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Delta Ferrite and Martensite Formation in Stainless Steels

From studies of 70 chill-cast stainless steel alloy types, nickel- and chromium-equivalents of 13 elements are evaluated for use in a revised Schaeffler diagram

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ABSTRACT. The effects of composition on delta ferrite and martensite formation were studied in chill-cast experimental stainless steel alloys. Nickel content was varied in each of seventy different alloy types to produce structures ranging from fully stable austenite to ones containing high percentages of delta ferrite or martensite. The nickel or chromium equivalents of Mn, Mo, Si, V, W, Ti, Cb, Ta, Al, C, N, Co and Cu were evaluated by regression analyses.

Introduction

Control of the structure of stainless steel weld deposits and castings is important because the microstructure of the steel influences many of its properties. For example, a certain amount of delta ferrite in stainless steel increases yield and tensile strength, improves the resistance to stress-corrosion cracking, reduces hot cracking in deposited weld metal, and reduces hot tearing in castings. Adverse effects of delta ferrite for some applications might include the higher magnetic permeability of alloys containing ferrite, or the decrease of impact strength during long-time high-temperature service through an increase in the rate of sigma phase formation.

Even though an alloy may be fully austenitic at high temperatures, if the total alloy content is low enough, a spontaneous transformation from austenite to martensite may occur on cooling. The temperature at which this transformation starts is called the M_s temperature, and it is considerably below the temperature at which austenite and ferrite would be at equilibrium. Deformation will cause the martensite reaction to occur at a temperature M_d, which is closer to the equilibrium temperature, because strain facilitates the transformation. Because of the adverse effect of uncontrolled transformation on dimensional stability and magnetic permeability, it is preferable to avoid martensite in alloys for such applications as cryogenic ball valves or liquid hydrogen or helium bubble chambers used to study nuclear particle reactions.

In order to facilitate the task of the alloy designer, who must obtain such particular combinations of physical, mechanical and chemical properties in weld deposits or castings as described above, the effects of fifteen elements on delta ferrite and martensite formation in stainless steels were experimentally measured. The results are expressed in terms of nickel and chromium equivalents of the elements for use in a revised Schaeffler diagram.

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Table 1 — Comparison of Delta Ferrite Contents of Welds and Castings with those of Remelted and Chill Cast Pins

Material	% delta ferrite in original weld or casting	% delta ferrite in remelted and chill cast pin
Type 307 stainless steel covered electrode weld, as deposited	5.2	6.2
Babcock and Wilcox type 16-8-2 stainless steel covered electrode weld, as deposited	1.0	0.5
CF-8 stainless steel valve casting	18.0	19.0

Experimental Procedure

Sample Preparation

For two previous studies[1,2] of the effects of composition on hot cracking, levitation melting was used because it provided a rapid and inexpensive method for the preparation of a large number of alloys. In the present instance, in order to determine whether small levitation melts-chill-cast in copper molds could be used to

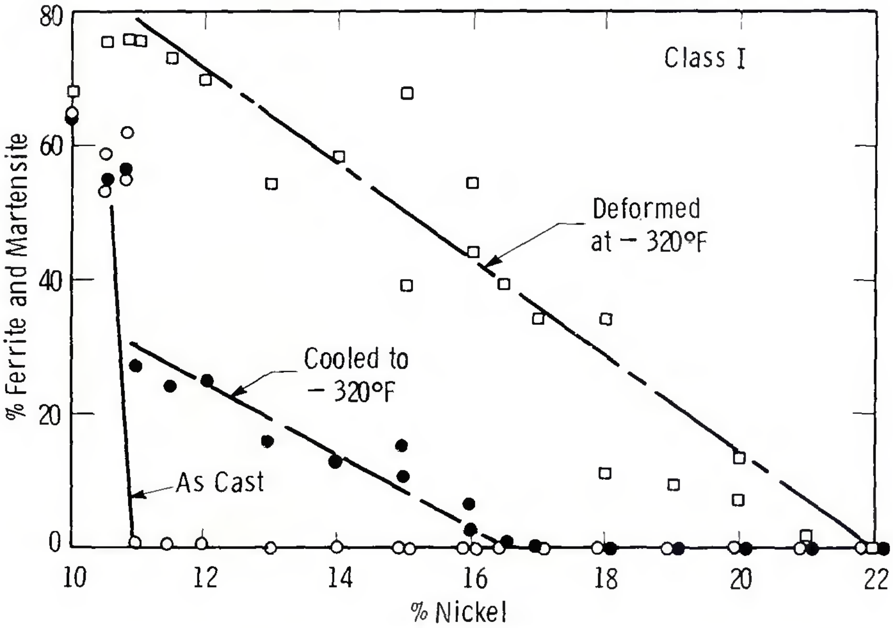

Fig. 1 — Effect of nickel on the structure of a cast stainless steel containing 14% Cr

simulate the microstructures of welds and castings, charges cut from two welds and a 7500 lb stainless casting were remelted and cast as small pins. As Table 1 shows, there was a good correlation between the delta ferrite contents of the three pins and those of the original materials. Since the cooling rate of these miniature castings is comparable to that of weld deposits, the structures produced and the composition correlations with the phase structure would be reasonably representative of as-deposited welds.

The test specimens for this study were prepared from materials which were pressed into 25-gram compacts, levitation melted in an argon atmosphere and chill-cast as approximately 2 in. long by ¼ in. diam tapered pins in copper molds. Vigorous stirring of the molten drop by the current of the high frequency induction coil insured that the melt was homogeneous prior to casting. Approximately 1400 specimens were prepared for this investigation.

Melting Stock

The materials used for melting stock were electrolytic grades of Fe, Cr, Ni, Co, Mn and Mn nitride; and pure grades of Al, Si, W, Mo, V, Cb, Ta, Cu, Ti and graphite. Typical levels of impurities (S, P and O) in the castings and of several of the elements when they were not added intentionally (Mn, Si, N and C) are shown in Table 2.

Alloy Compositions

The alloying element additions were made primarily to simple Cr-Ni stainless steels, although several series of heats contained 4, 8, 11, 14 or 20% Mn. These levels of manganese are much higher than those specified for the AISI 300 series of commercial stainless steels.

The recovery of alloying elements during melting was determined on a number of representative melts and typical nominal and analyzed compositions are given in Table 3. The losses for Cr, Ni and Mn were considered negligible for the purposes of this investigation and nominal compositions were used in the regression analyses. For the other alloying elements, the analyzed values were used. In the absence of an analysis, when these elements were added in smaller or larger amounts, the same fractional recovery was assumed. For example, the nominal 2% W alloy was assumed to have an actual composition of 2/5 of 4.54 or 1.82% W.

For each of the alloy series, in which chromium and one or more other alloying elements were held constant, 20 specimens on the average were cast with nickel varying over about a 12% range to include compositions, at the high side of the nickel range, which were fully austenitic as-cast or if deformed at −320 F (−196 C) and, at the low end of the nickel range, until more than 30% delta ferrite and/or martensite was present.

The seventy alloy types studied in this investigation and listed in Table 4 included steels with the following ranges of composition in weight %: 12-24 Cr, 0-22 Ni, 0-20 Mn, 0-6 Mo, 0-4 Si, 0-4 V, 0-5 W, 0-2 Ti, 0-4 Cb, 0-4 Ta, 0-2 Al, 0-6 Co, 0-4 Cu, 0-0.1 C and 0-.15 N. Of the nine alloys in Series

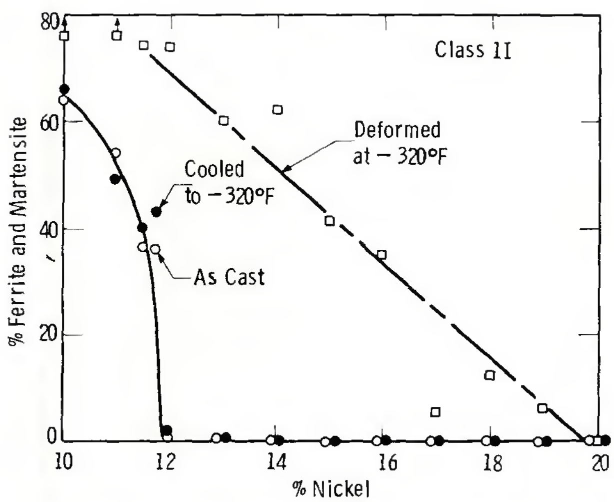

Fig. 2 — Effect of nickel on the structure of a cast stainless steel containing 14% Cr and 1% Al

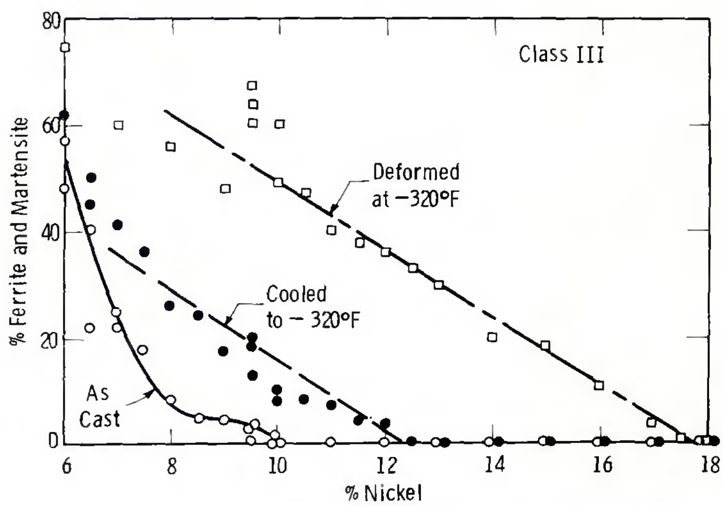

Fig. 3 — Effect of nickel on the structure of a cast stainless steel containing 16% Cr and 4% Mn

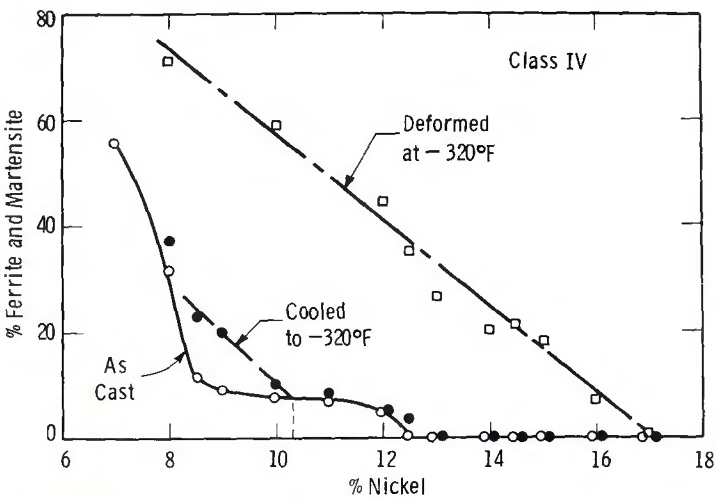

Fig. 4 — Effect of nickel on the structure of a cast stainless steel containing 19% Cr, 1% Mn and 0.5% Si

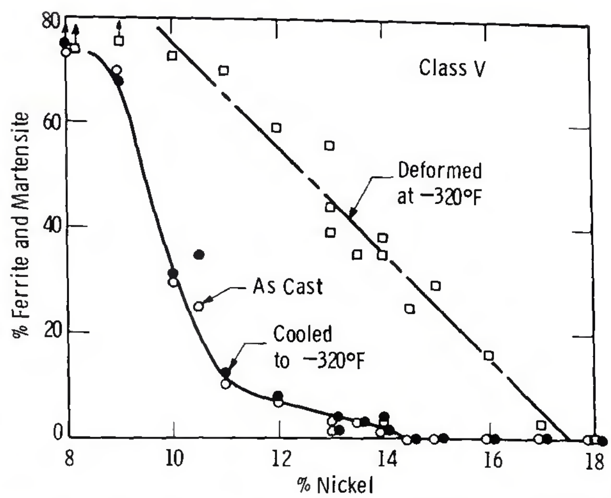

Fig. 5 — Effect of nickel on the structure of a cast stainless steel containing 16% Cr and 2% V

62-70, the first four represent extra low carbon versions of AISI Types 304, 316, 321 and 347 stainless steels, and the remaining steels contain two or three alloying elements in addition to Cr, Ni, Mn and Si.

Magnetic Measurements

The Aminco-Brenner Magne-Gage was used to determine the delta ferrite content of the stainless steel samples.[3,4,5] The values reported are the average of five readings taken on longitudinal and transverse sections of the cast pins. The accuracy of this and other methods for measuring the ferrite content of weld deposits has been summarized by Ratz and Gunia.[6] In order to measure high levels of delta ferrite or martensite, we extended the range of the gage to 75% ferrite by calibrating it with a series of iron-tin powder compacts.[7] The gage, of course, does not distinguish between delta ferrite and martensite, if both of these ferromagnetic phases are present, and one must then resort to microscopic examination to determine their relative proportions.

Martensite Transformation

The effects of composition on the transformation of austenite to martensite at −320 F were determined by cooling the specimen in liquid nitrogen and measuring the % (ferrite + martensite) after the specimen was returned to room temperature. For example, in Fig. 1, it is seen that an as-cast alloy of 14% Cr and 14% Ni was fully austenitic. However, when the sample was cooled to −320 F in liquid nitrogen and reheated to room temperature, it was found that 13% martensite had formed.

For the study of martensite transformation during deformation at low temperatures, specimens ¼ in. diam and 5/16 in. high were upset to a 50% reduction in height in a hydraulic press between 1 in. square by ½ in. thick blocks, the specimens and blocks being first cooled in liquid nitrogen. In the same 14% Cr, 14% Ni alloy mentioned above, 58% martensite formed during cooling to and deformation at −320 F.

Experimental Results

Curves of % (ferrite and martensite) versus % nickel were plotted from the test data for each alloy series. Since it is not practical to include all of the curves in this paper, the pertinent results are summarized in tabular form. Table 4 lists the nominal compositions and the specific values of % Ni for 0, 2, 5, 10 and 15% delta ferrite and the % Ni for M_s = −320 F and for M_d = −320 F for each alloy. Reference (a) in the column for 2, 5, 10 or 15% delta ferrite indicates that from the slope of the curve or metallographic examination it was concluded that martensite was forming during cooling to room temperature and the Magne Gage reading was not giving an accurate delta ferrite evaluation.

Discussion of Results

An examination and comparison of the curves mentioned above revealed many similarities, so that it was possible to describe the general characteristics of the 70 alloy types by only seven classifications. Typical curves illustrating these classes are presented in Figs. 1 to 7. Table 4

Table 2 — Typical Levels of Impurities and Other Elements When Not Deliberately Added, Wt %

Mn	Si	S	P	O	N	C
0.004	<0.03	0.007	0.006	0.03	0.004	0.004-0.016

Table 3 — Typical Nominal and Analyzed Compositions

Element	Nominal (Weight percent)	Analyzed (Weight percent)
Cr	16	16.0
	16	15.6
	20	19.7
Ni	12	11.2
	15	14.5
	15	14.6
Mn	14	13.5
Mo	1	0.98
	2	2.03
	4	3.97
	6	6.14
Si	3	2.89
V	3	2.98
W	5	4.54
Ti	2	1.75
Nb	2	1.62
Ta	2	1.55
N	0.10	0.050
N	0.15	0.11
C	0.10	0.082
Co	3	3.13
Co	6	5.97
Cu	2	1.74
Cu	3	3.0
Cu	4	3.9
Al	1	1.11
Al	2	2.13

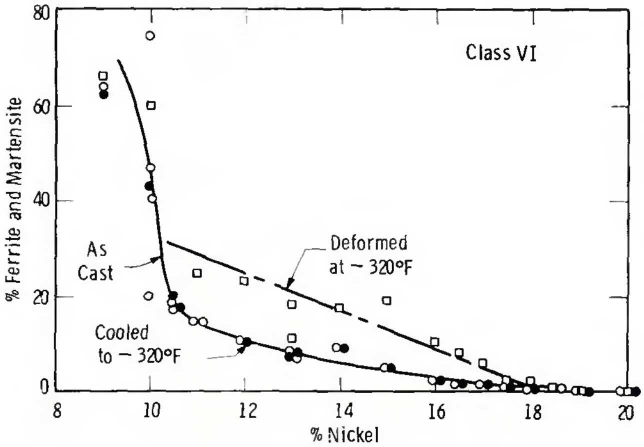

Fig. 6 — Effect of nickel on the structure of a cast stainless steel containing 16% Cr and 6% Mo

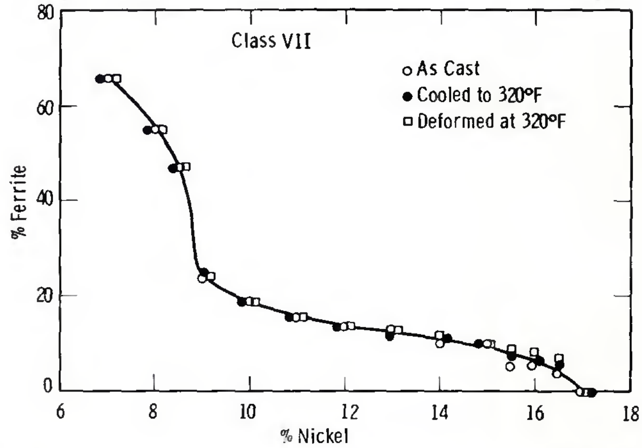

Fig. 7 — Effect of nickel on the structure of a cast stainless steel containing 16% Cr, 14% Mn and 3% V

classifies each of the alloys into one of these types.

The Class I curve (Fig. 1) is characteristic of steels with low total alloy content and low in ferrite formers. The distinguishing feature is the absence of delta ferrite. The abrupt rise in the curve (open circles) for as-cast alloys containing 14% Cr and less than 11% Ni was due to martensite formed on cooling to room temperature. At higher nickel levels the austenite was stable at room temperature, but cooling to −320 F (solid circles) or deformation at −320 F (open squares) produced martensite, as illustrated by the other two lines in Fig. 1. The intercepts of the two lines with the abscissa provided the nickel contents at which M_s and M_d = −320 F, respectively. Alloys with more than the latter amount of nickel would be stable at liquid nitrogen temperatures even if they were severely deformed.

Class II alloys (Fig. 2) are somewhat higher in alloy content and also show an abrupt increase in ferromagnetism as the nickel content is decreased. Alloying with Al, Ti or Cu lowered M_s to the point that no additional transformation to martensite occurred on cooling to −320 F.

The most general case of behavior is illustrated by Class III alloys (Fig. 3). Ferrite forming elements are sufficiently high that about 2-10% delta ferrite ispresent in castings containing an appropriate amount of nickel, but low enough that transformation to martensite will occur during cooling to −320 F and additional transformation during deformation at −320 F. In this alloy the amount of ferrite increased gradually as the nickel was decreased from 10% Ni to 8% Ni. Metallographic examination showed that the abrupt increase in slope of the curve (open circles) for alloys with

Fig. 8 — Effect of nickel and molybdenum on delta ferrite and martensite formation in chill cast-stainless steels containing 16% Cr

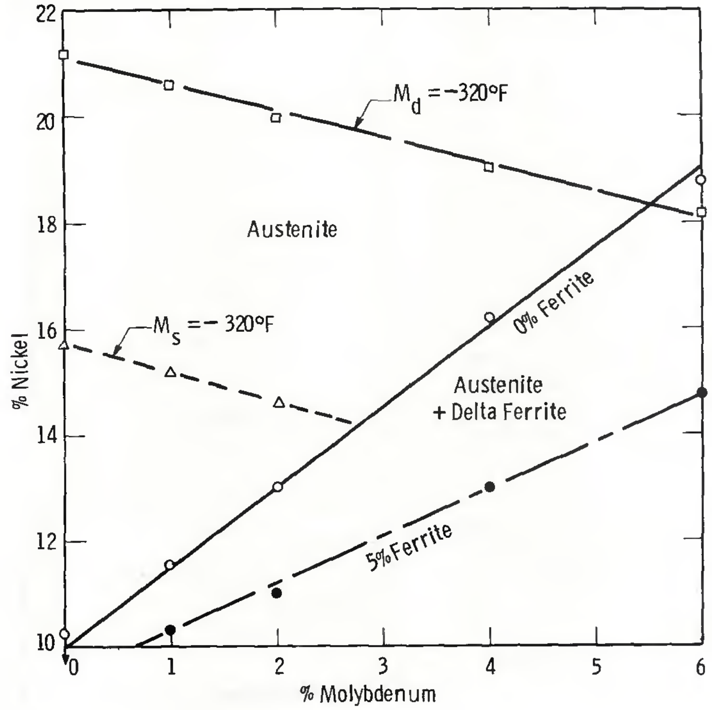

Fig. 9 — Effect of manganese on the nickel content at which a trace of delta ferrite is produced in eight as-cast stainless steels. Note that manganese acts as an austenite forming element below about 6% Mn and as a ferrite promoter above this level

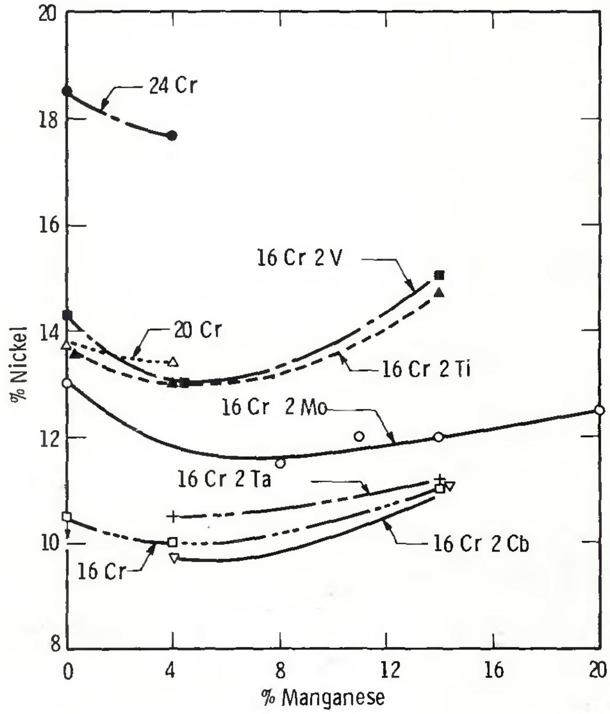

Table 4 — Nominal Compositions of the Seventy Alloy Series and the Nickel Contents for Various Amounts of Delta Ferrite and Martensite

Alloy series	Nominal composition, Wt % (bal. Fe)					Class	Percent nickel for indicated structure: Delta ferrite — %						
	Cr	Mn	Si	Mo	Other		0	2	5	10	15	M_s = −320 F	M_d = −320 F
1	14					I	<11	(a)				16.6	22.0
2	14				1 Al	II	<12	(a)				<12	19.8
3	14				2 Ti	II	<12	(a)				<12	20.2
4	14				2 V	IV	13.5	13.3	11.8	(a)		12.7	18.4
5	16					I	<10.5	(a)				15.4	20.8
6	16				1 Al	V	12.5	12.2	11.5	11.1	11.0[a]	<12.5	19.2
7	16				1 Ti	III	11.6	11.4	10.5	9.8[a]		13.0	19.3
8	16				2 Ti	V	13.6	13.2	11.4	10.1	9.9[a]	<13.6	19.6
9	16				1 V	III	12.5	11.8	11.1	10.6	10.3	14.0	19.1
10	16				2 V	V	14.3	14.0	12.8	11.1	10.7	<14.3	17.5
11	16				4 Cb	V	10.5	10.4	8.9	8.6	8.5[a]	<10.5	17.2
12	16				4 Ta	V	10.5	10.0	9.4	9.2	9.1[a]	<10.5	17.0
13	16				4 Cu	II	< 9	(a)				< 9	15.3
14	16				4 W	III	12.5	12.1	11.3	8.7	8.4	12.6	19.0
15	16		4			III	12.8	12.7	11.5	9.5[a]		13.1	19.5
16	16			1		III	11.6	11.1	10.3	10.0	9.9[a]	15.2	20.6
17	16			1	.1 C	III	10.6	9.8	8.5	8.4	8.3[a]	11.4	19.0
18	16			1	.1 N	III	10.5	10.2	9.5	9.3[a]		12.0	19.0
19	16			1	2 Cu	III	10.5	10.3	9.5	9.2[a]		11.6	18.0
20	16			2		III	13.0	12.7	11.1	9.9	9.7[a]	14.5	20.3
21	16			2	3 Co	III	11.5	11.0	8.9	8.5[a]		13.5	18.8
22	16			4		V	16.2	15.5	13.0	9.7	8.7	<16.2	19.1
23	16			6		VI	18.8	16.4	14.8	12.1	10.9	<18.1	18.1
24	16	4				III	10.0	9.8	8.6	7.8	7.4[a]	12.3	17.7
25	16	4			2 Al	V	15.5	15.4	14.0	10.0	9.8[a]	<15.5	16.1
26	16	4			2 Ti	V	13.0	12.8	12.0	9.0	8.0	<13.0	16.0
27	16	4			2 V	V	13.0	12.9	12.6	10.6	8.9	<13.0	16.1
28	16	4	2			III	10.8	10.0	7.0	6.5	6.1	11.7	17.3
29	16	4			2 W	III	10.4	10.2	8.5	6.2	5.8[a]	11.5	17.0
30	16	4			2 Cb	III	9.7	9.0	8.0	7.3	7.0[a]	10.6	16.1
31	16	4			2 Ta	IV	10.5	10.2	7.0	6.4	6.1[a]	10.0	16.4
32	16	4			3 Co	III	8.6	8.5	8.3	7.6	7.0	11.0	17.1
33	16	4			6 Co	III	7.6	7.4	7.2	6.7	6.3	10.5	16.0
34	16	4			3 Cu	IV	8.8	8.5	6.0	5.6	5.5[a]	7.9	14.7
35	16	14				VI	11.0	10.8	8.0	4.1	3.9[a]	<10.2	10.2
36	16	14			2 Ti	VII	14.7	14.3	13.0	9.0	7.6	<14.7	<14.7
37	16	14			3 V	VII	17.0	16.8	16.2	14.2	11.2	<17.0	<17.0
38	16	14	3			VI	12.0	11.9	10.5	6.3	6.0[a]	< 9.5	9.5
39	16	14			5 W	VII	13.8	13.5	12.7	10.0	6.9	<13.8	<13.8
40	16	14			2 Cb	VI	11.1	10.9	10.3	7.0	6.1	< 8.2	8.2
41	16	14			2 Ta	VI	11.2	11.0	9.0	6.2	5.5	< 8.7	8.7
42	16	14			.10 C	V	8.5	7.8	6.0	3.4	2.2	<10.5	10.5
43	16	14			.15 N	V	8.0	7.7	4.0	2.0	1.1	< 9.6	9.6
44	16	8		2		V	11.5	11.4	11.0	7.3	6.3	<11.5	14.2
45	16	11		2		V	12.0	11.6	10.9	8.0	6.8	<12.8	12.8
46	16	14		2		VII	12.0	11.8	11.3	7.8	7.0	<12.0	<12.0
47	16	20		2		VII	12.5	12.3	11.2	8.3	6.2	<12.5	<12.5
48	12	11		2		IV	8.5	7.0	4.5	4.0	3.6[a]	6.4	14.0
49	20	11		2		VII	16.1	15.9	15.5	14.1	11.5	<16.1	<16.1
50	17				0.5 Al	III	11.5	11.3	10.6	10.0	9.8[a]	12.0	19.5
51	17				1 Al	V	13.0	12.9	12.0	10.6	10.4[a]	<13.0	19.0
52	18					III	11.6	11.2	10.1	9.4	9.2[a]	14.7	20.0
53	18				1 Cu	III	11.5	11.4	10.5	8.8	8.6[a]	13.0	19.9
54	18				2 Cu	V	10.5	10.4	10.1	8.4	8.2[a]	<10.5	17.6
55	18				1 Al	V	14.1	14.0	12.8	10.6	10.3	<14.1	18.4
56	18				4 V	VII	21.7	20.5	18.0	15.6	14.0	<21.7	<21.7
57	20					V	13.7	13.5	12.5	11.5	10.5	<13.7	19.0
58	20				1 Al	V	15.5	15.3	14.5	11.3	11.0	<15.5	18.0
59	20	4				V	13.4	13.3	12.9	10.5	8.5	<13.4	16.3
60	24					VII	18.5	17.7	16.0	14.3	12.5	<18.5	<18.5
61	24	4				VII	17.7	17.4	16.8	15.6	14.1	<17.7	<17.7
62	19	1	.5			IV	12.4	12.3	12.0	8.8	8.4	10.3	17.0
63	17	1.5	.75	2.5		IV	13.1	12.9	12.0	9.5	8.8	10.1	16.3
64	18	.5	.5		1 Ti	V	13.5	13.3	12.0	9.8	8.8	<13.5	17.0
65	18	2			1 Cb	V	12.0	11.7	8.8	8.3	8.1[a]	<12.0	17.7
66	17	1	1	1	2 W	V	13.1	12.8	11.0	8.9	8.3	<13.1	18.0
67	15	1	.5	2	1 Cb	V	11.5	11.3	9.5	9.0[a]		<11.5	17.1
68	19	2	1		3 Co, 2 V	V	15.0	14.7	13.5	11.5	10.0	<15.0	15.5
69	19	2	1		3 Co, 2.5 V	VII	16.1	15.9	15.4	13.5	11.1	<16.1	<16.1
70	16	4	.5		1 Ti, 2 W	V	15.2	15.0	13.0	9.9	9.5	<15.2	15.8

(a) Delta ferrite plus martensite.

Table 5 — Coefficients, Standard Errors, and F-Ratios Determined by Regression Analyses for Empirical Equations Relating the % Ni for Various Microstructures to the Composition of As-Chill Cast Stainless Steels

	0% delta ferrite			2% delta ferrite			5% delta ferrite			M_s = −320 F			M_d = −320 F		
Element	Coeff.	Std. error	F-ratio	Coeff.	Std. error	F-ratio	Coeff.	Std. error	F-ratio	Coeff.	Std. error	F-ratio	Coeff.	Std. error	F-ratio
Constant	−4.706	.97		−4.930	.89		−7.017	1.37		28.531	3.0		26.82	1.12	
Cr	.917	.05	314	.917	.05	370	.979	.07	180	−.804	.17	21	−.399	.06	38
Mn	−.088	.059	2.3	−.094	.054	3.0	−.140	.08	2.9	−.919	.09	113	−.692	.02	1044
Mn^2	.0070	.0038	3.3	.0080	.0035	5.1	.0109	.005	4.1						
Mo	1.305	.09	187	1.101	.09	157	1.026	.13	58	−.944	.24	15	−.409	.09	21
Si	.514	.14	13.5	.528	.13	16.9	.312	.20	2.5	−.632	.22	8	−.343	.13	6.8
V	2.224	.12	345	2.120	.11	370	2.047	.17	147	−2.171	.49	20	−1.065	.18	36
W	.691	.12	34	.666	.11	37.6	.672	.17	16	−.727	.23	10	−.319	.15	4.8
Ti	2.122	.24	77	2.066	.22	86	1.960	.34	33	−3.064	1.05	9	−.787	.23	12
Cb	.171	.19	.8[a]	.153	.17	.7[a]	.060	.27	.05[a]	−.857	.56	2.4	−1.111	.18	40
Ta	.316	.21	2.4	.235	.19	1.5[a]	.042	.29	.02[a]	−1.283	.58	4.8	−1.093	.19	33
N	−14.6	6.2	5.5	−18.8	5.7	10.8	−21.8	8.7	6	−54.80	17.7	10	−5.35	5.9	.8[a]
C	−16.7	6.4	6.7	−20.3	5.9	11.7	−36.5	9.1	16	−40.7	10.8	14	−13.2	6.0	4.8
Co	−.472	.09	27.9	−.444	.08	29	−.311	.13	6	−.231	.13	3.2	−.213	.09	6.0
Cu	−.416	.20	4.5	−.386	.18	4.5	−.507	.27	3.3	−1.449	.26	30	−1.146	.13	74
Al	2.295	.27	74	2.342	.25	91	2.364	.38	40	−5.203	1.6	10	−.910	.24	14
No. of observations	65			65			65			27			60		
F-ratio for regression	60.0			67.5			31.9			12.8			91.9		
Std. error	.701			.646			.987			.828			.653		
Coeff. of determination, R^2	.948			.954			.907			.937			.966		

(a) Term is not statistically significant.

less than 8% Ni was because of the onset of martensite transformation on cooling to room temperature. The microstructure of the as-cast specimen containing 7.5% Ni consisted of 5% ferrite and 13% martensite.

Since all alloying elements lower M_s and M_d, as the total alloy content increases, the lines showing transformation to martensite on cooling to −320 F and on deformation at −320 F are progressively shifted to the left (lower nickel contents). If the alloying additions are strong ferrite formers, such as Cr, Mo, V, Ti or Al, the delta ferrite curve is simultaneously shifted to the right to substantially higher nickel levels. These opposing shifts in the three curves can lead to four other types of diagrams: Class IV alloys (Fig. 4) in which the M_s line intersects the delta ferrite curve, Class V alloys (Fig. 5) in which no additional transformation occurs during cooling to −320 F, Class VI alloys (Fig. 6) in which the M_d line intersects the delta ferrite curve, and finally Class VII alloys (Fig. 7) in which the austenite is fully stable at −320 F, i.e., M_d < −320 F. Metallographic examination showed that the ferromagnetic response of the Class VII alloy was caused solely by delta ferrite.

One approach to establishing the effects of alloying elements on delta ferrite and martensite formation is to compare appropriate alloy types with one another. For example, 16% Cr steels were prepared with 0, 1, 2, 4, and 6% Mo. As the content of molybdenum (a ferrite former) increased, the level of nickel also had to be increased to maintain a given structure, as illustrated in Fig. 8. The two lower curves shown are for 0 and 5% delta ferrite. The slopes of these two curves, 1.50 and 0.90 respectively, are the nickel equivalents of molybdenum. It will be seen that these depend upon the level of ferrite used for comparison, but are independent of the level of molybdenum. Molybdenum lowers M_s and M_d, as demonstrated by the fact that as molybdenum is increased, the nickel content must be decreased for the alloy to maintain the same degree of stability.

The effect of manganese on delta ferrite formation is of interest because of the considerable amounts of manganese added to AISI Type 200 Series steels and to a number of specialty steels. Figure 9 summarizes the results for eight alloys. At levels up to about 6%, manganese acted in the same way as nickel to reduce delta ferrite (i.e., as an austenite former). However, at higher levels manganese was a ferrite former.

An alternative way of obtaining the nickel equivalents of elements, utilizing all the available data, and at the

Table 6 — Effects of Elements on M_s and M_d

Element	Lowering of M_s in deg F for 1% increase of indicated element	Lowering of M_d in deg F for 1% increase of indicated element
Ni	106	106
Cr	85	42
Mn	97	73
Mo	100	43
Si	67	36
V	230	113
W	77	34
Ti	325	83
Cb	91	118
Ta	136	116
N	5800	570[a]
C	4300	1400
Co	24	23
Cu	153	121
Al	552	96

(a) Term is not statistically significant.

Table 7 — Nickel and Chromium Equivalent of Elements With Respect to Delta Ferrite Formation in Chill Cast Stainless Steels

Ni-Equiv. austenite promoters	Ni-Equiv. ferrite promoters	Cr-Equiv. ferrite promoters
+ 1.00 Ni	−0.94 Cr	+1.00 Cr
+ 0.11 Mn-0.0086 Mn^2	−1.14 Mo	+1.21 Mo
+18.4 N	−0.45 Si	+0.48 Si
+24.5 C	−2.13 V	+2.27 V
+ 0.41 Co	−0.68 W	+0.72 W
+ 0.44 Cu	−2.05 Ti	+2.20 Ti
	−0.13 Cb	+0.14 Cb
	−0.20 Ta	+0.21 Ta
	−2.33 Al	+2.48 Al

same time getting a quantitative evaluation of the experimental error, was to assume that the % Ni at which delta ferrite just became nil could be related to the composition by an empirical equation or model of the form:

$$\%Ni\ (\text{for } 0\%\delta) = k_0 + k_1 Cr + k_2 Mn + k_3 Mo + \ldots \quad (1)$$

where Cr stands for the weight % Cr in the alloy, etc., and the coefficients k_0, k_1, k_2, . . ., are constants whose values, as determined by a regression analysis, are the nickel equivalents of the respective elements.

The data in Table 4 provided several levels and many observations of Cr, Mn, and Mo so that both first and second order terms for these three elements were used in the first model. However, the squared terms for chromium and molybdenum were not significant. The final model was of the form:

$$\%\ Ni\ (\text{for } 0\%\ \delta) = -4.71 + .92\ Cr - .088\ Mn + .0070\ Mn^2 + 1.30\ Mo + .51\ Si + 2.22\ V + .69\ W + 2.12\ Ti + .17\ Cb + .32\ Ta - 14.6\ N - 16.7\ C - .47\ Co - .42\ Cu + 2.30\ Al \quad (2)$$

Table 5 lists coefficients, standard errors and F-ratios for the composition terms in this equation. In the equation for 0% ferrite, the F-ratio for the regression was 60, the standard error was 0.7% Ni and the coefficient of determination, R^2, was 0.95. This F-ratio indicates a high degree of significance for the result. An R^2 value of 0.95 indicates that the model chosen accounts for a large percentage of the observed variation. Similar equations are listed in Table 5 for calculating the % Ni to obtain 2% δ or 5% δ.

The coefficients for columbium and tantalum in Table 5 were not always significant, because the shifts in composition produced by even the relatively large amounts of these elements added were small compared to the experimental error. Cr, Mo, Si, V, W, Ti, Cb, Ta and Al with positive coefficients were ferrite formers; Ni, C, N, Co and Cu with negative coefficients were austenite formers. Because of its first and second order terms, manganese was an austenite former at low levels and a ferrite former at high levels, confirming the observations in Fig. 9. It is obviously possible with Eq. 2, if desired, to fix the nickel content of an alloy and calculate the percent of another element, such as chromium, that will produce 0% ferrite.

Least square analyses were also used to determine the nickel equivalents of elements as they affected M_s and M_d. Linear, first order relationships were assumed between % Ni for M_s and M_d = −320 F and the remaining alloy composition. Table 5 summarizes the results of these calculations. All elements lowered M_s and M_d. Eichelman and Hull[8] and later Monkman, Cuff and Grant[9] found that nickel in austenitic stainless steels lowered M_s by 110 and 102 F/% Ni, respectively. The effects of the other elements on M_s, as tabulated in Table 6, were calculated from the nickel equivalents and the average of the above coefficients for nickel.

In simple Cr-Ni stainless steels there is some evidence that the effects of composition on M_d are similar to their effects on M_s.[10] Based on the nickel equivalents of elements as they affect M_d and the assumption that the effect of nickel on M_d would be the same as its effect on M_s, the lowering of M_d for a 1% addition of each element was calculated. These results are also listed in Table 6. The lowerings of M_d for many elements were only about one half as great as their effects on M_s. Of the substitutional alloying elements, titanium and aluminum have extraordinarily large effects on M_s compared to their effects on M_d. No explanation for this phenomenon has been found.

Since the effect of nickel on M_s is known from prior work[8,9], the equation in Table 5, relating the nickel content for M_s = −320 F to the alloy composition, can be rewritten to provide a relationship between M_s and composition:

$$M_s\ (F) = 2700 - 106(Ni + Ni\ \text{equiv. for}\ M_s) \quad (3)$$

In the same way an equation relating M_d to composition can be obtained from Table 5:

$$M_d\ (F) = 2520 - 106(Ni + Ni\ \text{equiv. for}\ M_d) \quad (4)$$

The standard errors for these expressions are 88 and 69 F, respectively.

The coefficients of the elements for 0, 2 and 5% ferrite in Table 5 were averaged to arrive at the Ni-equivalents of each element with respect to delta ferrite formation. If these are

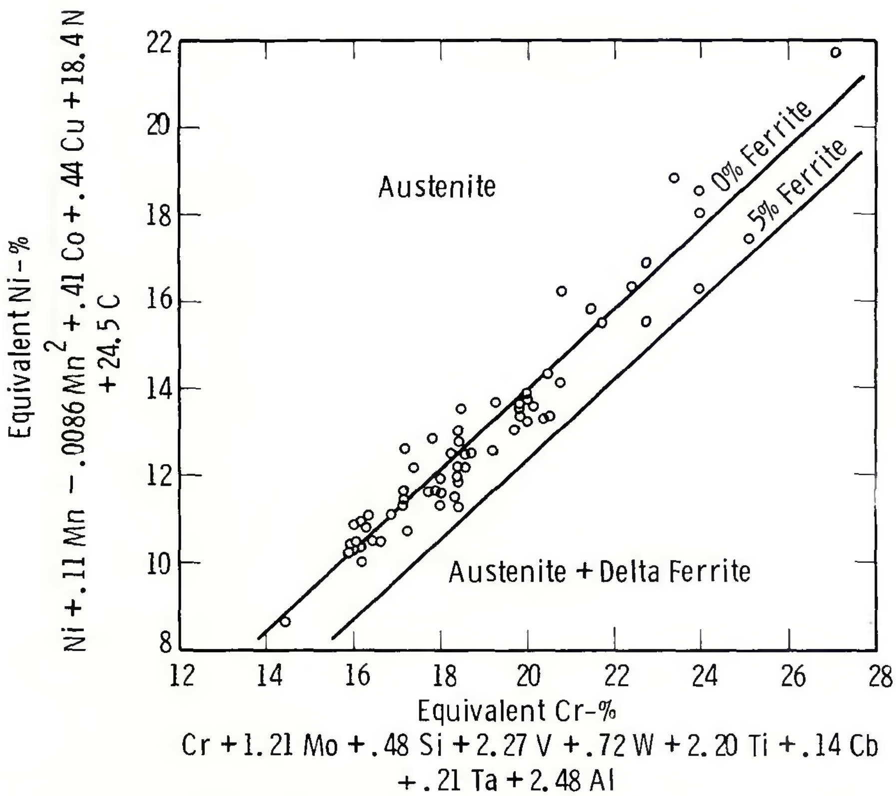

Fig. 10 — Portion of Schaeffler diagram based on the Ni- and Cr-equivalents of alloying additions evaluated in this paper for chill-cast stainless steels

0.45. Finally, in the present study (Table 5 and Fig. 9), manganese was found to have a dual role: austenite promoter at low levels and ferrite promoter at high levels.

The Schaeffler diagram[16] for predicting the microstructure of as-deposited welds utilizes the concept of "Equivalent Ni" and "Equivalent Cr" contents for handling Cr-Ni steels with additions of other elements. The present paper provides both new and modified coefficients for predicting structures for a greater variety of steels.

The Ni- and Cr-equivalents in Table 6 were used to calculate "Equivalent Ni" and "Equivalent Cr" contents of the 70 alloy types in Table 4. The points for 0% ferrite are shown in a portion of the Schaeffler diagram in Fig. 10. The line through these points agrees well with the 0% ferrite line established by previous work. The position of the present measured 5% ferrite line is also shown in Fig. 10, but the points were not plotted because of the confusion that would be caused by the overlap. The degree of scatter was comparable in both cases.

If terms are transposed and grouped, Eq. 2 takes a different form which is useful in making comparisons between alloys. Let us define a composition function, θ, such that

$$\theta = \Sigma \text{ (Ni equivalents)} - \text{Ni} - 4.7 \quad (5)$$

Note that (Ni equivalents) in Eq. 5 includes the Ni equivalents of both the austenite and ferrite formers for the case of 0% ferrite. Alloys for which $\theta \leq 0$ will be fully austenitic and alloys for which $\theta > 0$ will contain some delta ferrite. θ is a measure of the amount of nickel or the equivalent nickel that would have to be added to a given alloy containing ferrite, to restore a fully austenitic structure. It has the units of % Ni.

Equation 5 has the effect of producing mirror images of the original ferrite curves about a vertical axis and shifting origins so that all delta ferrite curves decrease to zero at $\theta = 0$. For a given alloy type, the larger the value of θ, the higher will be the amount of ferrite. When the base composition is different, however, comparisons between alloys can be misleading. Some typical curves of % delta ferrite versus θ are plotted in Figs. 11 to 14.

Percent ferrite versus θ curves are conveniently categorized in terms of their "effective width" and "height" (taken at one half the effective width). For example, in Fig. 11, the base alloy 16% Cr, 4% Mn had a width of about 2% Ni (before the rapid rise in % ferrite occurred) and a height of 5% ferrite. In some cases the rapid rise is partially related to martensite formation. An addition of 2% Si increased the width to about 4.5% Ni and decreased the height to 2% ferrite. Cobalt, on the other hand, doubled the height but did not affect the width. It would be very difficult to control composition closely enough to achieve a specific ferrite content with such an alloy because of the steep slope of the curve.

On the other hand, ferrite control would be easier in the case of the alloy with 2% V, in Fig. 11, since the width was 2.5 times as great. The effects of Mo, Cr and Mn additions are illustrated in Figs. 12, 13 and 14, respectively. Molybdenum and manganese increase width substantially with a small increase in height, whereas chromium increases height with only a slight increase in width.

For practical applications requiring precise control of the % ferrite, the ideal situation is one in which the basic composition has an approximately horizontal shelf of the proper "height" and a large "width" so that segregation or unintentional variations in composition will have the least effect on the amount of ferrite present. The current studies have shown that these objectives can be achieved by using alloys with about 11% Mn and 2% Mo to get a large effective width and selecting the amount of Cr to provide the desired shelf level of delta ferrite. These alloys are also characterized by exceptional resistance to hot cracking or hot tearing because of the optimum manganese and molybdenum contents.[23,24] Providing cost, properties, corrosion resistance and specifications permit, the following three alloys could be used to obtain the indicated ferrite levels:

Cr	Mn	Mo	Ni	% δ
12	11	2	7	2
16	11	2	9.5	8
20	11	2	12	16

If Si, C and N are present, as is likely in commercial steels, the nickel contents listed above for high purity alloys should be adjusted by the methods previously described to compensate for the actual Si, C and N contents of the steels.

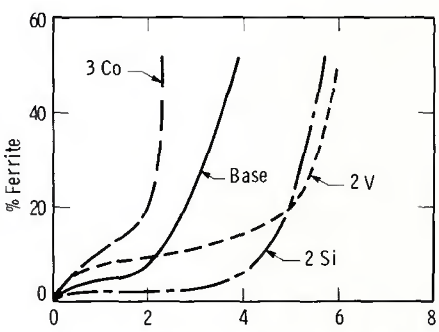

Fig. 11 — Effect of Co, V and Si on the shape of the delta ferrite versus θ curve for alloys containing 16% Cr, 4% Mn, variable nickel and balance iron

Table 8 — Nickel and Chromium Equivalents of Alloying Elements in Stainless Steels With Respect to Delta Ferrite Formation

Austenite formers	Avery[12] cast heat resistant alloys	Field, Bloom & Linnert[13] 20-10 weld metal	Campbell & Thomas[14] 25-20 weld metal	Henry, Clausson & Linnert[15] Cr-Ni weld metal	Schaeffler[15] Cr-Ni weld metal	Ferree[17]	Runov[18] Cr-Ni welds	DeLong[19] welds	Guiraldenq[20] castings	Potak & Sagalevich[21] castings	Hull chill castings
C	17	30	—	30	30	30	—	—	30	27	24.5
N	11	—	—	—	—	30	—	30	20	27	18.4
Ni	1	1	—	1	1	1	1	1	1	1	1
Mn	—	.5	—	.5	.5	.5	—	—	—	.5	.11 Mn-.0086Mn²
Cu	—	—	—	—	—	.3	—	—	—	.33	.44
Co	—	—	—	—	—		—	—	—	.4	.41
Ferrite Formers											
Al	—	—	—	—	—	—	—	—	3	4	2.48
V	—	—	—	—	—	—	—	—	—	1.5	2.27
Ti	—	—	—	5	—	—	3.5	—	4	4	2.20
Si	1.6	—	—	1	1.5	1.5	—	—	1.5	2	.48
Cb	2.8	—	2	2	.5	—	—	—	—	.9	.14
Mo	—	2	1.5	2	1	—	—	—	2	1	1.21
Ta	—	—	—	—	—	—	—	—	—	—	.21
W	—	—	—	—	—	—	—	—	—	.5	.72
Cr	1	1	1	1	1	1	1	—	1	1	1
Mn	—	—	—	—	—	—	—	—	.45	—	—

grouped according to austenite or ferrite forming tendencies, we obtain the results listed in the first two columns of Table 7. The Cr-equivalents of the ferrite promoters were obtained by taking the ratios of the Ni-equivalents of the elements to the Ni-equivalent for chromium, for example, the Cr-equivalent of molybdenum is 1.14/0.94 or 1.21.

In 1950 Thielsch[11] summarized the nickel and chromium equivalents of alloying elements in castings and welds as determined by several investigators.[12-16] In Table 8 the earlier data are compared with more recent equivalents determined by Ferree[17], Runov[18], DeLong[19], Guiraldenq[20], Potak and Sagalevich[21] and the results of the current study.

In the present investigation, unless carbon or nitrogen were intentionally added, their contents were very low (Table 1). Hence when the effects of Ti, Cb and Ta were studied, in alloys which were essentially free of carbon and nitrogen, it was the solid solution effect of Ti, Cb or Ta that was measured. Pryce and Andrews[22] determined Cr-equivalents for titanium and columbium in annealed, wrought stainless steels in order to be able to limit delta ferrite in hot rolled products. These authors assumed that titanium or columbium combined with all the nitrogen and all but 0.03% C, thus somewhat reducing the effective titanium or columbium content of the alloys. Potak and Sagalevich[21] point out that in welds and castings the carbide and nitride forming tendencies of the Ti, Al and Cb must be taken into account.

The previously determined Cr-equivalents for columbium and titanium (Table 8) are considerably larger than the coefficients obtained in this study. This difference may be caused by the fact that in commercial steels the removal of carbon and nitrogen from solution by titanium and columbium represents a decrease of austenite formers in solution (which is equivalent to a ferritizing effect), in addition to the ferrite forming tendency of the titanium and columbium which remain in solution. If the whole effect were to be ascribed to titanium or columbium, the coefficients assigned to these elements would be fictitiously high.

There is disagreement on the effect of manganese on the structure of weld deposits and castings. Several investigators[13,15,16] have assigned manganese a role as an austenite former with a Ni-equivalent of 0.5. In Fig. 38 of Ref. 20, Guiraldenq showed that manganese promoted the formation of ferrite in as-cast specimens containing 18.5% Cr, 7.5 to 10.5% Ni and 1 to 8% Mn. The Cr-equivalent of manganese was about

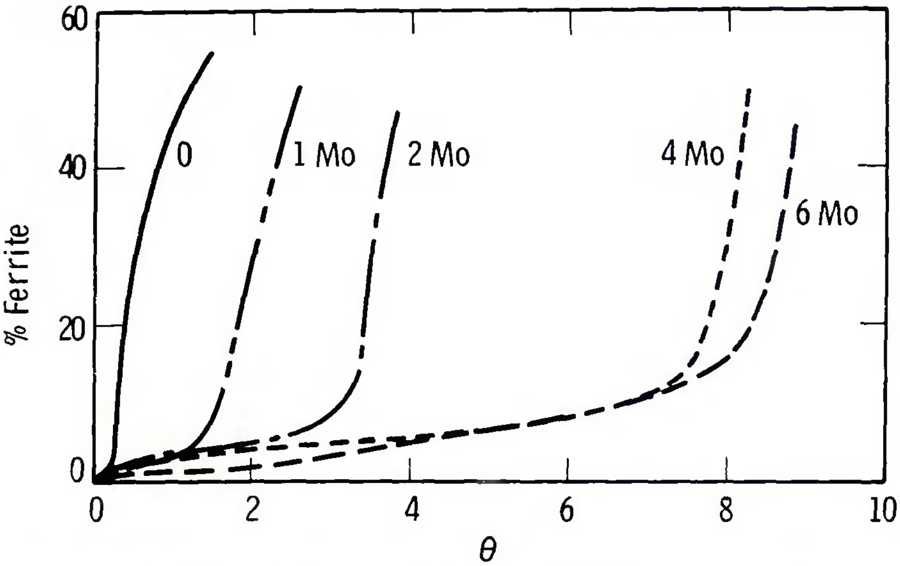

Fig. 12 — Effect of molybdenum on the shape of the delta ferrite versus θ curve for alloys containing 16% Cr, variable nickel and balance iron

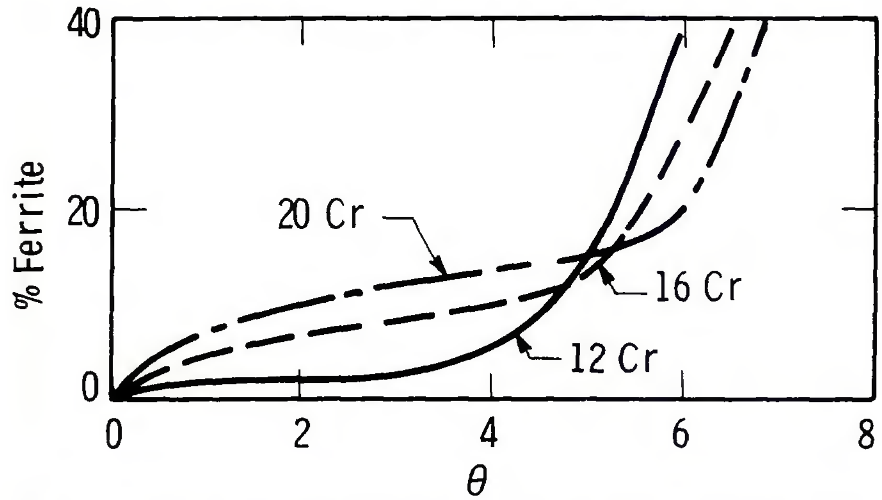

Fig. 13 — Effect of chromium on the shape of the delta ferrite versus θ curve for alloys containing 11% Mn, 2% Mo, variable nickel and balance iron

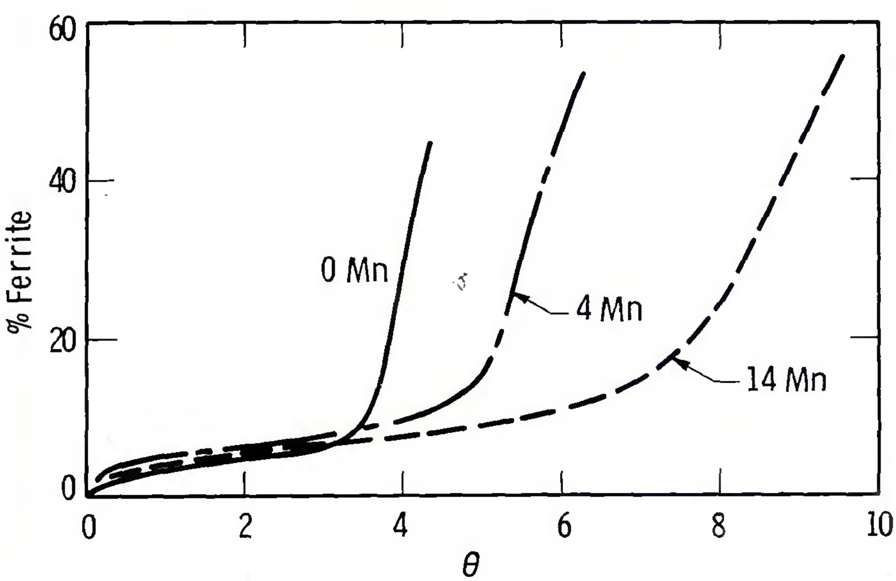

Fig. 14 — Effect of manganese on the shape of the delta ferrite versus θ curve for alloys containing 16% Cr, 2% Ti, variable nickel and balance iron

Summary and Conclusions

The effects of 15 alloying elements on delta ferrite and martensite formation in cast austenitic Cr-Ni stainless steels were evaluated. Small chill-cast pins were selected for this study for experimental convenience and because they provided a reasonable approximation to the microstructures and cooling rates of weld deposits. Nickel and chromium equivalents of Mn, Mo, Si, V, W, Ti, Al, Cb, Ta, C, N, Co and Cu, with respect to delta ferrite formation and also M_s and M_d temperatures, were determined by regression analyses.

By using the quantitative relationships derived and adjusting both the total alloy content and the balance between austenite and ferrite forming elements, different delta ferrite contents, combined with varying M_s or M_d temperatures can be obtained in order to achieve particular combinations of properties. For example, through composition selection, dimensionally stable stainless steel castings for cryogenic service could be designed to contain 5% delta ferrite, to increase strength and to minimize hot tearing, but at the same time have an austenite that would not transform to martensite if deformed at low temperatures.

The ease of control of delta ferrite at a predetermined level depends upon the slope of the curve of % ferrite versus composition. Alloying elements affect this slope in widely different ways. Steels with 11% Mn, 2% Mo, 12 to 20% Cr, 7 to 12% Ni and balance Fe possess the desirable characteristic of having particularly wide, flat curves, with the height of the delta ferrite shelf determined primarily by the amount of chromium present.

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