	112.4 (775)	112.9 (778)	113.7 (784)	—	—	—	—	126.3 (871)
Yield, ksi (MPa)	60.4 (416)	—	—	63.4 (437)	67.4 (465)	72.8 (502)	65.7 (453)	—	—	—	—	76.2 (525)
% Elong. in 2 in.	34.0	—	—	34.0	34.5	34.0	35.0	—	—	—	—	29.0
ft-lb (J) @ −50°F	50.6 (68.6)	—	—	25.4 (34.4)	32.3 (43.8)	9.5 (12.9)	37.5 (50.9)	—	—	—	—	21.0 (28.5)
Ferrite, FN	42	—	—	51	46	66	45	—	—	—	—	35

Temperature conversions: −50°F = −46°C, 1900°F = 1038°C, 2000°F = 1093°C, 2050°F = 1121°C, 2100°F = 1149°C.

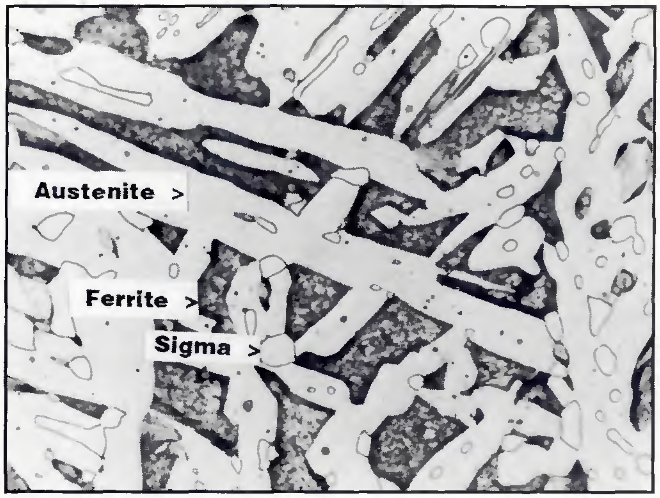


Fig. 4—Microstructure of weld from Experiment 9292-109 (8.3% Ni Alloy 2205). Annealed 96 h at 1900°F (1038°C)

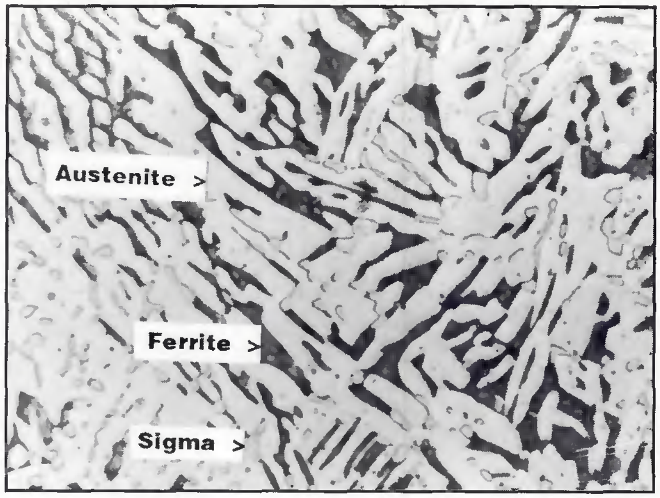


Fig. 5—Microstructure of Experiment 9292-109 (8.3% Ni Alloy 2205). Annealed at 1950°F (1066°C) for 4 h

the annealing behavior, except where specifically noted.

Experiment 9292-112 is the same as the optimum as-welded composition (Ref. 3), although slightly lower nitrogen was observed. The as-welded properties exceed all base metal minimum requirements from ASTM A240 as well as the supplementary Charpy V-notch requirement of 20 ft-lb at −50°F.

However, the sample of this weld annealed at 1900°F was severely embrittled by sigma phase, just as was the optimum as-welded Alloy 2205-type weld metal. The sample annealed at 2050°F showed no sigma. Microstructures from these two tensile specimens are shown in Figs. 6 and 7. As with the optimum as-welded Alloy 2205-type weld metal, small samples of these two tensile specimens were subjected to further heat treatment at 1900°F for various times. Again, the ferrite content of the sigma-embrittled sample rose with increasing time at 1900°F, while that of the initially sigma-free sample fell with increasing time at 1900°F—Fig. 8. Eventually, the FN of the two samples reached the same value. After 96 h at 1900°F, the microstructure consists of an apparently equilibrium mix of austenite, ferrite, and sigma—Fig. 9. Again, this indicated that sigma formed during heating to 1900°F was slow to dissolve at 1900°F, and that some sigma is stable at 1900°F in this composition.

It is noteworthy that the yield strength of the weld metal of Experiment 9292-112 annealed at 2050°F dropped markedly as compared to the as-welded condition. It meets neither the wrought metal requirements of ASTM A240 (80 ksi/550 MPa) nor the cast metal requirements of ASTM A743 or A744 (70 ksi/485MPa), (see Table 1 versus Table 3).

The step-annealed weld metal is even lower in strength in this particular case, although it is also more than adequate in ductility and toughness. Then, if the recommendation of the supplier of Ferralium 255 base metal is to be followed, this weld metal could be used wth step-annealing, albeit with lower yield strength.

It was considered that the low yield strength after annealing in 9292-112 was at least in part due to nitrogen being at the low end of the composition range of base metal. Accordingly, Experiments 9292-136 and 9292-137 were prepared with higher nitrogen at two molybdenum levels. Because higher nitrogen could be expected to reduce ferrite, nickel was reduced in these experiments to keep ferrite in balance (30-60 FN as-welded was considered optimum based on Ref. 3). Nitrogen over 0.20% was achieved in weld metal from both experiments—Table 3.

The as-welded properties of both Experiments 9292-136 and 9292-137 meet base metal requirements, although the ductilities are lower than that of 9292-112. The toughness does not meet the supplementary criterion, however. Only annealing at 2000°F was considered for heat treatment information because the as-welded properties were not satisfactory.

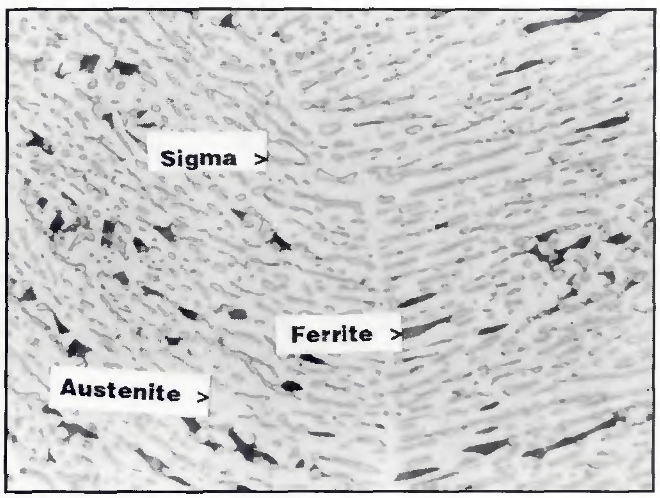


Fig. 6—Microstructure of weld from Experiment 9292-112 (10.2% Ni Ferralium 255). Annealed 2 h at 1900°F (1038°C)

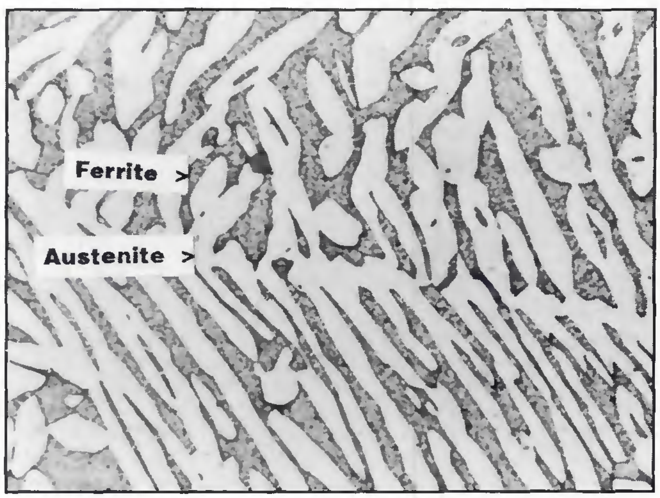


Fig. 7—Microstructure of weld from Experiment 9292-112 (10.2% Ni Ferralium 255). Annealed 2 h at 2050°F (1121°C)

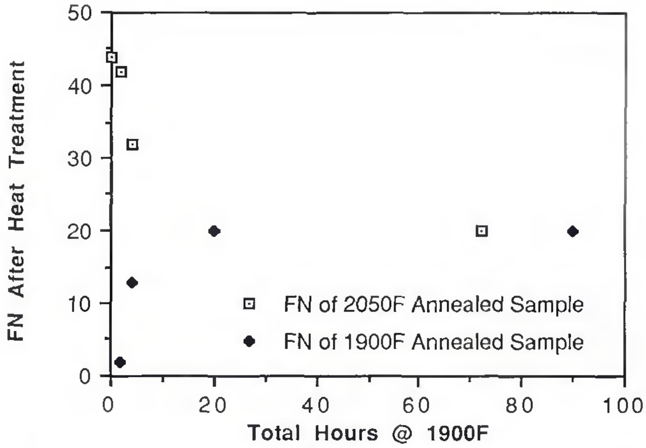


Fig. 8 — Effect of extended heat treatment at 1900°F on ferrite content of Weld 9292-112

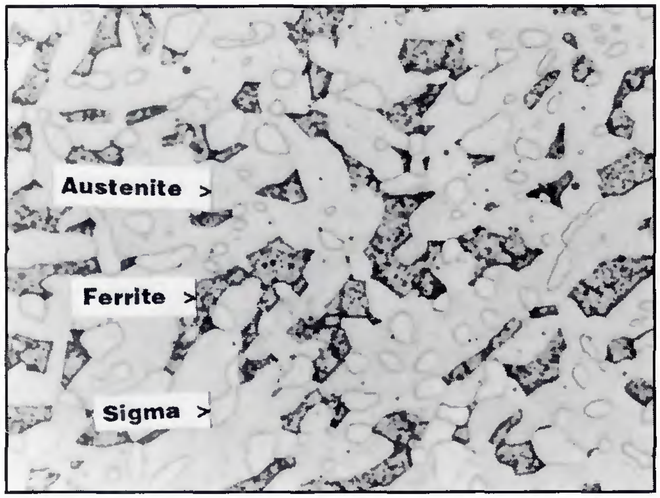


Fig. 9 — Microstructure of weld from Experiment 9212-112 (10.2% Ni Ferralium 255). Annealed 96 h at 1900°F (1038°C)

No sigma was found in these annealed welds. The ductility and toughness of both annealed welds were improved compared to the as-welded condition. And the annealed yield strength for both experiments exceeded the 70 ksi (485 MPa) requirement for cast CD-4MCu, but not the Ferralium 255 yield strength requirement of 80 ksi (550 MPa). The higher molybdenum of experiment 9292-137 had at best only a minor improving effect on annealed yield strength.

The next two experimental wires for Ferralium 255-type weld metal (9292-161 and 9292-174) were made with reduced molybdenum because the base metal manufacturer suggested this would reduce sigma problems after 1900°F anneal. Nickel was increased to improve toughness, and two levels of nitrogen were considered. The as-welded properties (Table 3) meet all base metal requirements and the supplementary toughness criterion. The properties after 1900°F anneal do not meet the wrought material requirements. The higher nitrogen weld metal 9292-174 meets the cast material requirements but not the supplementary toughness criterion. No sigma was found in this weld metal (Fig. 10) although the toughness is surprisingly low compared to the as-welded condition or to higher temperature-annealed conditions — Table 3.

The weld metals of 9292-161 and 9292-174 annealed at 2050°F or higher had high toughness and ductility. Although the higher nitrogen weld metal does meet the cast metal yield strength requirement, neither meets the wrought material requirement. The step-annealed weld metal, in both cases, has still lower yield strength, neither sample meeting the cast material requirement.

At this point, it seemed advisable to examine weld metal that matched the base metal composition, Experiment 9292-202. This wire was produced in 3/32-in. (2.4-mm) diameter using a low-carbon mild steel tube, in contrast to all other Ferralium 255 experiments which were made with a 304L stainless steel tube in 1/16-in. (1.6-mm) diameter. This resulted in weld metal of much lower silicon and phosphorus than from the other wires — Table 3. The as-welded ferrite content is extremely high (100 FN, which is appreciably less than 100% ferrite, Ref. 11). The as-welded mechanical properties meet all base metal tensile requirements, but not the supplementary toughness criterion.

Annealing weld metal of 9292-202 at 1900°F greatly reduced its ferrite content, but left no sigma — Fig. 11. As before, the yield strength dropped markedly due to annealing. However, the toughness did not improve significantly as compared to the as-welded condition. In this case, step-annealing did not further reduce the yield strength. Neither heat treatment resulted in weld metal meeting the wrought base metal yield strength requirement.

The next two experimental wires (9292-203 and 9292-231) were made with nickel above 9% and molybdenum aimed at 3.0 and 3.4%, respectively — Table 3. The as-

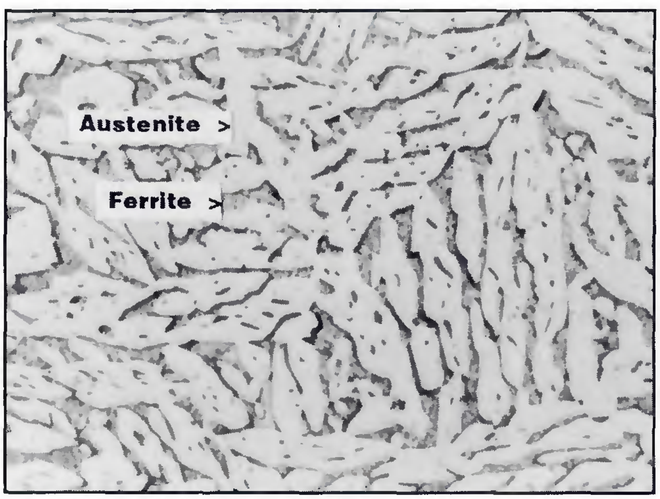


Fig. 10 — Microstructure of weld from Experiment 9292-174 (8.5% Ni, 2.7% Mo Ferralium 255). Annealed 4 h at 1900°F (1038°C)

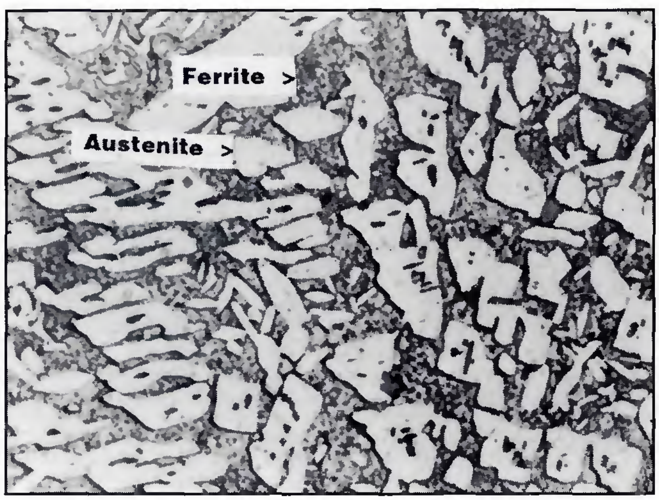


Fig. 11 — Microstructure of weld from Experiment 9292-202 (5.9% Ni Ferralium 255). Annealed 4 h at 1900°F (1038°C)

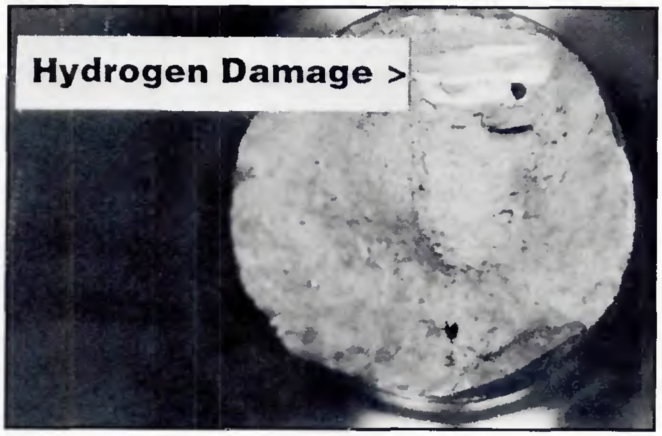


Fig. 12 — Tensile specimen fracture surface of weld from Experiment 9292-231, (9.5% Ni, 3.4% Mo) as-welded

welded properties of the lower Mo weld (9292-203) meet base metal requirements, but those of the higher Mo weld (9292-231) fall short of requirements in ductility (% elongation). The ferrite of this weld is nearly 60 and the tensile specimen showed hydrogen damage (Fig. 12), also noted in high-ferrite welds of Ferralium 255-type in the as-welded study (Ref. 3). The lower Ni, lower Mo weld (9292-203) after 1900°F had nearly half of its original ferrite converted to sigma, evidenced by the ferrite number as-welded versus 1900°F annealed, and shown by its microstructure — Fig. 13. On the other hand, the higher Ni, higher Mo weld (9292-231) after 1900°F had nearly all of its ferrite converted to sigma — Fig. 14.

The only sigma-free weld of 9292-203 was step-annealed — no high-temperature anneal was tried. This weld was ductile and tough, but of very low yield strength. On the other hand, only a 2100°F anneal was evaluated with 9292-231. This produced ductile, tough weld metal meeting the casting yield strength requirement, but not the wrought base metal yield strength requirement.

The inability at this point to achieve 80 ksi (550 MPa) yield strength in sigma-free annealed weld metal in Ferralium 255-type alloys was somewhat surprising. Since the most potent strengthener in these alloys was considered to be nitrogen, the next experimental wire (9292-358) was aimed at 0.25% nitrogen, and chromium was aimed at 26% to enhance nitrogen solubility. The as-welded properties (Table 3) meet base metal requirements, but not the supplemental toughness criterion. The weld metal annealed at 1900°F contained extensive sigma and was very brittle. The weld metal annealed at 2100°F only barely met the 80 ksi yield strength objective and had more than adequate ductility and toughness.

Step-annealing of Experiment 9292-358 was not tried. But, since the nitrogen was much higher in this weld metal than in that of the first Ferralium 255-type weld (9292-112), it was considered that the nitrogen might reduce sigma stability so that longer times at 1900°F would cause some sigma to dissolve or revert to ferrite. Yet, the higher chromium of 9292-358 might work in the opposite direction. Accordingly, separate weldments were annealed for 8 h and for 16 h. As compared to the 4-h anneal at 1900°F shown in Table 3, the 8-h and 16-h anneals produced no improvement whatsoever in ductility or toughness, and no increase in ferrite number. It must therefore be concluded that sigma is very stable at 1900°F in this composition.

Assuming that the high nitrogen of 9292-358 was the necessary requirement to achieve 80 ksi after an anneal that avoided sigma, and that the high chromium of this experiment stabilized sigma at 1900°F, two new experiments were produced with similar high nitrogen, but reduced chromium, at two molybdenum levels. These are Experiments 9292-622 and 9292-650 — Table 3. The as-welded properties of both are quite similar and meet the base metal requirements, but not the supplementary toughness criterion. Annealing of weld metal from both wires for 4 h at 1900°F again resulted in extensive sigma with resulting poor ductility and toughness.

Annealing weld metal from these two experimental wires at 2100°F produced no sigma, good ductility and toughness, but yield strengths below the 80 ksi base metal requirement. In comparing these results to the same anneal with 9292-358, it seemed clear that nitrogen alone was insufficient for meeting the yield strength requirement. Higher chromium might also be necessary.

The last experimental wire, Experiment 9292-678, returned to chromium above 26% (like 9292-358) and raised the nitrogen still higher — 0.289% was measured in the broken tensile specimen. The as-welded tensile, yield and ductility were all very high. The as-welded Charpy impacts were short of the supplemental requirement. The weldment annealed at 1900°F was severely embrittled by sigma. The weld annealed at 2100°F was ductile and tough. Its yield strength nearly reached the 80 ksi base metal requirement. Again, the step-annealed weld metal provided a

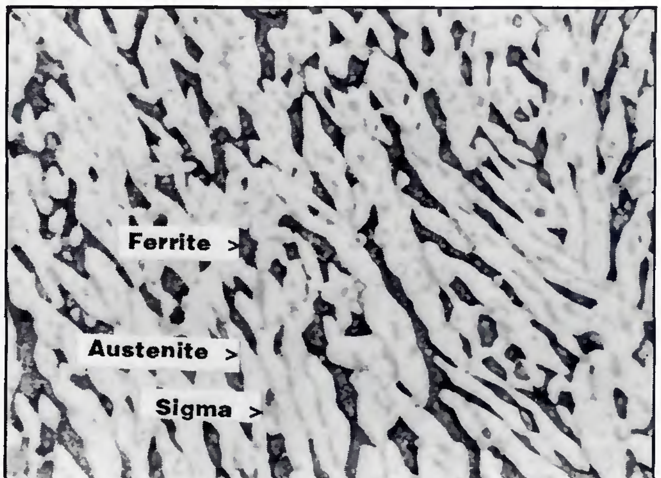


Fig. 13 — Microstructure of weld from experiment 9292-203 (9% Ni, 3% Mo Ferralium 255). Annealed 4 h at 1900°F (1038°C)

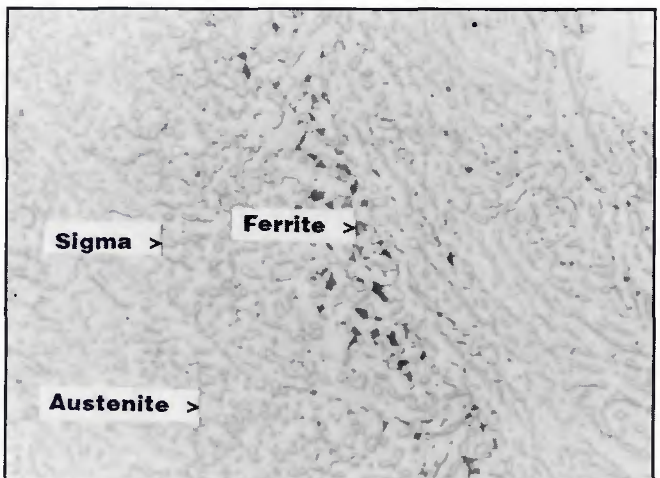


Fig. 14 — Microstructure of weld metal from Experiment 9292-231 (9.5% Ni, 3.4% Mo Ferralium 255). Annealed 2 h at 1900°F (1038°C)

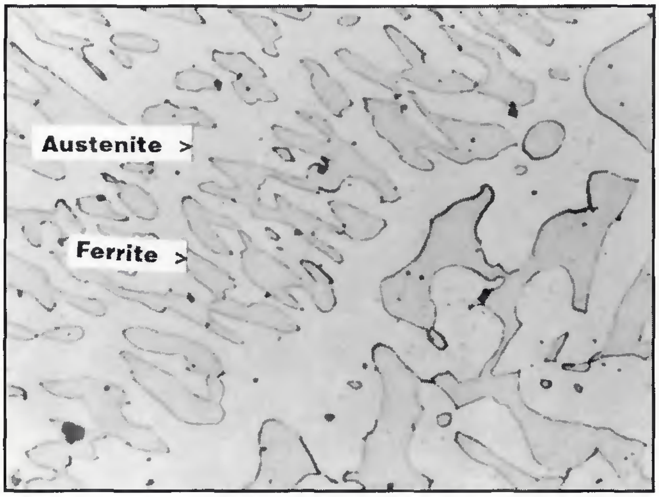


Fig. 15 — Microstructure of weld from Experiment 9292-678 (26% Cr, 0.29% N Ferralium 255). Annealed 4 h at 2100°F (1149°C)

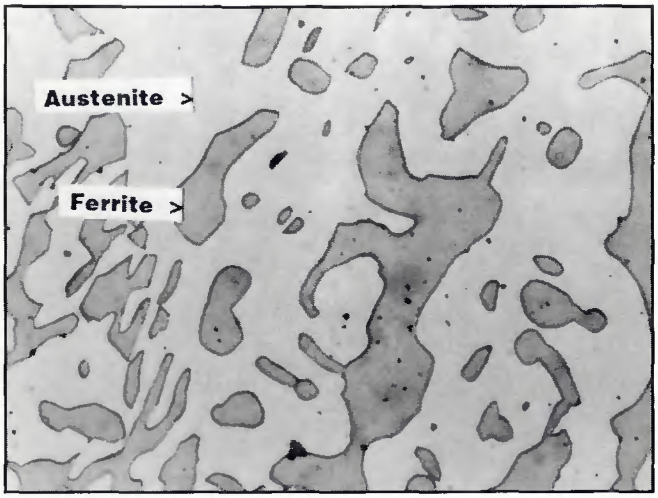


Fig. 16 — Microstructure of weld from Experiment 9292-678 (26% Cr, 0.29% N Ferralium 255). Step-annealed 4 h at 2100°F (1149°C) and 2 h at 1900°F (1038°C)

somewhat lower yield strength than the simple 2100°F anneal.

Figures 15 and 16 compare the microstructures resulting from simple 2100°F anneal and from step-anneal of Experiment 9292-678. It will be noted that a different etchant was used for these samples as compared to previous microstructures. Kalling's Reagent had no effect on this higher chromium weld metal (a micro was not prepared of the other 26% Cr weld, Experiment 9292-358) at room temperature. Heating the Kalling's Reagent caused severe pitting in the ferrite. Murakami's Reagent was tried at room temperature also, with no effect. Heating Murakami's Reagent slowly with the specimen immersed produced the desired etching with only very minor pitting. So, these microstructures are presented after etching with hot Murakami's Reagent. No sigma is present either in the 2100°F annealed weld metal nor in the step-annealed weld metal. The step-annealed microstructure may be somewhat coarser.

Discussion of Results

This study has considered three main concerns relating to annealed duplex stainless steel weld metals. These are:

1) the formation and stability of sigma phase during annealing,

2) the achievement of base metal yield strength requirements in sigma-free weld metal,

3) the achievement of a supplementary impact requirement of 20 ft-lb at −50°F (27J at −46°C).

Most of the compositions considered herein were embrittled by sigma phase after 1900°F (1038°C) anneals. Both the low-nickel weld metals that matched their respective base metals, 9292-204 (Alloy 2205, Table 2) and 9292-902 (Ferralium 255, Table 3), were exceptions. It is quite clear from this that higher nickel in the weld metal increases the stability of sigma. Weld metals of increased nickel for good as-welded properties have to be annealed at higher temperatures than weld metals that match base metal composition in order to avoid sigma.

It appears that high chromium and high molybdenum also work to stabilize sigma. Of course, one could aim weld metal compositions at the bottom of the acceptable ranges, but this would be at the risk of inferior corrosion resistance in the weld metal. High chromium, and especially high molybdenum, are preferred for pitting resistance in particular, which is why most compositions examined herein were above 3% Mo. High nitrogen, up to nearly 0.3%, did not appear to be very effective in preventing sigma formation.

If a final annealing temperature of 1900°F must be used for optimum corrosion resistance, as suggested by Ref. 13, with high-nickel weld metal, then step-annealing seems a viable method of achieving this. It must be accepted that any sizeable weldment cannot be heated fast enough to annealing temperatures to prevent sigma formation during heating. If one overshoots the final annealing temperature to put all sigma back into solution, then when the weldment cools back to 1900°F, it becomes necessary to nucleate sigma again (assuming that a high-nickel composition is in use so that sigma will be stable at 1900°F). This nucleation apparently takes some time. Ferralium 255-type weld metals high in nickel, which formed vast quantities of sigma in a simple 1900°F anneal, were sigma-free when step-annealed, first at 2100°F (1149°C), then furnace cooled to 1900°F and held for 2 h before quenching. So it must take more than 2 h to nucleate sigma at 1900°F, provided that the weldment can get to 1900°F sigma-free. It can do this from higher temperatures, but not from lower temperatures.

In order to obtain higher weld metal yield strengths after sigma-free anneals, higher nitrogen, especially in combination with higher chromium, seemed beneficial in this study. Figure 17 presents the sigma-free anneal data of Table 3 (not step-annealed) as a plot of yield strength versus nitrogen content. The nitrogen values are those measured in these broken tensile specimens. A regression line is included in Fig. 17. The correlation coefficient, R^2, is not large, but the trend of increasing annealed yield strength with increasing nitrogen content is clear.

Coupled with high nitrogen, high chromium seems beneficial for obtaining high annealed yield strength. The two highest annealed yield strengths in Ferralium 255-type weld metal were achieved with over 26% Cr, Experiments 9292-358 and 9292-678 — Table 3. Perhaps the higher chromium makes nitrogen more soluble in ferrite. At any rate, it enhances the overall solubility of nitrogen in the weld metal — porosity was not observed even at 0.29% nitrogen with 26% Cr. When the weld metal solidifies, it is entirely ferrite, so the solubility of nitrogen in ferrite at the solidification temperature, at least, must be high to avert porosity.

It is unsettling that, despite nearly 0.3% N and over 26% Cr, the 80 ksi (550 MPa) yield strength requirement of Ferralium 255 base metal was not comfortably exceeded, in the annealed condition. The same weld metals that, in the as-welded condition, reached close to 100 ksi (695 MPa), lost on the order of 20% of their as-welded yield strength in annealing, without losing much ferrite, if any.

If ferrite is not being lost due to annealing, then one must wonder what is the mechanism whereby the yield strength drops in annealing. Some apparent micro-

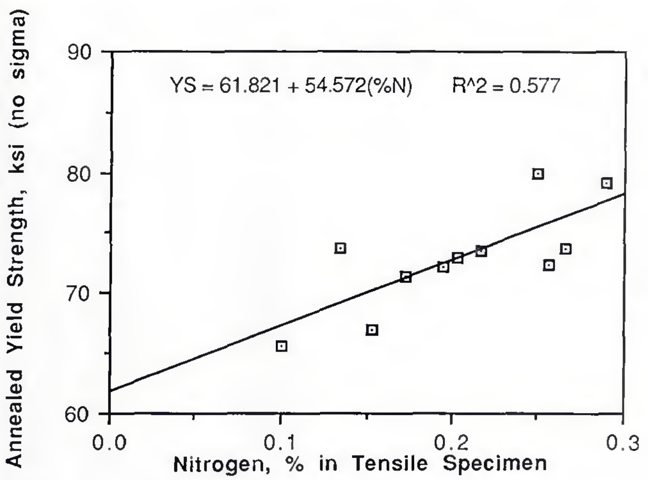


Fig. 17 — Annealed (sigma-free) yield strength versus nitrogen content of Ferralium 255-type weld metals of Table 3

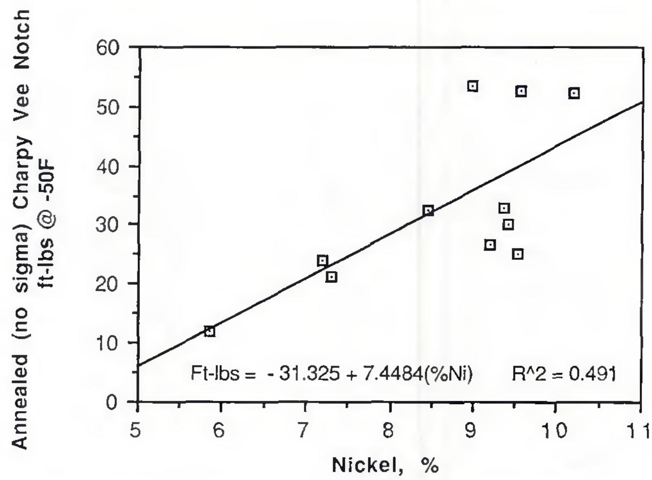


Fig. 18 — Annealed Charpy V-notch energy as a function of nickel content for Ferralium 255-type weld metals of Table 3

structural coarsening appears to occur during annealing, as noted earlier, but the change is not drastic. An alternate explanation, that appears more plausible to the writer, is available.

Kokawa, *et al.* (Ref. 15), describes in detail the fact that, when austenite must nucleate in solid ferrite due to solidification as 100% ferrite, then the resulting austenite has a Kurdjumov-Sachs relationship with the parent ferrite, with a high degree of coherency across the interface between ferrite and austenite. Further, he shows that coherency is retained in high-temperature heat treatment provided that sigma does not form. Presumably, however, if sigma forms, coherency is destroyed and is not recovered when the sigma reverts back to ferrite, as would occur during relatively slow heating of a large weldment. In this hypothesis, the coherency across the austenite-ferrite interface would account for the high yield strength as-welded. And the loss of coherency due to sigma formation during heating through intermediate temperatures (sigma forms in 2 min at 1650°F (900°C) in an alloy similar to 2205 (Ref. 5), and presumably even more quickly in the higher nickel, higher chromium weld metals studied herein), without recovery of coherency when the sigma reverts back to ferrite at higher temperatures, accounts for the loss of the yield strength in annealing.

If this hypothesis is correct, then, if one could heat a small specimen very rapidly to annealing temperature without forming sigma during heating, high yield strength could be retained after annealing because coherency would be retained. This approach would be impossible with any sizeable weldment because heating could not be rapid enough, but it does offer a way to test the hypothesis. Use of a Gleeble for very rapid heating might accomplish annealing of duplex stainless weld metal without forming sigma. Such equipment was not available to the author, so this hypothesis is untested.

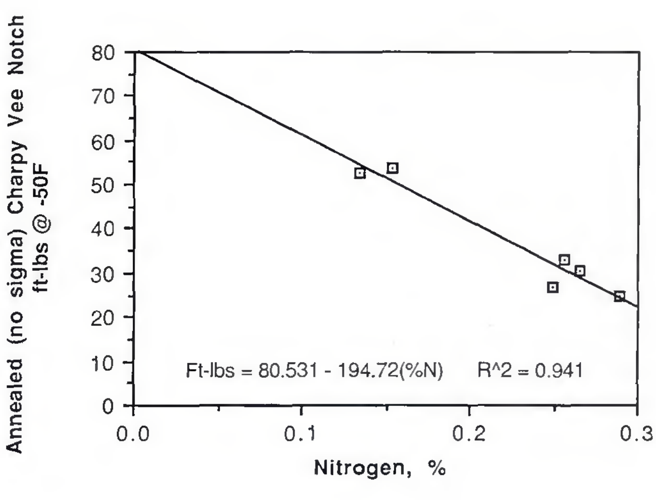
The achievement of Charpy V-notch energy exceeding 20 ft-lb at −50°F in the annealed condition appears to be linked mainly to nickel content in the weld metal. Figure 18 presents the annealed (no sigma) Charpy results for the Ferralium 255-type weld metals from Table 3 as a function of nickel content. A regression line is included in the figure. Although the correlation coefficient is not high, the trend of increasing toughness with increasing nickel is evident. Not enough data on Alloy 2205-type weld metals are available to present a similar figure for that weld metal, but it is noteworthy that the low-nickel weld (Experiment 9292-204, Table 2) did not meet 20 ft-lb at −50°F. The low-nickel weld (Experiment 9292-202, Table 3) of Ferralium 255-type weld metal did not meet that criteria either.

There is a second effect also evident in the annealed toughness data. Higher nitrogen at the same nickel level tends to reduce the toughness. In Table 3, there are six weld metals with nickel in the range of 8.96–9.55%, with annealed (no sigma) toughness data. If other compositional effects on toughness can be ignored, a clear trend of decreasing toughness with increasing nitrogen is visible. The correlation coefficient is high for this regression line — Fig. 19.

It is also evident that the highest nitrogen Ferralium 255-type welds, though having adequate toughness in the annealed sigma-free condition, do not meet the supplemental toughness requirement in the as-welded condition — Table 3. None of the weld metals above 0.2% nitrogen met 20 ft-lb at −50°F. Therefore, while high nitrogen may be desirable for annealed yield strength, it may not be desirable for as-welded toughness. Then a Ferralium 255 type weld metal optimized for annealed properties may not be appropriate for as-welded properties, and vice versa.

On the other hand, the weld metal of Alloy 2205-type, Experiment 9292-109, optimized for as-welded properties, also meets the annealed property requirements for the base metal. The more modest yield strength requirement for Alloy 2205 makes this possible.

Fig. 19 — Toughness versus nitrogen in annealed Ferralium 255-type weld metal for 8.96–9.55% nickel



Conclusions

The results of this study lead to the following conclusions:

1) Duplex stainless steel weld metals, enriched in nickel for optimum as-welded properties or for good toughness after annealing, are prone to sigma formation during heating to the annealing temperature. This sigma is likely to be stable at temperatures up to or above 1900°F (1038°C). To eliminate sigma from the weld metal, annealing temperatures of 2000°F (1093°C) or higher are appropriate.

2) If it is necessary, for whatever purpose, to use 1900°F as the final anneal, this temperature should be approached from above to be sure that sigma is dissolved. Then the time at 1900°F should be short to prevent sigma reformation at 1900°F in the weld metal.

3) High nitrogen is important for keeping annealed weld metal yield strength high. About 0.2% N minimum is needed to keep the yield strength above 70 ksi (485 MPa), and 0.3% is needed to get near 80 ksi (550 MPa).

4) Even if a weld metal is intended for annealed use only, it is advantageous to have high nickel. In the annealed condition, high nickel is necessary to meet a requirement of 20 ft-lb at −50°F (27J at −46°C).

5) In Alloy 2205-type weld metal, about 8.3% nickel produces properties adequate for base metal requirements in both the as-welded and annealed condition.

6) In Ferralium 255-type weld metal, above 9% nickel in combination with high nitrogen (nearly 0.3%) can be used to obtain good toughness in the annealed condition along with yield strength approaching base metal requirements, but such weld metal will have low toughness in the as-welded condition.

Acknowledgments

Teledyne McKay provided the opportunity to conduct this work and the environment to encourage it. Mr. Stanley Merrick assisted in the long-time annealing studies. Mr. Lee Flasche of Haynes International offered helpful insights into Ferralium 255 needs and behavior.

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Appendix

Etchants

1) Kalling's Reagent: 2g $CuCl_2$, 40 mL HCl, 40 mL ethanol, 40 mL distilled water. Immerse specimen about 1 min.

2) Hot Murakami's Reagent: 10g $K_3Fe(CN)_6$, 10g KOH or NaOH, 100 mL distilled water. Use fresh. Immerse specimen and heat. Remove specimen from bath when etching is as desired.