

197-24-83 QS (1)
ANL-82-43

I-10878

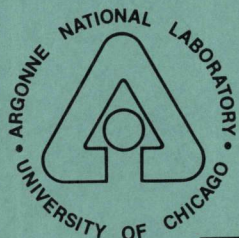
Dr. 1702-1
ANL-82-43

STUDY OF CHROMIUM-FREE AND CHROMIUM-REDUCED STEELS

by

T. C. Wiencek and H. R. Thresh

DO NOT MICROFILM
THIS PAGE



ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated by THE UNIVERSITY OF CHICAGO

for the U. S. DEPARTMENT OF ENERGY

under Contract W-31-109-Eng-38

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ANL-82-43

ANL--82-43

DE83 016717

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

STUDY OF CHROMIUM-FREE
AND CHROMIUM-REDUCED STEELS

by

T. C. Wiencek and H. R. Thresh

Materials Science and Technology Division

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

May 1983

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
A. Formability Studies	2
B. Production of Pilot-Scale Heats	2
C. Evaluation of Engineering Properties	4
II. EXPERIMENTAL PROCEDURES	4
A. Sample Preparation	4
B. Evaluation of Engineering Properties	4
III. RESULTS AND DISCUSSION	5
A. Formability Studies	5
B. Production of Pilot-Scale Heats	6
C. Evaluation of Engineering Properties	9
IV. SUMMARY AND CONCLUSIONS	17
ACKNOWLEDGMENTS	18
REFERENCES	18

List of Figures

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Schaeffler Diagram as Modified by Schneider	3
2.	Formability of 7.5% Si Alloys, Based on Bend Tests of Ref. 4	3
3.	Extruded CFS-6 Sample, Heat Treated 1 h at 1000°C and Water Quenched	10
4.	Extruded CFS-7 Sample, Heat Treated 1 h at 1000°C and Water Quenched	10
5.	Extruded CFS-10 Sample, Heat Treated 1 h at 1000°C and Air Cooled	10
6.	Extruded CFS-10 Sample, Heat Treated at 1000°C for 1 h and Furnace Cooled	10
7.	Age-hardening Curves for CFS-6, CFS-7, and CFS-10 at 780°C	11
8.	As-cleaned Specimens after 1416-h Oxidation Test at 1000°C in Still Air	17

List of Tables

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Composition Ranges of High-Silicon Alloys That Showed the Best Formability in Previous Studies	6
II.	Effect of Composition on Hardness of Small Alloy Specimens	7
III.	Compositions of Pilot-Scale Alloys Chosen for Extrusion ...	8
IV.	Extrusion Data for Pilot-Scale Alloys	8
V.	Effect of Heat Treatment on Hardness of Pilot-Scale Alloys	9
VI.	Tensile Properties of Extruded and Hot-rolled Alloys at Room Temperature	12
VII.	Effect of Cold Reduction on Hardness of Pilot-Scale Alloys	14
VIII.	Degrees of Surface Pitting Observed in Alloy Samples after Salt Water Corrosion Tests	14
IX.	Effect of Composition on Salt Water Corrosion Rate of Small Alloy Specimens	15
X.	Effect of Composition on Oxidation of Small Alloy Specimens after 1416 h in Still Air at 1000°C	16

STUDY OF CHROMIUM-FREE AND CHROMIUM-REDUCED STEELS

by

T. C. Wiencek and H. R. Thresh

ABSTRACT

The goal of this study was to develop an iron-based alloy, similar to Type 316 stainless steel in mechanical and corrosion properties but with a reduced Cr content or, ideally, no Cr. The major market for such an alloy would be applications in which materials must withstand aggressive environments and the cost of stainless steel is prohibitive.

A total of twenty-six 225-g ingots and ten 2.5 to 12 kg ingots of various compositions in the Fe-Si-Mn-Ni-C system were prepared. All ingots contained from 5 to 11 w/o silicon and drew their corrosion resistance primarily from this component. The composition ranges of the remaining major alloying elements were (in w/o) 0-24 Mn, 0-35 Ni, and 0.08-0.95 C. Most of the alloys were reduced to sheet, demonstrating the hot fabricability of these high-silicon alloys.

The mechanical and corrosion properties of these alloys are attractive. Tensile tests showed yield strengths of 303 to 379 MPa (44 to 55 ksi), ultimate tensile strengths of 731 to 882 MPa (106 to 128 ksi), and elongations of 34 to 77%. Air oxidation rates were lower than those of 300-series stainless steels at 1000°C. Salt water corrosion rates for these alloys fall between those of stainless steels and plain carbon steels and are 5 to 10 times lower than the rates for plain carbon steels.

The results are sufficiently encouraging to suggest that a more complete data base of optimized alloys be established. This should include information on the role of silicon and silicon/chromium combinations in the establishment of a protective oxide layer.

I. INTRODUCTION

There is a well-recognized need for an economical class of iron-based alloys with corrosion and oxidation properties intermediate between those of plain carbon steels and stainless steels. Further, since the United States is almost totally dependent on imported chromium from Zimbabwe (formerly Rhodesia) and the Republic of South Africa, the possibility of a chromium

embargo makes the investigation of possible chromium substitutes a subject of national interest.² A government-funded study³ has discussed the possibility of creating a new family of chromium-free austenitic stainless alloys, which would draw their resistance to corrosive environments from silicon and/or aluminum. Such alloys could be useful in many engineering applications, including coal liquefaction and gasification systems, where stainless steels are now specified. Preliminary work⁴ has demonstrated that a processable iron-based high-silicon alloy is feasible and warrants a more thorough investigation.

The primary criterion for the usefulness of a reduced-Cr or Cr-free alloy is formability similar to that of an austenitic stainless steel. An austenitic structure would be preferred since it is usually soft, ductile, and well suited to fabrication processes. However, duplex or even ferritic alloys could also meet the formability criterion. The Schaeffler diagram⁵ shown in Fig. 1 illustrates the effects of alloying elements on the phases present in iron-based alloys and was the major guide for selection of elements to produce an austenitic high-silicon alloy. Additions of the Ni-equivalent elements Co, C, N, Mn, and Cu promote the formation of an austenitic structure, while additions of the Cr-equivalent elements Si, Mo, V, Al, Nb, Ti, and W produce a ferritic structure.

Two other important requirements for a useful stainless steel substitute alloy are ambient-temperature corrosion resistance and high-temperature oxidation resistance. A recent study on stainless steels by Sedriks⁶ has shown that in terms of resistance to corrosion in chloride solution, the most beneficial alloying elements of commercial interest are Si, Ni, Mo, and Cu; small additions of less common alloying elements such as Ag or Re are also effective. In the same study, Ni, Al, and Si were identified as the most beneficial alloying elements for improved oxidation resistance in steels.

In the present investigation, the effects of a variety of alloying elements on the fabricability, corrosion resistance, and oxidation resistance of high-silicon iron-based alloys were systematically examined. The study was divided into three phases:

A. Formability Studies

Results from a previous study,⁴ shown in Fig. 2, demonstrated the existence of three distinct composition ranges for 7.5 w/o silicon alloys with good formability: high-nickel, high-manganese, and high-manganese plus nickel (Table I). In the present study, alloy samples in these three composition ranges, with or without additional alloying elements, were arc-cast in the form of small (225-g) ingots. These samples were then examined to determine (1) the maximum silicon level attainable with acceptable formability, and (2) the effects of minor alloying elements on formability.

B. Production of Pilot-Scale Heats

On the basis of the formability studies, three alloys were selected to cast as large heats (~10 kg). The objective was to develop the process metallurgy for these alloys to the pilot-scale level.

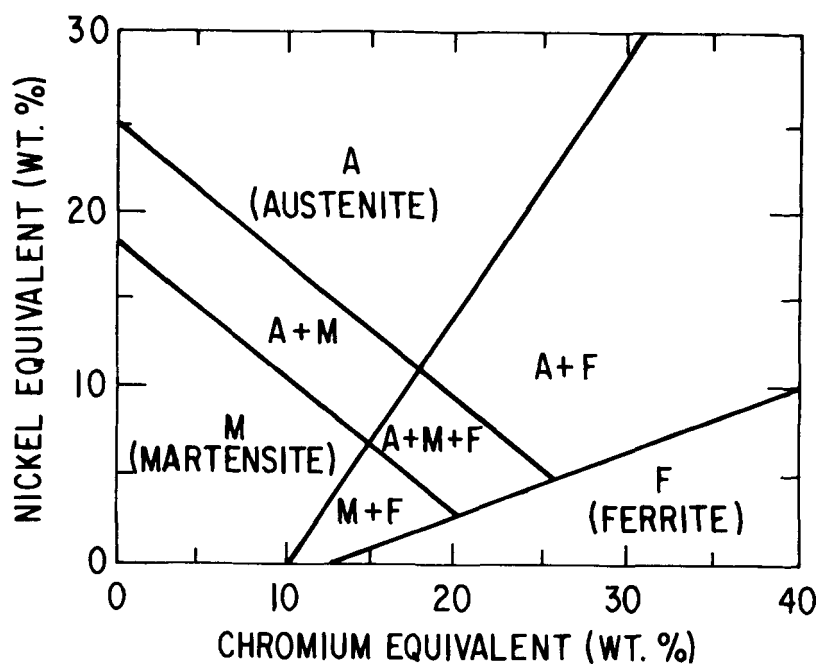


Fig. 1. Schaeffler Diagram as Modified by Schneider. Weight percent Ni equivalent = $\%Ni + \%Co + 30(\%C) + 25(\%N) + 0.5(\%Mn) + 0.3(\%Cu)$. Weight percent Cr equivalent = $\%Cr + 2(\%Si) + 1.5(\%Mo) + 5(\%V) + 5.5(\%Al) + 1.75(\%Cb) + 1.5(\%Ti) + 0.75(\%W)$. Reproduced from Ref. 5.

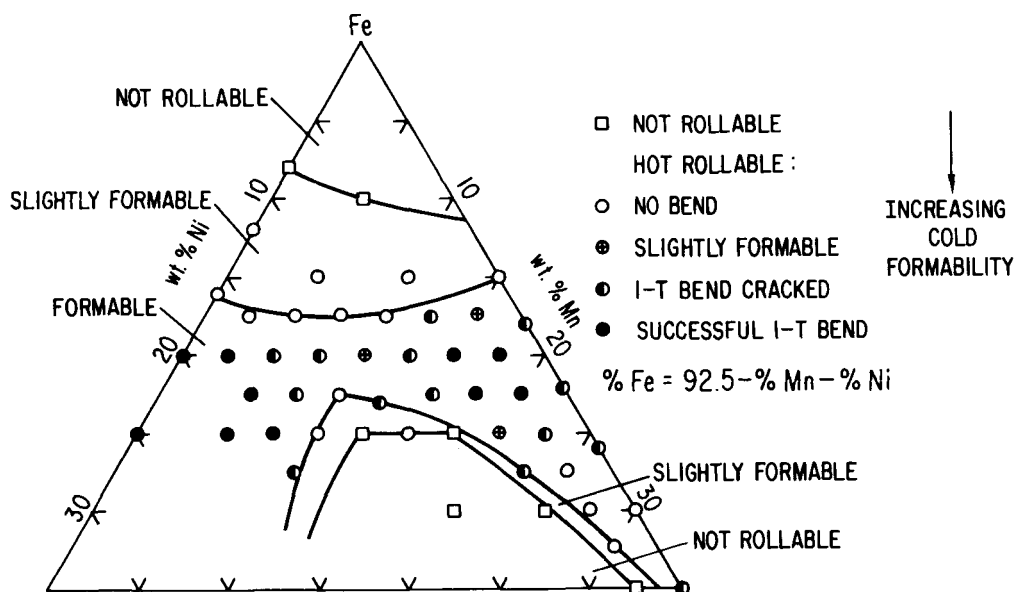


Fig. 2. Formability of 7.5% Si ($\sim 0.06\%$ C) Alloys, Based on Bend Tests of Ref. 4.

C. Evaluation of Engineering Properties

Pilot-scale samples were tested to determine their response to heat treatment, age-hardening properties, tensile properties, and cold reduction behavior. Small samples were used to measure room temperature corrosion rates in salt water and high-temperature oxidation rates in still air.

II. EXPERIMENTAL PROCEDURES

A. Sample Preparation

Small heats (~225 g) were produced in an arc-melting furnace. Melts were made under an atmosphere of argon and helium at slightly more than 10^{-5} Pa (1 atm). Charge materials were Fe (as commercial 1008, 1018, or 1095 steel), Inco Ni pellets (99.5%), electrolytic Mn (99.0%), pure Mo (99.0%), pure Cu (99.0%), pure Si (97.0%), pure Al (99.9%), and electrolytic Cr (99.0%). The arc-cast ingots were annealed at 1000°C for a minimum of 8 hours. The samples were then hot rolled at 1000°C to ~0.5 to 1.0-mm (~0.020 to 0.040-in.) sheet on a two high 3 x 6 in. rolling mill.

Large heats were prepared as ~10-kg vacuum induction melts. The initial ingots were slab cast to dimensions of ~76 x 25 x 152 mm (~3 x 1 x 6 in.). Later, a cylindrical ingot, ~114 mm (~4.5 in.) in diameter and 178 mm (7 in.) long, was cast. The charge materials were the same as those used for the small heats, except that 1018 steel was used exclusively as the source of iron.

The melting procedure consisted of heating a complete charge in a MgO crucible coated with yttrium oxide under vacuum to ~800°C, then backfilling the furnace with argon to $\sim 9 \times 10^{-4}$ Pa (~0.9 atm). After melt-down, the heat was held at ~1450°C for a minimum of 20 minutes. The heats were then bottom poured at ~1450°C into a graphite mold coated with yttrium oxide as a release agent. Three of the castings were extruded and hot rolled to sheet.

B. Evaluation of Engineering Properties

1. Heat Treatments

Pilot-scale alloy samples were heated to 1000°C for 60 minutes with subsequent water quenching, air cooling, or furnace cooling. Hardness readings and metallographic samples were taken.

2. Age-hardening Experiments

Samples of the pilot-scale heats were solution treated at 1000°C for 60 minutes and water quenched. Hardness readings were taken after aging periods of 1, 2, 4, 8, and 16 hours at 780°C.

3. Tensile Tests

Sheet tensile specimens, 152 x 25.4 x 3.2 mm (6 x 1 x 0.125 in.) in size with a 50.1-mm (2-in.) gage length, were machined from extruded and

hot-rolled sheet. Some samples were age-hardened as described above. The yield strength, ultimate tensile strength, and percent elongation were measured.

4. Cold Reduction

Samples of the pilot-scale heats, 12.7 x 12.7 x 12.7 mm (0.5 x 0.5 x 0.5 in.) in size, were cold rolled to thickness reductions of 10%, 20%, 30%, and where possible, 40% and 50%. Hardness readings were taken after each reduction.

5. Salt Water Corrosion Tests

Samples of the small (225-g) heats, 25.4 x 25.4 x 0.76 mm (1 x 1 x 0.03 in.) in size, were subjected to alternate immersion in 3.5% NaCl for 1512 h, in accordance with ASTM Standard G44-75.⁷ This is an "all-purpose" test that produces useful comparisons of salt water corrosion of most metals and alloys. Reference samples of commercially produced Type 304 and Type 316 stainless steels and 1018 carbon steel were included in these tests. Some of the samples were passivated in a 50% nitric acid dip at room temperature before the corrosion testing was initiated. After testing, the samples were wiped with acetone and buffed with a soft cloth. To calculate the corrosion rates, the densities of the alloys were measured by the Archimedes method.

6. Static Oxidation Tests

Simple static oxidation tests (1000°C for 1416 h) were conducted on ten of the experimental small-heat alloys, in accordance with ASTM Standard G54-77.⁸ The 1000°C temperature was chosen to provide a very hostile test environment. Samples of Type 304 and Type 316 stainless steel and 1018 carbon steel were also included for comparison.

III. RESULTS AND DISCUSSION

A. Formability Studies

For this part of the investigation, a variety of alloy samples were fabricated as small (~225-g) heats. Some had compositions within the approximate ranges listed in Table I; others had either a higher Si content or small additions of Al, Mo, Cu, or Cr. Since most of the weight losses during arc-melting were much less than 1%, the final compositions of the small heats were not analyzed. Table II summarizes the nominal compositions and hardness data for 24 different alloy samples. In general, alloys with hardness readings below 95 R_B are quite formable, with tensile elongations in the 20-30% range. This amount of formability is acceptable for most engineering applications.

The data for Groups 1 and 2 show the effects of increased silicon content on the hardness of the high-Ni and high-Mn alloys, respectively. Alloys with more than 8.5 w/o Si were brittle and difficult to roll. This is most likely due to the formation of Si-rich intermediate phases, which have an embrittling effect.

Table I. Composition Ranges of High-Silicon Alloys That Showed the Best Formability in Previous Studies^a

Type	Composition (w/o) ^b			
	Mn	Ni	Si	C
High-Ni	-	20-30	7.5	0.1-0.7
High-Mn	20-30	-	7.5	0.1-0.2
High-Mn + Ni	20-30	3-7	7.5	0.1-0.3

^aSee Ref. 4, p. 60.

^bBalance Fe.

The data for group 3 show the effect of a 5 w/o Al addition. These alloys were castable but were extremely brittle and could not be hot worked at 1000°C. An investigation of the literature suggests that as little as 2 w/o Al would improve the corrosion resistance of these alloys; with 2 rather than 5 w/o Al, the alloys might have acceptable formability.

Molybdenum additions in the 2-3% range reduce the amount of pitting corrosion in 316 stainless steel at low temperatures. It was thought that Mo might have the same effect on the high-silicon alloys. However, the addition of 3 w/o Mo (group 4) severely reduced the formability of the high-Mn alloy, and slightly reduced the formability of both the high-Ni and the high-Mn + Ni alloys.

Copper additions (group 5) had only a slight negative effect on formability.

The investigation of chromium additions (group 6) led to a particularly interesting result. Since Cr is a ferrite stabilizer, it was believed that a combination of high Si and Cr might severely embrittle these alloys. However, the high-Ni alloy and the high-Mn alloy were able to form solid solutions containing substantial amounts of Cr without embrittlement. This finding supports the idea that a high-Si, low-Cr alloy would be a feasible substitute for some high-Cr alloys.

B. Production of Pilot-Scale Heats

A total of ten pilot-scale heats were cast; three of these heats, representing the three alloy types of Table I (high-Ni, high-Mn, and high-Mn + Ni), were selected for extrusion to bar or round stock. Table III gives the compositions of the alloys chosen for extrusion, and Table IV summarizes the

Table II. Effect of Composition on Hardness of Small Alloy Specimens^a

Table II. Effect of Composition on Hardness of Small Alloy Specimens^a

Alloy No.	Nominal Composition (w/o) ^b					Hardness ^c	
	Mn	Ni	Si	C ^d	Other	R _B Scale	R _C Scale
<u>Group 1</u>							
2	-	20.00	7.5	0.08	-	80	-
3A	-	25.00	8.5	0.95	-	94	-
7	-	30.00	9.0	0.95	-	-	38
8	-	30.00	10.0	0.95	-	-	50
11	-	35.00	11.0	0.95	-	-	54
<u>Group 2</u>							
5	24.0	-	7.0	0.08	-	80	-
1	17.5	3.75	7.5	0.08	-	80	-
18	20.0	-	7.5	0.18	-	84	-
4	24.0	-	7.5	0.08	-	86	-
12	24.0	-	8.0	0.18	-	95	-
9	24.0	-	9.0	0.18	-	-	35
<u>Group 3</u>							
21	-	25.00	7.0	0.18	<u>Al</u> 5.0	-	53
22	17.5	3.75	7.0	0.18	5.0	-	43
23	24.0	-	7.0	0.18	5.0	-	40
<u>Group 4</u>							
24	-	22.00	7.0	0.18	<u>Mo</u> 3.0	83	-
25	17.5	3.75	7.0	0.18	3.0	99	-
26	24.0	-	7.0	0.18	3.0	-	34
<u>Group 5</u>							
16	17.5	3.75	7.5	0.18	<u>Cu</u> 1.0	96	-
17	-	25.00	8.0	0.18	1.0	99	-
<u>Group 6</u>							
10	-	30.00	7.0	0.18	<u>Cr</u> 3.0	70	-
15	17.5	3.75	7.0	0.18	6.0	89	-
14	-	25.00	7.0	0.18	10.0	81	-
20	-	25.00	7.0	0.95	10.0	88	-
19	-	25.00	7.0	0.18	15.0	89	-

^a Alloy samples were heat treated for 1 h at 1000°C and air-cooled to room temperature before testing.

^b Balance Fe.

^c Hardness values that exceeded the R_B range (100-kg load) were measured on the R_C scale (150-kg load).

^d Based on carbon content of steel used in charge.

Table III. Compositions^a of Pilot-Scale Alloys Chosen for Extrusion

Alloy No.	Charged Composition/Analyzed Composition (w/o)			
	Mn	Ni	Si	C
CFS-6	-/0.55	22/22.6	7.5/7.2	0.18/0.14
CFS-7	17.5/17.7	3.75/3.75	7.5/7.6	0.18/0.15
CFS-10	24/24.3	-/0.01	7.0/7.2	0.18/0.25

^aBalance Fe.

Table IV. Extrusion Data for Pilot-Scale Alloys

Alloy No.	Extrusion Temperature (°C)	Die Size ^a (mm)	Extrusion Ratio	Break-through Pressure		Mean Flow Stress ^b		Estimated Mean Flow Stress for 316 SS	
				MPa	ksi	MPa	ksi	MPa	ksi
CFS-6	1020	41.1 x 16.6	12.5	958 ^c	139	510	74	414	60
CFS-7	1020	33.7 x 16.1	15.7	1130 ^c	164	579	84	414	60
CFS-10	1130	37.7 diam	7.6	813	118	317	46	383	41

^aDie angle = 45°.^bBased on Siebel calculation (see text).^cPress stalled after extruding approximately 80% of casting.

extrusion results. The mean flow stresses were determined from the extrusion ratio, breakthrough pressure, die size, and lubrication data by use of the Siebel calculation (Ref. 4, p. 51) with modifications to include the friction of the wall. The high-temperature strength of the alloys was similar to that of stainless steels.

Samples of the extruded bars were hot rolled at 1000°C to sheet. The alloys showed excellent formability and were easily hot worked to a thickness of 3.2 mm (1/8 in.).

C. Evaluation of Engineering Properties

1. Heat Treatments

Samples of the as-extruded bar fabricated from alloys CFS-6, CFS-7, and CFS-10 were heat treated as shown in Table V. Typical microstructures resulting from these treatments are illustrated in Figs. 3-6. All of these alloys have an austenitic matrix; other phases present are probably ferrite or a compound precipitate.

Table V. Effect of Heat Treatment on Hardness^a (R_A Scale)
of Pilot-Scale Alloys

Condition	Hardness		
	CFS-6	CFS-7	CFS-10
As extruded	57	60	60
1000°C for 60 min., water quenched	51	60	57
1000°C for 60 min., air cooled	51	60	59
1000°C for 60 min., furnace cooled	61	61	59

^aHardnesses of ~6.4-mm (~0.25-in.) cubic samples were measured with a Brale indenter (60-kg load) and a conventional Rockwell hardness tester.

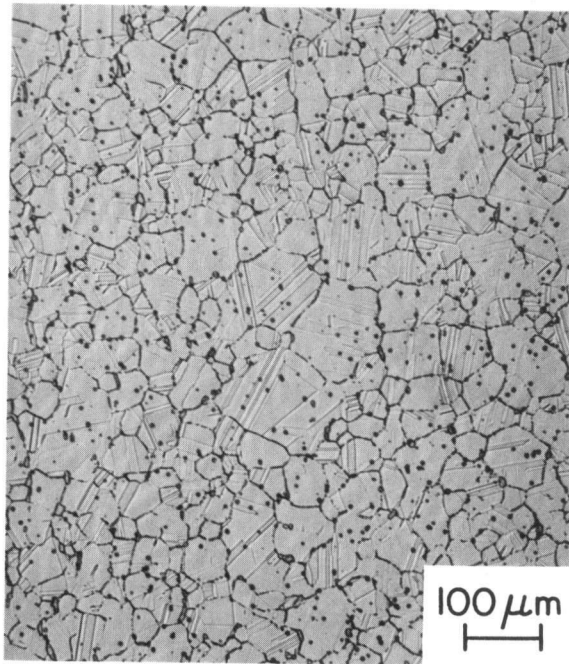


Fig. 3. Extruded CFS-6 Sample, Heat Treated 1 h at 1000°C and Water Quenched. Matrix is austenite; dark phase is ferrite. Nital etch.

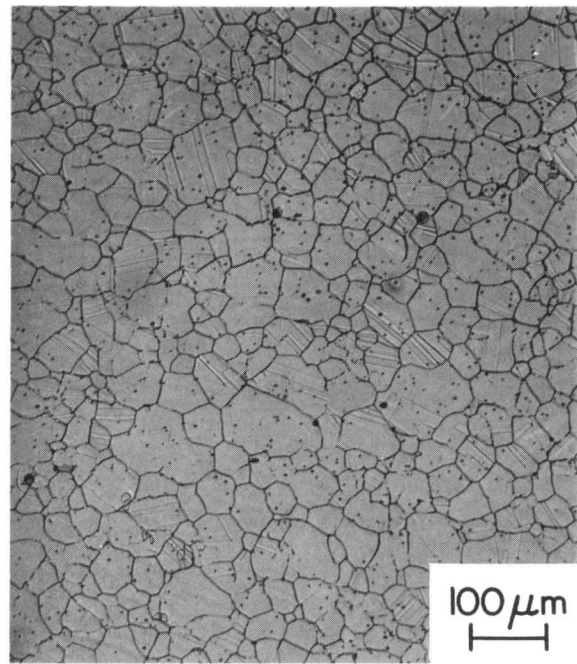


Fig. 4. Extruded CFS-7 Sample, Heat Treated 1 h at 1000°C and Water Quenched. Matrix is austenite; dark phase is ferrite. Nital etch.

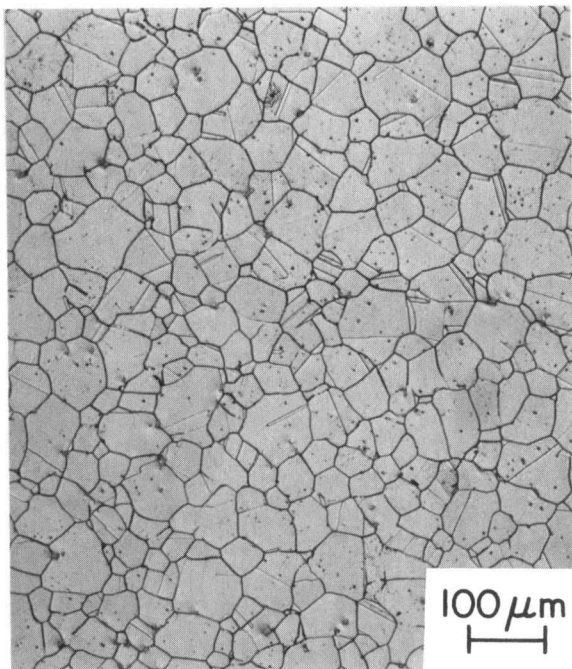


Fig. 5. Extruded CFS-10 Sample, Heat Treated 1 h at 1000°C and Air Cooled. Fully austenitic structure. Nital etch.

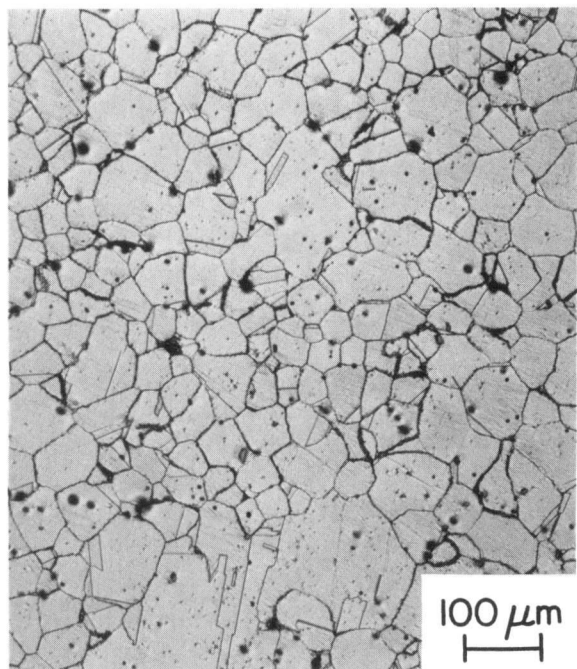


Fig. 6. Extruded CFS-10 Sample, Heat Treated at 1000°C for 1 h and Furnace Cooled. Matrix is austenite; dark phase is ferrite. Nital etch.

The data in Table V demonstrate that these alloys are not heat treatable to martensite at these carbon levels (~ 0.14 to 0.25% C). At higher carbon levels, conventional quench-and-temper⁴ heat treatment may lead to martensitic transformation, but previous work⁴ has shown that for acceptable ductility the carbon level in CFS-7 and CFS-10 must be limited to less than 0.3% . Only CFS-6, which can tolerate a carbon content of 0.8% , could possibly be hardened in this manner.

One interesting result shown in Table V is the increase in hardness of CFS-6 after furnace cooling. The increase of 10 points on the R_A scale is equivalent to a change of approximately 20 points on the R_C scale, a significant increase which warrants further investigation.

2. Age Hardening Experiments

A simple aging experiment was conducted on alloys CFS-6, CFS-7, and CFS-10; the results are shown in Fig. 7. Both CFS-6 (Fe-Ni-Si) and CFS-7 (Fe-Mn-Ni-Si) showed age hardening, whereas CFS-10 (Fe-Mn-Si) did not. These results can be explained by attributing the age hardening to the precipitation of a nickel-silicon compound. The Ni-Si phase diagram shows decreasing solid solubility with decreasing temperature, which is the prime requirement for age-hardening.

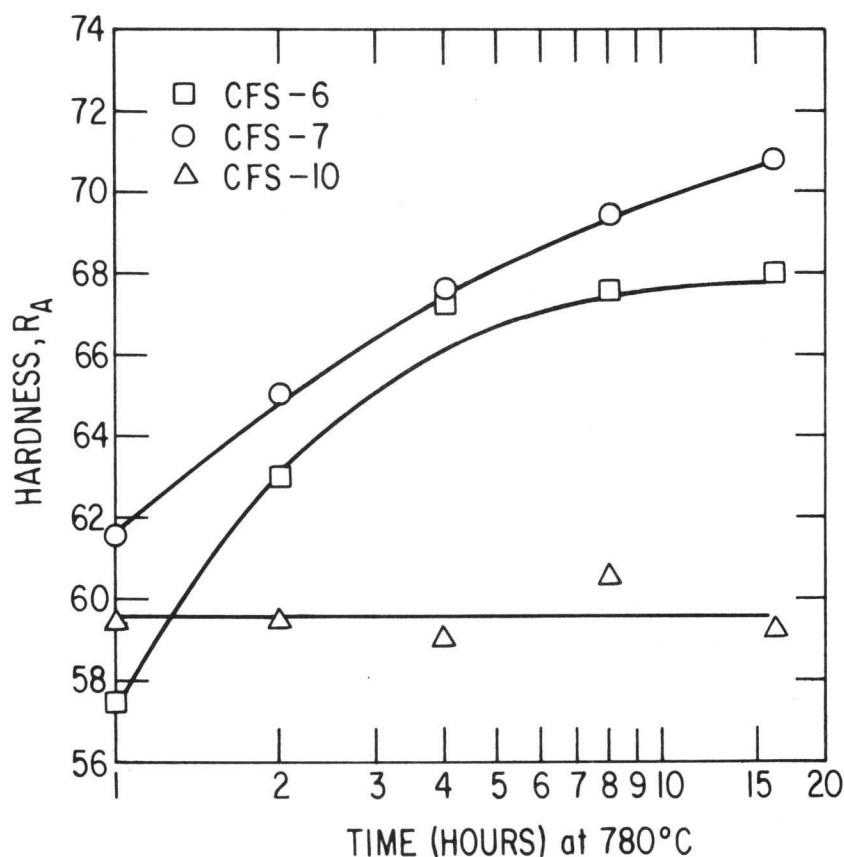


Fig. 7. Age-hardening Curves for CFS-6, CFS-7, and CFS-10 at 780°C .

3. Tensile Tests

Hot-rolled samples of the pilot-scale alloys were heat treated as shown in Table VI. The results indicate that in the annealed condition all three alloys have very acceptable mechanical properties. The yield strengths range from 303 to 379 MPa (44 to 55 ksi) and the ultimate tensile strengths range from 731 to 882 MPa (106 to 128 ksi). The elongations are also quite acceptable, varying from 35% to a high of 77%.

However, the alloys lost almost all ductility after heat treatment, probably owing to the formation of a brittle nickel silicide precipitate. Because of this loss of ductility, these alloys can have no useful engineering application in the age-hardened condition. Also, this temperature range would have to be avoided in processing or application to prevent brittle failure.

Table VI. Tensile Properties of Extruded and Hot-rolled Alloys at Room Temperature^a

	Alloy No.		
	CFS-6	CFS-7	CFS-10
	<u>Air Cooled</u>		
Yield Strength (MPa/ksi)	303/43.9	382/55.4	332/48.2
Ultimate Tensile Strength (MPa/ksi)	733/106.3	884/128.2	856/124.1
% Elongation (in./in.)	77.2	41.6	34.6
	<u>1 h at 780°C</u>		
Yield Strength (MPa/ksi)	387/56.2	418/60.7	Not Tested
Ultimate Tensile Strength (MPa/ksi)	874/126.8	603/87.5	Not Tested
% Elongation (in./in.)	10.3	0.8	Not Tested
	<u>16 h at 780°C</u>		
Yield Strength (MPa/ksi)	365/53.0	Brittle Failure;	Not Tested
Ultimate Tensile Strength (MPa/ksi)	570/82.7	No Data	Not Tested
% Elongation (in./in.)	1.3		Not Tested

^a Alloy samples with a 51-mm (2-in.) gage length were cut parallel to the rolling direction. All samples were heated to 1100°C and then water quenched as a base condition. Average values of measurements on three samples are given.

4. Cold Reduction

Table VII shows the hardness of each pilot-scale alloy as a function of the percent cold reduction. All three alloys showed a significant increase in hardness after cold rolling. It is possible that by cold rolling, yield strengths in excess of 689 MPa (100 ksi) could be attained. However, the probable accompanying loss in ductility may limit the applications of these materials.

5. Salt Water Corrosion Tests

Salt water corrosion tests were carried out on most of the small alloy samples, and on three reference samples of commercially produced steels. The experimental alloys formed a thick, dark, tenacious scale during these tests. The amount of surface pitting was quantified as shown in Table VIII. Table IX shows the effects of alloying elements on the salt water corrosion rates and pitting of the samples. The corrosion rates for all the experimental alloys were lower than that of 1018 steel but higher than those of the stainless steels. The results for Group 1 show the effect of increased silicon. There seems to be an optimum level of silicon for good corrosion resistance; at higher silicon levels the corrosion rate increases. This could be due to the formation of silicides or the transition to a two-phase alloy (austenite and ferrite). The addition of Mo or Cu (Group 2) produced no significant change in corrosion rate relative to the corresponding Group 1 alloys. The Group 3 results show that, as expected, even small amounts of chromium (3-6%) reduced the corrosion rates relative to the corresponding Group 1 alloys. This supports the concept of an optimized high-silicon, low-chromium alloy as a substitute for high-chromium stainless steels.

6. Static Oxidation Tests


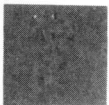
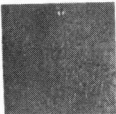
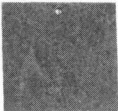

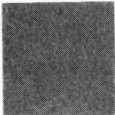
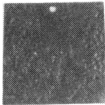
The results of static oxidation tests on 10 alloy samples and 3 commercial steels are summarized in Table X. The oxidation rates of the experimental alloys at short times (<200 h) were comparable to or, in some cases, lower than those of the stainless steels. At longer times the oxides that formed on the silicon-rich alloys were much more stable than those on either 304 or 316 stainless steel. The surface appearances of the samples after testing are illustrated in Fig. 8. A comparison of the oxidation data (Table X) for alloys 2 and 7, and for alloys 4 and 9, shows that increasing the silicon level actually increased the oxidation rate. However, this effect could be counteracted by other elements; for example, alloy 6, which has only 6% Si, oxidized at a comparable rate to alloy 2, which had 7.5% Si and double the nickel content. Overall, it is clear that these preliminary alloys were not optimized for oxidation resistance and that a more thorough investigation could lead to significant improvements.

Table VII. Effect of Cold Reduction^a on Hardness of Pilot-Scale Alloys

Alloy No.	Hardness (R _A Scale)						
	After Cold Reduction of						
	As Extruded	0%	10%	20%	30%	40%	50%
CFS-6	57.4	51	62.8	66.7	71.2	71.8	72
CFS-7	62.0	60	64.5	68.0	71.0	-	-
CFS-10	63.5	57	68.0	71.2	71.6	-	-

^aAll alloy samples were solution heat treated for 1 h at 1000°C and water quenched before cold rolling.

Table VIII. Degrees of Surface Pitting Observed in Alloy Samples after Salt Water Corrosion Tests

Surface Rating		Example ^a
1 - No pitting		17 (high-Ni + Cu)
2 - Very slight pitting		18 (high-Mn)
3 - Slight pitting		2 (high-Ni)
4 - Uniform small pits		4 (high-Mn)
5 - Some large pits		15 (high-Mn + Ni + Cr)
6 - Numerous large pits		9 (high-Mn)
7 - Very numerous large pits		16 (high-Mn + Ni + Cu)

^aPhotographs are one-half actual size.

Table IX. Effect of Composition on Salt Water Corrosion Rate of Small Alloy Specimens

Alloy No.	Nominal Composition (w/o) ^a						Density (g/cm ³)	Corrosion Rate (One Side)		Surface Rating ^c
	Mn	Ni	Si	C ^b	Other			mm/yr	mils/yr	
					<u>Cr</u>	<u>Mo</u>				
304 SS	2.00	9.50	1.00	0.08	19.0	-	8.00	<0.0003	<0.01	1
	max		max	max						
316 SS	2.00	12.00	1.00	0.08	17.0	2.5	8.00	<0.0003	<0.01	1
	max		max	max						
1018	0.75	-	0.25	0.16-0.20	-	-	7.86	0.63	24.9	4
Group 1										
2	-	20.00	7.5	0.08	-		7.63	0.03	1.3	3
3A	-	25.00	8.5	0.95	-		7.45	0.02	0.8	1
7	-	30.00	9.0	0.95	-		7.46	0.01	0.5	1
8	-	30.00	10.0	0.95	-		7.37	0.02	0.6	1
5	24.0	-	7.0	0.08	-		7.42	0.14	5.4	4
1	17.5	3.75	7.5	0.08	-		7.45	0.14	5.4	5
18	20.0	-	7.5	0.18	-		7.41	0.09	3.5	2
4	24.0	-	7.5	0.08	-		7.37	0.09	3.7	4
12	24.0	-	8.0	0.18	-		7.37	0.07	2.9	3
9	24.0	-	9.0	0.18	-		7.29	0.19	7.6	6
Group 2										
					<u>Mo</u>					
24	-	22.00	7	0.18	3.0		7.71	0.04	1.4	2
25	17.5	3.75	7	0.18	3.0		7.50	0.14	5.4	7
26	24.0	-	7	0.18	3.0		7.42	0.20	7.7	7
					<u>Cu</u>					
16	17.5	3.75	7.5	0.18	1.0		7.42	0.21	8.4	7
17	-	25.00	8	0.18	1.0		7.49	0.02	0.8	1
Group 3										
					<u>Cr</u>					
10	-	30.00	7	0.18	3.0		7.66	0.01	0.4	1
15	17.5	3.75	7	0.18	6.0		7.41	0.04	1.4	5
14	-	25.00	7	0.18	10.0		7.61	0.001	0.05	2
20	-	25.00	7	0.95	10.0		7.54	0.005	0.2	2
19	-	25.00	7	0.18	15.0		7.54	0.001	0.04	2

^aBalance Fe.

^bBased on carbon content of steel used in charge.

^cSee Table VIII.

Table X. Effect of Composition on Oxidation of Small Alloy Specimens^a after 1416 h in Still Air at 1000°C

Alloy No.	Nominal Composition (w/o) ^b					Oxidation Rate (One Side)		Comments
	Mn	Ni	Si	Cr	Mo	mm/yr	mils/yr	
2	-	20	7.5	-	-	0.13	5.0	Uniform oxidation
7	-	30	9	-	-	0.46	18.2	Questionable value (uneven oxidation)
6	10	10	6	-	-	0.14	5.4	Uniform oxidation
1	17.5	3.75	7.5	-	-	0.40	15.8	Questionable value (severe oxide growth on edges)
4	24	-	7.5	-	-	0.46	18.2	Uniform oxidation
9	24	-	9	-	-	0.65	25.4	Uniform oxidation
15	17.5	3.75	7	6	-	-	-	Severe oxidation
19	-	25	7	15	-	0.10	4.1	Uniform oxidation
25	17.5	3.75	7	-	3	-	-	Severe oxidation
26	24.0	-	7	-	3	-	-	Severe oxidation
304 SS	2.00 max	9.5	1.00 max	19.00	-	1.75 ^c	69 ^c	Severe oxidation
316 SS	2.00 max	12	1.00 max	17.00	2.5	0.46	18	Severe oxidation
1018	0.75	-	0.25	-	-	660	26,000 ^d	Uniform oxidation

^aAlloy specimens were heat treated for 1 h at 1000°C and air-cooled to room temperature before testing.

^bBalance Fe.

^cBased on 792-h test (Ref. 4, p. 76).

^dBased on 1-h test.

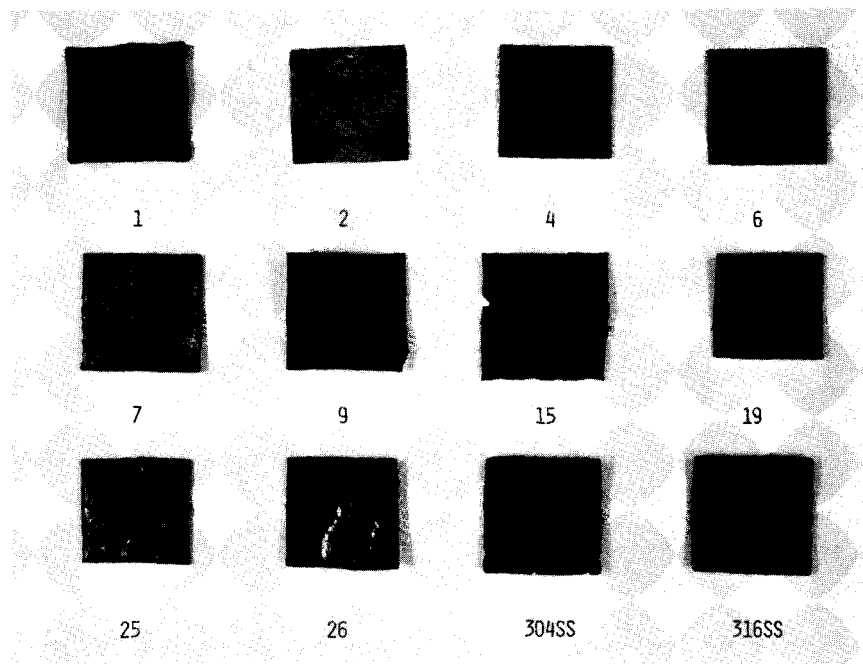


Fig. 8. As-cleaned Specimens after 1416-h Oxidation Test at 1000°C in Still Air (ASTM G54-77). Photographs are one-half actual size.

IV. SUMMARY AND CONCLUSIONS

The following can be concluded about high-silicon iron-base alloys:

1. The formability of the alloys with 7 w/o silicon is similar to that of 300 series stainless steels.
2. The high-silicon alloys have yield strengths of 303 to 379 MPa (44 to 55 ksi) and ultimate tensile strengths of 731 to 882 MPa (106 to 128 ksi) in the annealed condition. They offer an increase in strength over 300-series stainless steels in a similar condition.
3. The oxidation rates of selected high-silicon alloys are significantly lower than those of 300-series stainless steels after extended (over 1400 hours) exposure to still air at 1000°C.
4. The salt-water corrosion rates are 5 to 10 times lower than those of plain carbon steel.

By design, this study was of limited scope. The results to date have been sufficiently encouraging to suggest that a more complete data base of optimized alloys be established. This should include information on the role of silicon and silicon/chromium combinations in the establishment of a protective oxide layer.

From an application point of view, the alloys studied can be placed in two distinct categories. The most promising market for the high-nickel alloys, which are very expensive, is superalloy applications. Mechanical alloying or other state-of-the-art methods could be used to optimize an Fe-Ni-Si-Cr alloy. The high-manganese alloys are the most likely candidates for a stainless steel substitute alloy. Further studies should optimize an alloy in the 20-30% Mn, 5-10% Si, 5-10% Cr ranges. This nickel-free alloy would be very competitive in cost with the 300-series stainless steels.

ACKNOWLEDGMENTS

We would like to thank J. A. Zic for his fine technical work and C. Steves for his excellent metallography. Special thanks are extended to R. F. Domagala, who provided suggestions and solutions to many problems during the investigation. Finally, we wish to thank ANL management for supporting this work through the allocation of discretionary funding.

REFERENCES

1. Contingency Plans for Chromium Utilization, The National Research Council, National Materials Advisory Board NMAB-335 (1978).
2. J. C. Bittence, "Can There Be 'Stainless' Without Chromium?," Materials Engineering, March 1979, pp. 28-32.
3. Materials Technology in the New-Term Energy Program, The National Academy of Sciences (1974).
4. T. C. Wiencek, Development of a Formable Chromium-Free High Silicon Alloy, Thesis, University of Illinois at Chicago Circle (1979).
5. Chromium Substitution in Stainless Steels, S. Floreen Center Bureau of Mines report OFR 110-81 (1980).
6. A. J. Sedriks, Corrosion of Stainless Steels, John Wiley and Sons, New York (1980).
7. "Alternate Immersion Stress Corrosion Testing in 3.5% Sodium Chloride Solution," G44-75, Part 10, in 1978 Annual Book of ASTM Standards.
8. "Simple Static Oxidation Testing," G54-77, Part 10, ibid.
9. D. Peckner and I. M. Bernstein, in Handbook of Stainless Steels, McGraw-Hill, New York (1977), Chapter 23, pp. 3-4.

Distribution for ANL-82-43Internal:

E. S. Beckjord	A. G. Hins	V. A. Maroni
C. E. Till	G. L. Fogle	T. F. Kassner
E. L. Martinec	F. J. Karasek	J. B. Darby (3)
A. A. Jonke	G. W. Klimczak	T. C. Wienczek (10)
B. R. T. Frost	C. Steves	E. M. Stefanski
R. W. Weeks	D. R. Schmitt	ANL Patent Dept.
H. R. Thresh (10)	J. R. Summers	ANL Contract File
R. F. Domagala	C. F. Konicek	ANL Libraries (3)
W. A. Ellingson	J. A. Zic	TIS Files (6)

External:

DOE-TIC, for distribution per UC-25 (197)

Manager, Chicago Operations Office, DOE

Materials Science and Technology Division Review Committee:

- G. S. Ansell, Rensselaer Polytechnic Inst.
- A. Arrott, Simon Fraser U.
- A. L. Bement, Jr., TRW, Inc., Cleveland
- R. C. Dynes, Bell Labs., Murray Hill
- L. M. Falicov, U. California, Berkeley
- E. Kay, IBM San Jose Research Lab.
- M. E. Shank, Pratt & Whitney, East Hartford
- P. G. Shewmon, Ohio State U.