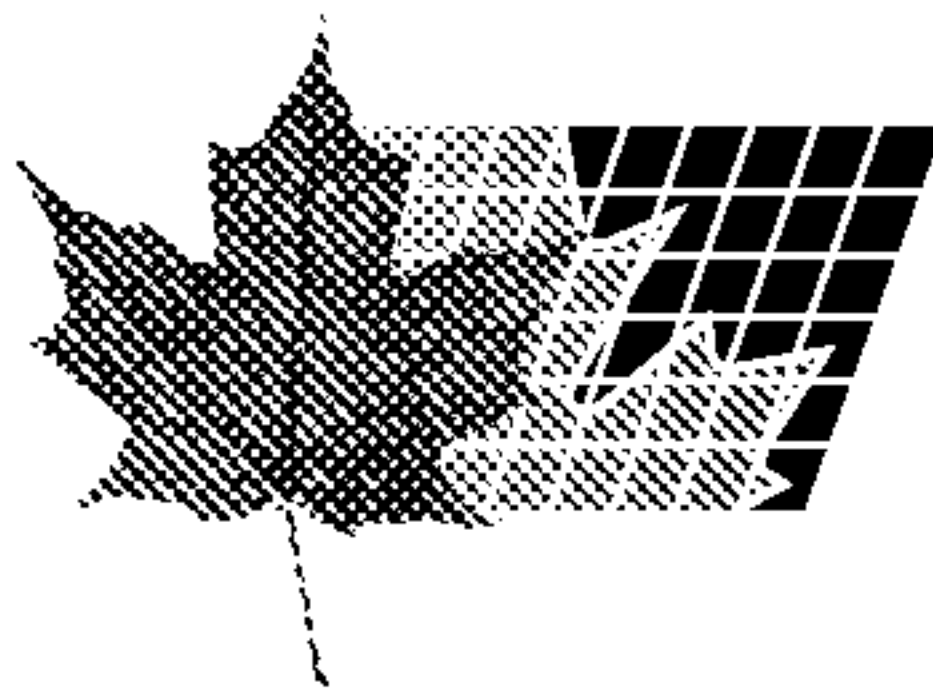




(72) CAMERON, GORDON, CA

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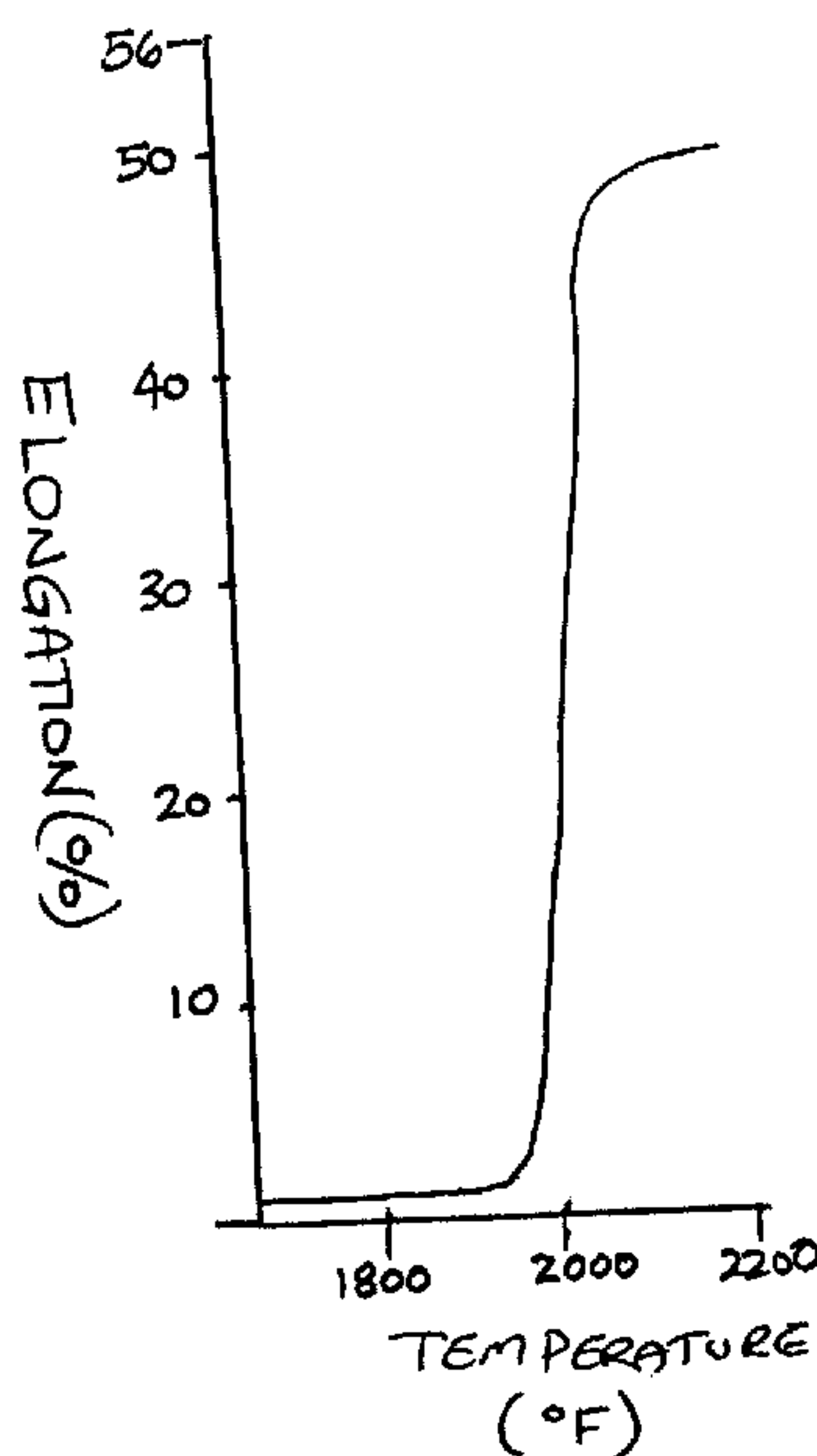
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(54) **ALLIAGES INOXYDABLES POSSEDANT UNE RESISTANCE
ACCRUE A LA CORROSION**

(54) **STAINLESS ALLOYS FOR ENHANCED CORROSION
RESISTANCE**



(57) An improved stainless alloy has application in handling concentrated sulfuric acid. The alloy of the invention preferably comprises 23 to 33% chromium, more than 20% nickel, 6% or more of silicon, 0.2% to 0.4% nitrogen and minor amounts of molybdenum, copper, and tungsten with the balance iron. The alloy offers superior corrosion resistance by comparison with the standard stainless steels over the range from 90% sulfuric acid into the oleum range. The alloy is readily weldable and may be used in either cast or wrought form. After heat treating the alloy acquires a duplex structure which has a mixture of austenite and ferrite phases. The heat-treated alloy is ductile.

ABSTRACT

An improved stainless alloy has application in handling concentrated sulfuric acid. The alloy of the invention preferably comprises 23 to 33% chromium, more than 20% nickel, 6% or
5 more of silicon, 0.2% to 0.4% nitrogen and minor amounts of molybdenum, copper, and tungsten with the balance iron. The alloy offers superior corrosion resistance by comparison with the standard stainless steels over the range from 90% sulfuric acid into the oleum range. The alloy is readily weldable and may be used in either cast or wrought form. After heat treating the alloy acquires a duplex structure which has a mixture of
10 austenite and ferrite phases. The heat-treated alloy is ductile.

STAINLESS ALLOYS FOR ENHANCED CORROSION RESISTANCE

Field of the Invention

This invention relates to alloys containing silicon, chromium, iron and nickel which
5 have enhanced resistance to corrosion in acidic environments. The alloys of the invention
have particular application in handling sulfuric acid over a wide range of concentrations.

Background of the Invention

In many areas stainless steels and higher alloys have replaced cast irons as the
10 materials of choice for handling sulfuric acid. In sulfuric acid plants which operate by the
contact process, high volume circulating streams of sulfuric acid are used to dry process
gases and absorb sulfur trioxide. In such plants, sulfuric acid contacts various pieces of
process equipment including distributors, towers, pumps, valves, acid coolers and piping.
Currently-available stainless steel compositions corrode much more quickly than is
15 desirable for such applications, particularly under process conditions which involve high
temperatures and/or high flow velocities.

Some alloys perform well in specific ranges of acid strength and/or temperature
but none perform well under the full wide range of acid concentrations and temperatures
that may be encountered in some chemical processes. Some cast iron materials offer
20 reasonably good corrosion resistance properties. However, cast iron materials are brittle
and can fail catastrophically. When better materials are available, the cost of such materials
is often sufficiently high that thin walls must be used to keep costs down. The use of thin
walls introduces risks of failure.

Keeping a sulfuric acid plant in safe operation requires continuous maintenance.
25 Components which contact concentrated acids suffer undesirably premature corrosive
degradation and must be periodically replaced. The operator of a sulfuric acid plant must
keep up a program of continual inspection and replacement of acid-contacting
components. This is true even when components are made with thick materials having
heavy corrosion allowances. It is very expensive to replace corroded components in plants
30 handling sulfuric acids. The components are often large and some are difficult to obtain.

It is now possible to operate sulfuric acid plants at higher efficiencies than were
formerly possible by doing things such as using streams of acid as a heat recovery
medium. These efficiencies are achieved at the expense of harsher process conditions, such

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as much higher acid temperatures. For example, the contact process for making sulfuric acid involves the absorption of sulfur trioxide in concentrated sulfuric acid. This reaction is highly exothermic and is typically performed in an absorbing tower. It was formerly considered necessary to maintain the acid in the absorbing tower at low temperatures to avoid rapid corrosion of acid-contacting components. This can make large acid flow rates necessary. A small increase in acid temperature can dramatically increase corrosion rates.

It has been realized that the heat generated by the absorption of sulfur trioxide may be used to heat feed water to make steam or to heat some other medium. Where heat is recovered from the acid exiting an absorbing tower it is desirable to maintain the acid temperature high to maximize the amount of energy which can be recovered from the hot acid. It is therefore desirable to allow the acid to reach temperatures higher than were previously considered prudent.

Further advantages can be obtained if acid handling components are able to withstand acid at higher temperatures. For example, if it is acceptable to allow higher acid temperatures then the flow rate of acid through some components, such as absorption towers, can be reduced. This can lead to savings in pumping, pipe, towers and heat exchangers and also provides greater freedom to design absorption towers.

Harsher process conditions accelerate corrosion and increase the potential harm caused by failed components. Most plants are operated under process conditions near limits imposed by the materials from which the components of process equipment are made. Such plants must be operated and maintained very carefully to avoid catastrophic equipment failures.

The standard stainless steels used for handling sulfuric acid are austenitic. A.I.S.I. 304, 316, 309, and 310 type stainless steel alloys are most common. In most cases these alloys can handle cooled product acid or strong acid having a concentration of about 98% without anodic protection as long as flow velocities, temperatures and turbulence are low. With anodic protection, these materials can be used in hotter acids and the ability to withstand turbulence is increased. Even with anodic protection, however, the use of such materials is normally restricted to solutions containing more than 93% sulfuric acid.

Many alternative materials have been suggested for use in the handling of concentrated sulfuric acids. However, all of these materials lack desirable features. For

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example, while some materials are more highly resistant to corrosion than conventional materials at certain acid concentrations they are more susceptible to corrosion at other acid concentrations. Many materials which are highly corrosion resistant are extremely brittle and therefore cannot be easily worked and may fail catastrophically. Some corrosion resistant materials are not weldable or can only be welded under stringent conditions. Many of these materials also lack versatility. Others are prohibitively expensive for use in most applications.

Jones et al., Canadian Patent No. 1,181,569 discloses that addition of a significant quantity of silicon (preferably about 5.3% silicon) to an austenitic stainless steel greatly improves corrosion resistance to 98% sulfuric acid and to tolerance of turbulence and high velocity. Stainless steel materials having the compositions described by Jones et al. are used widely in sulfuric acid plants in pump tanks, towers, acid piping, and distributors. A typical such material is designated A611 and has the composition Ni 17.5%, Cr 17.5%, Si 5.3%, C < 0.015% with the balance being Fe. Unfortunately, while the compositions disclosed by Jones et al., including A611, are corrosion resistant at absorbing acid strength (98 - 99.5%), the compositions are heavily corroded in oleum or "fuming sulfuric acid" (which contains free liquid SO₃). The compositions also exhibit accelerated corrosion rates at lower acid concentrations. At 50°C, A611 corrodes faster in 70% sulfuric acid than does conventional 316L stainless steel. Furthermore, the Jones et al. materials typically require anodic protection to achieve the lowest corrosion rates. It has also been found that the Jones et al. compositions must contain a number of trace elements and require special care in welding and fabrication. Jones et al. do not explain how to select trace elements to maintain the desired austenitic structure.

Culling, U.S. patent No. 5,306,464 suggests alloys having the formulation: Ni - 15-25%, Si - 4.5-8%, Cr - 15-26%, Cu - 1-4%, Mo 0.3-3% and the balance Fe. Culling '464 does not give any examples of alloys having more than 21.35% Cr. The alloys described in Culling '464 have high carbon contents in the range of 0.5 to 1.7% to produce an acceptable microstructure with acceptable mechanical properties. The high carbon content prevents Culling's alloy from being ductile. The maximum tensile elongation reported in Culling '464 is 4.7%. Culling determined that alloys with high

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silicon contents and low carbon contents tended to be even more brittle and to have other undesirable mechanical properties.

Culling, U.S. patent No. 4,836,985 discloses a nickel based alloy with very little iron and, therefore, a negligible tendency to form ferritic phases. Culling, U.S. patent No. 4,917,860 discloses alloys which have silicon contents of less than 4.5%.

U.K. patent No. 1,534,926 proposes a broad range of alloys said to be resistant to concentrated sulfuric acid but only provides examples of low-nickel stainless steel alloys.

Horn, U.S. patent Nos. 5,051,253 and 5,120,496 disclose alloys of 4-9% silicon with iron, chromium, and nickel. None of the examples given by Horn show both high silicon contents in excess of 6% and high chromium contents in excess of 22%. Horn provides no results of mechanical tests or corrosion resistance data for any materials having 6% or more silicon.

Sridar, U.S. patent No. 5,063,023 discloses a nickel-based alloy containing about 20% chromium, 2% copper, 2% iron, 2% molybdenum, 5% silicon and the balance nickel.

Despite over a century of research directed to identifying materials which can be used in equipment for handling industrial quantities of sulfuric acid there is still much room for improvement. The teachings of prior patents and other publications are sometimes contradictory and often do not provide data to support the full range of suggested compositions.

Currently available silicon stainless steels are relatively corrosion resistant in very strong acid but the corrosion resistance falls off rapidly as the acid strength drops below 95%. While there has been speculation that higher silicon content stainless steels might have more desirable corrosion resistance properties, until now nobody has succeeded in making such a stainless steel alloy which is workable. Those who have tried to make stainless steels with increased silicon contents have found that the materials become essentially unworkable at high silicon levels. High silicon materials such as **DURIRON™** a cast iron material which contains a large amount of iron silicide and has a silicon content of 14%, are typically extremely brittle, sensitive to thermal shock and are not available in wrought form.

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There is a need for materials capable of handling strong sulfuric acids, including oleum, which have better corrosion resistance than the alloys which are currently used. Such materials should have low corrosion rates under the worst conditions expected in sulfuric acid plants. Preferably such materials should retain corrosion resistance at high
5 temperatures to allow the use of process conditions not feasible with present materials. There is a particular need for such materials that can be formed into components of required shapes at reasonable cost by a variety of industrial processes and which can be easily welded.

10 Summary of the Invention

Surprisingly, the inventors have found that workable stainless steel compositions which include significant amounts of both silicon and chromium yield corrosion resistance significantly better than that of alloys having enhanced chromium content or enhanced silicon content alone. The prior art generally teaches that to increase corrosion resistance
15 one should decrease chromium content, or at least hold the chromium content fixed, and thereby make room for extra silicon. Furthermore, the prior art generally teaches that increasing the silicon content of stainless steels or stainless alloys tends to yield materials that are very brittle and not workable.

The inventors have found that certain stainless steel alloys having in excess of 22%
20 chromium and in excess of 6% silicon by weight have exceptional resistance to corrosion and erosion in concentrated sulfuric acids and are workable. The workability of these materials combined with their high degree of resistance to corrosion by concentrated sulfuric acids is completely unexpected as is the wide range of acid concentrations over which the materials are usable. Upon heat treatment, materials according to preferred
25 embodiments of the invention exhibit a duplex microstructure consisting of a mixture of austenite and ferrite. To maintain this microstructure the materials of the invention preferably have a nickel content in excess of 19%.

The inventors have discovered that adding a modest amount of copper and/or molybdenum in the presence of some nitrogen further remarkably increases
30 corrosion resistance to sulfuric acid having a concentration of 98% or lower. Also, adding

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small amounts of vanadium and/or tungsten was found to increase corrosion resistance in 98% to 100% sulfuric acid.

Accordingly, the invention provides a corrosion resistant stainless steel alloy comprising at least 22% by weight chromium and at least 6% by weight silicon.

5 Another aspect of the invention provides a corrosion resistant alloy comprising 22% to 36% by weight chromium, 6% to 10% by weight silicon (in some embodiments 6% to 8% silicon), substantially the balance nickel and iron. In some embodiments the nickel content is in the range of about 18% to about 32% by weight nickel.

10 In one preferred embodiment of the invention the alloy consists essentially of: 25% by weight chromium; 6.5% by weight silicon; 20% by weight nickel; and, 51.5% by weight iron. Upon suitable heat treatment, as described below, materials according to preferred embodiments of the invention become ductile and are readily welded and formed.

15 Another aspect of the invention provides a method for making a workable metallic alloy which is resistant to corrosion by sulfuric acid. The method comprises: alloying at least 22% chromium, at least 6% silicon, at least 20% nickel, up to 4% copper, and iron; and, heat treating the resulting alloy at a temperature sufficient to cause the alloy to become ductile and to have a duplex structure consisting of a mixture of ferrite and austenite. Preferably the heat treatment temperature is a temperature in the range of
20 1100°C to 1200°C.

Further advantages and aspects of the invention are described below.

Brief Description of the Drawings

25 The invention is described in more detail below in conjunction with the accompanying drawings in which:

Figure 1 is a curve relating elongation to heat treatment temperature for an alloy according to an embodiment of the invention;

Figure 2 is a plot showing acid temperatures at which the corrosion rate is 5 mils per year as a function of concentration of sulfuric acid;

30 Figures 3A through 3D are respectively histograms which compare corrosion rates of alloys according to the invention to corrosion rates of some commercial stainless steel

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alloys under the following conditions: 90% sulfuric acid at 100°C; 98% sulfuric acid at 160°C; 105% sulfuric acid at 70°C; and, 105% sulfuric acid at 100°C;

Figure 4 is a histogram showing corrosion rate in 90% H₂SO₄ at 160C as a function of silicon content for several alloys;

5 Figure 5 is a histogram illustrating the relationship between corrosion rate in 90% H₂SO₄ at 100C, 130C and 160C and chromium content for several alloys;

Figure 6 is a histogram illustrating the relationship between corrosion rate in 90% H₂SO₄ and chromium content in the base alloy for alloys having varying silicon contents;

10 Figure 7 is a histogram illustrating the relationship between corrosion rate in 98% H₂SO₄ at 320C and silicon content for several alloys; and

Figure 8 is a histogram illustrating the relationship between corrosion rate in 98% H₂SO₄ at 320C and chromium content in the base alloy for alloys having various silicon contents.

Detailed Description

15 Samples of several alloys designated A1 through A8 having the compositions set out in Table I were made and subjected to accelerated corrosion tests in concentrated H₂SO₄. Except where otherwise stated, all references to elemental compositions in this specification and the appended claims are to percentages by weight of the named element(s). For comparison purposes samples of 310 stainless steel, A611 stainless steel
20 and 700Si stainless steel having the compositions set out in Table I were also subjected to identical accelerated corrosion tests.

Table I: Nominal Composition of Alloys Tested (wt.%)						
Alloy	Cr	Si	Ni	Cu	Mo	Fe
25 A1	24	6.5	19.5	0.19	0.30	balance
A2	24	6.5	19.5	3.19	0.30	balance
A3	24	6.5	19.5	0.19	4.30	balance
A4	24	6.5	19.5	2.19	2.30	balance
A5	24	6.5	24.5	3.19	0.30	balance
30 A6	24	6.5	29.5	3.19	0.30	balance
A7	24	8.5	19.5	0.19	0.30	balance
A8	24	10.5	19.5	0.19	0.30	balance
310	25	0.5	20	-	-	balance
A611	17.5	5.3	17.5	-	-	balance
35 700Si	9	7	25	-	-	balance

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Each alloy was tested by exposing a sample of the alloy for 7 days to agitated 90 wt.% H₂SO₄ at 100°C. Each alloy was also tested by exposing a sample of the alloy for 7 days to agitated 98 wt.% H₂SO₄ at 160°C. Table II shows the measured corrosion rates for each tested alloy in each of these environments.

Table II: Alloy Corrosion Rates in H ₂ SO ₄		
Alloy	90 wt.% H ₂ SO ₄ at 100°C (mils/year)	98 wt.% H ₂ SO ₄ at 160°C (mils/year)
A1	11	20
A2	0.61	13.6
A3	0.61	23.5
A4	0.7	26.8
A5	0.08	8.14
A6	0.58	3.56
A7	5.93	9.2
A8	0.64	0.46
310	278	1.5
A611	523	32.4
700Si	6,900	0.4

The results tabulated in Tables I and II show the following:

- For a constant chromium content of 24 wt.%, an increase in the silicon content from 0.5 to 6.5 very significantly decreased the corrosion rate in both environments. Further increase in the silicon content to 8.5% and 10.5% further decreases the corrosion rate in both 90% and 98% sulfuric acid.
- Simultaneously increasing both the chromium content from 17.5 wt.% to 24 wt.% and the silicon content from 5.3 wt.% to 6.5 wt.% significantly decreased the corrosion rate in both environments.
- For a constant silicon content of about 6.5 wt.%, an increase in the chromium content from 9 wt.% to 24 wt.% significantly decreases the corrosion rate in both environments.

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4. The 700Si material, which has a high silicon content combined with a reduced chromium content unexpectedly has a corrosion rate in 90% sulfuric acid greatly in excess of that of the other materials tested.

5 The inventors have also discovered that the addition to the alloys of the invention of vanadium and tungsten adds significantly to corrosion resistance in 98-100% sulfuric acid while the addition of copper, in amounts up to 4% or molybdenum in amounts of up to 6% , or mixtures of copper and molybdenum in amounts up to 6% (with copper not exceeding 4%), dramatically reduces corrosion rates in sulfuric acid concentrations below
10 98%. The addition of some nitrogen is beneficial in such alloys. Mixtures of copper and molybdenum may provide better corrosion resistance to sulfuric acids having concentrations of less than 98% than either copper or molybdenum alone. If a mixture of copper and molybdenum is used then copper should make up less than 4% of the alloy.

The above results are surprising. Providing a quantity of more than 22% chromium
15 in the presence of more than 6% silicon unexpectedly provides drastically improved corrosion resistance in the alloys of the invention without destroying the workability or weldability of the resulting alloys. Having a high chromium content in addition to a high silicon content can be seen to increase resistance to corrosion by weaker (<98%) sulfuric acid.

20 While both Horn, U.S. patent No. 5,120,496 and Culling, U.S. patent No. 5,306,464 suggest a wide range of alloys which includes some alloys having silicon contents in excess of 6% and chromium contents in excess of 22%, neither Horn nor Culling provide any examples of such alloys and neither Horn nor Culling suggest that
25 such alloys might be both workable and have exceptional resistance to corrosion. Culling's alloys demonstrate good corrosion resistance but have a high carbon content and are not workable, as evidenced by tensile elongation values of less than 5%. Horn provides no corrosion data for silicon contents of 6.45% or more.

A stainless steel alloy according to this invention comprises at least 22% chromium and at least 6% silicon and preferably contains 0.5% to 6% copper and molybdenum.
30 Preferably the alloy of the invention comprises:
a) chromium 22% to 33% ;

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- b) silicon 6% to 10% , and most preferably 6% to 8% ;
- c) copper and/or molybdenum totalling 0.2% to 6% (preferably 0.5% to 6%) with:
 - i) up to 4% copper; and,
 - ii) up to 6% molybdenum;
- 5 d) manganese 0%-3%;
- e) nitrogen in the range of 0.1% to 0.5%; and,
- f) the balance nickel and iron.

Preferably the alloy contains in excess of 18% nickel. More preferably the alloy contains at least 20% nickel. The alloy may contain, for example, 20% to 30%, or more
10 nickel.

Preferably for alloys to be used in 98% -100% sulfuric acid the alloy contains 2% to 4% of one or both of tungsten and vanadium. Minor amounts of other elements may also be present.

It is thought that the ratio of silicon to chromium should be kept in the range of
15 0.25 to 0.36. For one range of alloys according to the invention the preferred relative amounts of silicon and chromium are expressed by the formula:

$$W_{Si} = (0.33 \pm 0.06) \times W_{Cr}$$

where W_{Si} is the percentage of silicon and W_{Cr} is the percentage of chromium.

On casting the alloys of the invention have structure containing austenite and a
20 eutectic phase. On heat treatment the alloys become ductile. After heat treatment, most alloys of the invention acquire a duplex microstructure which has a mixture of austenite and ferrite. Preferably the duplex structure should have about 24% to about 30% by volume ferrite and the balance austenite. The relative amounts of nickel and iron may be varied to adjust the relative amounts of austenite and ferrite in the heat-treated material.
25 Increasing iron content at the expense of nickel tends to increase the ferrite content of the heat-treated material at the expense of austenite content. Increasing nickel content at the expense of iron content tends to increase austenite content of the heat-treated material at the expense of ferrite content. Since chromium and silicon are known to promote the formation of ferrite phases. It is therefore generally desirable to increase the amount of
30 nickel relative to iron as the silicon and chromium content is increased in order to achieve a duplex structure containing a mixture of austenite and ferrite after heat treating. In

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preferred embodiments of the invention the ferrite and austenite phases have very similar elemental compositions. Preferably the ratios of the chromium contents of the ferritic and austenitic phases are 1 ± 0.2 , more preferably 1 ± 0.15 , and the silicon contents of the ferritic and austenitic phases are 1 ± 0.07 , more preferably 1 ± 0.05 .

- 5 A preferred stainless steel alloy according to the invention consists essentially of:
chromium 24-26% ;
silicon 6.5-7.5% ;
nickel in excess of 19% , for example, 19-32%;
copper 3%-3.5% ;
10 molybdenum 2%-3% ;
carbon less than 0.08% ;
trace amounts of other elements such as aluminum, boron and/or cerium which may be
chosen by those skilled in the art, as is known in the art, for functions such as controlling
grain growth or scavenging oxygen; and,
15 iron the balance.

For use in 98% to 100% sulfuric acid the alloy may additionally contain tungsten 2%-4% and/or vanadium 2%-4%.

The alloy of the invention may be used in either cast or wrought form and has been found to be weldable in both cast and wrought forms.

20

Example 1

- An alloy designated A9 having a composition of, 24.7% Cr, 19.2% Ni, 6.0% Si, 0.12% Cu, 0.001% Mo, 0.7%Mn, 0.01% C, and 0.045%N was cast. The as-cast alloy had a microstructure consisting of an austenitic matrix with a eutectic phase occupying
25 approximately 20% to 25% of the volume. The grains of eutectic phase material tended to be acicular. The as-cast alloy was quite brittle. Several samples of the A9 alloy were heat treated. Each sample was heated to a selected temperature for two hours and then quenched in water. Mechanical properties of the as-cast alloy and the heat-treated samples are set out in Table III.

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TABLE III VARIATION IN MECHANICAL PROPERTIES OF A9 ALLOY WITH HEAT TREATMENT AT VARIOUS TEMPERATURES							
Heat Treatment (°F)	Ferrite Content (%)	Magnetic Response	Hardness Rc	Yield Strength (ksi)	Ultimate Tensile Strength (ksi)	Elongation (%)	Charpy Impact (ft lbs.)
None	0	NO	21.3	51.9	84.0	2.0	1.5
1800	0	NO	26.6	63.2	80.7	1.2	1.5
1950	0	NO	22.3	60.5	83.9	1.9	2.0
2000	24.5	YES					
2050	23.0	YES	15.6	57.0	113.5	45.0	45.3
2100	25.9	YES	16.0	58.6	114.2	52.1	58.3
2150	26.4	YES	14.6	58.3	113.2	48.2	59.0
2200	27.0	YES					

15 It can be seen that heat treatment at temperatures in excess of about 2000 °F causes a distinct change in mechanical properties including an increase in tensile strength from approximately 80 ksi to in excess of 110 ksi, an increase in elongation from less than 2% to more than 40%, and an increase in impact strength from less than 3 ft lbs. to more than 45 ft. lbs.

20 In studying the microstructure of the heat-treated A9 alloy it was found that at a heat treatment temperature of 1950 °F (1065 C) the eutectic phase was converted to an intermetallic. At a slightly higher heat treatment temperature of 2000 °F (1093 C) the intermetallic phase begins to transform into a delta ferrite so that the alloy is a duplex alloy having a microstructure characterized by regions of ferrite and regions of austenite. As the
25 heat treatment temperature is increased the ferrite content increases gradually to 27% at a heat treatment temperature of 2200 °F (1204C). Figure 1 is a curve relating elongation to heat treatment temperature which illustrates the marked increase in ductility obtained by heat treating at temperatures in excess of approximately 2000 °F.

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Table IV compares the mechanical properties of a sample of the A9 alloy heat treated at 2100 degrees to the mechanical properties of some commercially available stainless steel alloys.

5

TABLE IV COMPARISON OF MECHANICAL PROPERTIES				
Alloy	Yield Strength (ksi)	Ultimate Tensile Strength (ksi)	Elongation (%)	Ferrite Content (%)
A9	58.6	114.2	52.1	27
A611	51.5	99.3	65	0
SANDVIK™ SX	32	98	30	0
CEI™ XS3390	55.9	126	38	<40
WEIR™ S32760	80	110	25	18
304SS	25	70	40	0

10

15

While the inventors do not wish to be bound by any particular theory of operation it was observed that the elemental composition of austenitic phases and ferritic phases in the A9 alloy were very closely similar. The inventors believe that the even distribution of elements, particularly silicon and chromium, between the ferritic and austenitic phases promotes corrosion resistance and enhances weldability. Corrosion resistance in stainless steels is typically provided by a passive layer. Corrosion is known to occur where one phase within an alloy has a lower concentration of elements capable of forming a stable passive layer than other phases within the alloy. In duplex alloys according to the invention where the elemental composition of austenitic phases and ferritic phases is substantially the same there is no weak point for corrosive attack to occur.

20

25

It was found that the A9 alloy could be worked either hot or cold after heat treatment at 2100 °F. Both the as-cast A9 alloy and the heat-treated A9 alloy could be welded with good results. For example, a joint in a section of as-cast pipe was MIG welded under argon shielding gas at 100 Amperes DC using FOX™ SZW 23 filler material. The

Alloy	Cr	Si	Mo	Cu	W	V	C	Ni	Fe.
310	24	0.5	0.31	0.19			0.048	19.5	balance
E1	24	6.5	0.31	0.19			0.048	19.5	balance
E2	24	6.5	2.3	0.19			0.048	19.5	balance
E3	24	6.5	4.3	0.19			0.048	19.5	balance
E4	24	6.5	0.31	2.19			0.048	19.5	balance
E5	24	6.5	0.31	3.19			0.048	19.5	balance
E6	24	6.5	0.31	4.19			0.048	19.5	balance
E7	24	8.5	0.31	0.19			0.048	19.5	balance
E8	24	10.5	0.31	0.19			0.048	19.5	balance
E9	24	6.5	0.31	0.19			0.048	24.5	balance
E10	24	6.5	0.31	3.19			0.048	24.5	balance
E1 [†]	24	6.5	0.31	3.19			0.048	29.5	balance
E12	27	6.5	0.31	0.19			0.048	19.5	balance
E13	29	6.5	0.31	0.19			0.048	19.5	balance
E14	24	6.5	0.31	0.19	4		0.048	19.5	balance
E15	24	6.5	2.3	0.19	2		0.048	19.5	balance
E16	24	6.5	2.3	2.19			0.048	19.5	balance
E17	24	6.5	4.3	4.19			0.048	19.5	balance
E18	24	6.5	0.31	0.19		2	0.048	19.5	balance
E19	24	6.5	0.31	0.19		4	0.048	19.5	balance
E20 [*]	24	6.5	0.31	3.19			0.048	19.5	balance
E21 ^{**}	24	6.5	0.31	3.19			0.048	19.5	balance
E22	32.75	6.3	1.49	0.54			0.012	31.4	balance
E23	32.75	8.3	1.49	0.54			0.012	31.4	balance
E24	32.75	8.3	1.49	0.54			0.012	31.4	balance

* low nitrogen
** high nitrogen

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Tables VI and VII lists the corrosion rates of alloys E1 through E24 under various conditions.

TABLE VI CORROSION RATES OF TEST ALLOYS IN H ₂ SO ₄								
Alloy	70% 100°C	90% 100°C	90% 130°C	98% 160°C	98% 200°C	98% 250°C	98.5% 200°C	99% 250°C
E1	3460	9	132	17	6.2		9.3	8.4
E2	2000	1	96	23	5		13	6.2
E3	200	0.6	94	24	2.6		8.6	4.7
E4	1160	0.7	5	14	1.1		9.2	5.1
E5		0.6		14	11	11	7.9	6.6
E6	650	0.4	6	8.8	0.1		11	6.7
E7		5.9		9.2	0.6	4.9	2.3	3.9
E8		0.64		0.5	0.2	0.8	0.3	0.1
E9	3300	26	91	6.6	12	8.4	10	5.5
E10	50	0.08		8.1	23.5		17	6.4
E11	33	0.58		3.56			9.7	6.9
E12		48		13	7.3		14	5.9
E13		19		18	7.6		12	8.8
E14		26		22	10		11	4.5
E15	2070	29		18	7		7	6
E16	75	0.73	14.5	27	1.9		19	7.6
E17		1.1		22				
E18		19.5		25	12		3	
E19		30.5		12	6.3		3.6	
E20		1.5		12			12	12
E21		0.95		13			12	12
E22	1180	5.8	77	13			12	7.2
E23		11		13	1.6	2.9		
E24		0.65		0.07	5.4	1.1		

Alloy E10 was exposed to various concentrations of sulfuric acid at various temperatures and the corrosion rate was measured. Figure 2 is a plot showing the temperatures at which the corrosion rate is 5 mils per year as a function of acid concentration. The curve labelled **A** pertains to alloy E10 of table V. For comparison purposes, the curve labelled **B** is for A611 stainless steel alloy and, the curve labelled **C** is for SANDVIK™ SX stainless steel alloy. The curve labelled **D** is the boiling temperature of sulfuric acid at 1 atmosphere pressure.

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TABLE VII CORROSION RATES OF TEST ALLOYS IN OLEUM			
Alloy	101% 160°C	105.12% 100°C	105% 70°C
E1	1.55	7.83	0.70
E2	2.81	8.95	1.42
E3	23.0	7.7	0.73
E4	2.1	13.0	0.68
E5	1.87	6.97	0.44
E6	1.99	25.5	1.73
E7		6.48	
E8		105	
E9	1.95	7.84	0.70
E10	2.06	7.5	
E11	2.26	14.4	
E12	2.05	9.4	
E13	1.27	5.18	
E14		5.99	
E15		8.23	
E16	5.72	10.0	1.18
E18		6.50	
E19	6.04	7.68	
E20	1.74	14.7	
E21	1.48	14.1	
E22	1.79	10.3	0.73

Figures 3A through 3D are histograms which compare the corrosion rate of alloys according to the invention to the corrosion rates of various commercially available alloys under the same conditions. Figure 3A is for alloy E10 in 90% sulfuric acid at 100°C. Figure 3B is for alloys E8 and E24 in 98% sulfuric acid at 160°C. Figure 3C is for alloy E13 in 105% sulfuric acid at 100°C. Figure 3D is for alloy E5 in 105% sulfuric acid at 70°C.

Example 3

Table VIII lists other alloys according to various embodiments of the invention.

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Table VIII: Nominal Composition of Example Alloys (wt.%)									
Alloy	Cr	Si	Mo	Cu	W	V	C	Ni	Fe.
P1	22	6.5	0	3	0	0	<0.05	20	Bal.
P2	22	6.5	6	0	0	0	<0.05	20	Bal.
P3	22	6.5	0	0	4	0	<0.05	20	Bal.
P4	22	6.5	0	0	0	4	<0.05	20	Bal.
P5	28	7.5	0	3	0	0	<0.05	26	Bal.
P6	28	7.5	4	2	0	0	<0.05	26	Bal.
P7	28	7.5	0.5	0.5	2	2	<0.05	26	Bal.
P8	33	9.5	0.5	0.5	2	2	<0.05	35	Bal.
P9	33	9.5	0	0	0	0	<0.05	35	Bal.
P10	33	7.5	0.5	3	0	0	<0.05	35	Bal.
P11	25	6.9	0.5	3	0	0	<0.05	30	Bal.
P12	23	6.8		0	0	0	<0.05	24	Bal.
P13	23	6.5	0	2.5	0	0		22	Bal.

Example 4

Table IX shows measured corrosion rates in sulphuric acid at various concentrations and temperatures, for the stainless steel alloys, 1815LCSI, (hereafter called 1915), 310, and Alloy 33 with added silicon.

Table IX								
H ₂ SO ₄ Concentration and Temperature				70.0% 100C	90.0% 100C	90.0% 130C	90.0% 160C	98.0% 320C
Alloy Code	Composition, bal Fe			Corrosion Rate, mpy				
	%Si	%Cr	%Ni					
1815	4.35	18.25	15.4	10665.6	579.0	54873.8	216800.0	45.2
1815-2	6.35	18.25	15.4	24356.4		349.6	40280.0	10.7
1815-4	8.35	18.25	15.4	2516.6	62.6	145.4	16750.0	18.5
1815-6	10.4	18.25	15.4	1820.6	27.7	39.6	92.0	4.3
1815-8	12.4	18.25	15.4	293.9	0.1	6.3	4.0	0.7
310	0.54	24.0	19.14		228.0	142770		4406
310-A3	6.54	24.0	19.14	3459.90	6.6	110.9	300.7	14.7
310-J	8.54	24.0	19.14	341.10	5.9	52.8	132.0	6.8
310-K	10.54	24.0	19.14	66.40	0.6	4.1	9.5	1.2
33	0.3	32.75	31.35		2796.0	12447		176.5

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33-Z3	6.3	32.75	31.35	1181.10	2.5	83.8	222.3	14.3
33-Y	8.3	32.75	31.35	425.80	10.9	45.3	92.0	7.9
33-X	10.3	32.75	31.35	36.60	0.6	31.3	1.5	0.7

5 It can be seen that at 70% H₂SO₄ at 100C, the corrosion rate is very high for the 1815 alloy, and the silicon would have to be carried above 12% to reduce the corrosion rate to acceptable levels. The 310 and Alloy 33 bases with added silicon again show that the levels would have to be carried above 10% Si to reduce corrosion to acceptable levels.

10 However, in 90.0% H₂SO₄ and as hot as 160C and 90% H₂SO₄ as hot as 320C it can be seen that silicon has a beneficial effect at levels of 10% and even lower for the higher chromium alloy.

Figure 4 is a histogram showing the corrosion rate of stainless steel alloys, 1815, 310, and Alloy 33, in 90.0% H₂SO₄ at 160C with added silicon. It can be seen that the added silicon has a beneficial effect on corrosion rates in all alloy bases.

15 Example 5

Table X, shows the corrosion rate in sulphuric acid on high silicon and chromium stainless steel alloys bearing copper, with additional Ni, Ce and Nb. The Ce and Nb are normally added to highly alloyed stainless steels for grain refinement and deoxidation, while the Ni is added to stabilize the austenite phase in the microstructure. It can be seen that

20 these elements have only a minor effect on corrosion resistance.

Table X								
H ₂ SO ₄ Concentration and Temperature, C							90.0% at 160C	98.0% at 320C
Alloy Code	Composition, Balance Fe						Corrosion Rate, mpy	
	%Si	%Cr	%Ni	%Cu	%Ce	%Nb		
F9064	9.3	23.0	26.0	2.8			56.5	4490
F9064-A	9.3	23.0	31.0	2.8	0.1		97.1	7.3
F9104	6.9	28.0	32.0	3.2				
F9104-A	6.9	28.0	32.0	3.2	0.1		218.4	19.1
30 F9104-B	8.4	28.0	32.0	3.2	0.1		114.2	9.0
F9104-C	6.9	28.0	32.0	3.2	0.1	2.0	214.0	14.9
F9104-D	8.4	28.0	32.0	3.2	0.1	2.0	105.0	11.8

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Example 6

Hardness measurements in Rockwell C were done. They are marked in numbers in square brackets in Table XI. Those which are marked 'Brittle, break in test' were in sections from 3 to 5 mm thick, they fractured under the test load. Generally, for Si levels about 6%, the thin sample sections fractured under the test load. Alloy 33 base and the Ni base, D205 were thick enough to obtain measurements at 8 and 10% Si respectively. They are in the same range of hardness as silicon iron. The samples were tested in "as cast" condition.

10

15

20

Table XI						
Base Alloy	4% Si	6% Si	8% Si	10% Si	12% Si	14% Si
SiFe						[44,44]
1815LCSI	[19, 15.8]	[60, 60]	Brittle, Breaks in hardness test	Brittle, Breaks in hardness test	Brittle Breaks during sectioning	
310 7.5, 4.8			Brittle, Breaks in hardness test	Brittle Breaks during sectioning		
Alloy 33 16, 13		[40, 39]	Brittle One sample broke during polishing [47.5, 51]	Brittle Very glass like, breaks with sharp edges		
Hast, D205 96, 93.5, 95 Ni Base		There is 5% Si in base alloy		Has not broken during sample preparation [54, 53.5, 53.5]		

25

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Example 7

Table XII further demonstrates the beneficial effect of further additions of Ni, Nb and C, in that alloy F9064, which has 9.3% Si and cracked during casting, although still hard, is now only moderately harder than silicon iron. Annealed samples were solution
 5 annealed at 1150 C for 2 hours followed by a water quench. It can be seen that annealing makes the alloys more ductile. Internal oxidation may have reduced the effectiveness of the annealing on some higher silicon alloys.

Table XII				
Alloy Description	#1	#2	Rockwell C Average	Elcometer Ferrite No.
F9064 + 5Ni + 2Nb + 0.1 Ce	57.5	58.0	57.8	0
Above annealed, but cracked during annealing				21
F9104 + 0.1Ce	39.5	38.9	39.2	0
Above annealed	30.5	30.0	30.3	0
15 F9104 + 1.5Si + 0.1Ce	56.0	58.0	57.0	0
Above annealed, but cracked during annealing				2
F9104 + 2Nb + 0.1Ce	42.5	42.5	42.5	0
Above annealed	32.0	32.5	32.3	0
F9104 + 1.5Si + 2Nb + 0.1Ce	Brittle, chips in test			0
20 Above annealed, but cracked during annealing, chips in test				3
310 + 6Si + 5Ni + 3Cu + 0.2Ta	30.0	28.5	29.3	1
Above annealed	19.0	21.0	20.0	8

Example 8

25 Figure 5 is a histogram showing the corrosion rate of stainless steel alloys 1815, 310 and Alloy 33, in 90.0% H₂SO₄ at 160C, with 6.3-6.5% added silicon, plotted against the chromium level in the base alloys at 3 temperature levels. It can be seen that increasing chromium decreases corrosion rates at lower temperatures with this level of silicon.

Example 9

30 Figure 6 is a histogram showing the corrosion rate of 1815, 310 and Alloy 33, in 90.0% H₂SO₄ at 160C, with 6 and 10% added silicon, showing the effect of chromium in the base alloy. The beneficial effect of chromium is apparent at higher silicon levels.

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Example 10

Figure 7 is a histogram showing the corrosion rate of stainless steel alloys, 1815, 310 and Alloy 33 with added silicon in 98.0% H₂SO₄ at 320C, plotted against %Si. The beneficial effect of silicon is shown with acceptable corrosion rates at the 10% level.

5 Example 11

Figure 8 is a histogram showing the corrosion rates of stainless steel alloys 1815, 310 and Alloy 33 with 6.5% Si and with 10% Si in 98.0% H₂SO₄ at 320C, plotted against the chromium content of the base alloy. It can be seen that the chromium is beneficial when the silicon content is about 10% or higher. Silicon must be at 10%. This shows that
10 for best corrosion resistance the ratio of Cr/Si should be controlled..

Applications

The inventors consider that the alloys of this invention have particular application when used for acid contacting components in sulfuric acid plants. Such components include
15 heat exchangers, pipes, absorption towers, pumps, and the like. The alloys have particular application in handling sulfuric acid having concentrations in the range of 85% sulfuric acid to 40% oleum in plants which use the contact process to manufacture sulfuric acids. The alloys are also especially useful in situations where they are used in contact with acid having a concentration in the range of 90% to 98% at temperatures in excess of 130°C. For
20 example, the alloys may be used to make vessels for concentrating sulfuric acid by boiling off water at 180°C.

The alloys of this invention may also be formed into and used as an acid-contacting component in a heat exchanger wherein one surface of the component is in contact with concentrated sulfuric acid and another surface of the component is in contact with
25 concentrated phosphoric acid.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the following claims.

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We claim:

1. A weldable alloy comprising at least 22% chromium and at least 6% silicon and having a tensile elongation in excess of 40%.
- 5 2. The alloy of claim 1 comprising 20% or more nickel.
3. The alloy of claim 1 wherein the relative amounts of silicon and chromium are expressed by the formula:

$$W_{\text{Si}} = (0.33 \pm 0.06) \times W_{\text{Cr}}$$
10 where W_{Si} is the percentage of silicon and W_{Cr} is the percentage of chromium.
4. The alloy of claim 1 wherein the ratio of silicon to chromium is in the range of 0.25 to 0.36.
- 15 5. The alloy of any one of the above comprising 0.2% to 4% copper.
6. The alloy of claim 5 comprising 2% to 4% copper.
7. The alloy of any one of the above claims comprising 0.2% to 5% molybdenum with
20 the combined amount of copper and molybdenum not exceeding about 6% .
8. The alloy of any one of the above claims comprising 0.05% to 0.5% nitrogen .
9. The alloy of any one of the above claims comprising 2% to 4% tungsten.
- 25 10. The alloy of any one of the above claims comprising 2% to 4% vanadium .
11. The alloy of any of the above claims characterized by a duplex structure containing a mixture of ferrite and austenite upon heat treatment at a temperature in the range
30 of 1100°C to 1200°C.

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12. The alloy of claim 9 wherein the structure consists of about 24% by volume to about 30% by volume ferrite and the balance austenite.
13. The alloy of one of claims 10 and 11 wherein the concentration of silicon in the austenite phase is substantially the same as the concentration of silicon in the ferrite phase and the concentration of chromium in the austenite phase is substantially the same as the concentration of chromium in the ferrite phase.
14. An acid contacting component in a plant for manufacturing concentrated sulfuric acid by the contact process, the component having an acid-contacting surface made from the alloy of any one of the above claims.
15. The use of the alloy of any one of claims 1 through 13, as an acid-contacting component in a heat exchanger in a process for recovering heat from acid having a concentration in excess of 95% and temperature in excess of 130°C.
16. The use of the alloy of any one of claims 1 through 13, as an acid-contacting component in a heat exchanger wherein one surface of the component is in contact with concentrated sulfuric acid and another face of the component is in contact with concentrated phosphoric acid.
17. An alloy comprising
22% to 36% chromium,
6% to 10% silicon,
0.5 to 6% of an alloying element selected from the group consisting of up to 4% copper, molybdenum, and a mixture of up to 4% copper and molybdenum;
0.05 to 0.45% nitrogen; and,
the balance iron and nickel.
18. The alloy of claim 17 comprising molybdenum in an amount of less than 5% .

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19. The alloy of any one of claims 17 or 18 comprising chromium in an amount greater than 23% .
20. The alloy of claim 19 wherein the relative amounts of silicon and chromium are expressed by the formula:
5 $W_{\text{Si}} = (0.33 \pm .06) \times W_{\text{Cr}}$
where W_{Si} is the percentage of silicon and W_{Cr} is the percentage of chromium.
21. The alloy of claim 19 wherein the ratio of silicon to chromium is in the range of
10 0.25 to 0.35.
22. The alloy of any one of claims 17, 18 or 19 comprising approximately 6.6% silicon and approximately 23% chromium.
- 15 23. The alloy of any one of claims 17, 18, 19, 20 or 21 comprising 0.2% to 0.4% nitrogen.
24. The alloy of any one of claims 17, 18, 19, 20, 21, 22, or 23 comprising 2% to 4% tungsten.
20
25. The alloy of any one of claims 17, 18, 19, 20, 21, 22, 23, or 24 comprising 2% to 4% vanadium.
26. The alloy of claim 17 comprising copper in an amount of less than 4%.
25
27. A stainless steel alloy consisting essentially of:
25% chromium;
6.5% silicon;
25% nickel; and,
30 the balance iron.
28. A stainless steel alloy consisting essentially of:

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22% to 36% chromium;

6% to 8% silicon;

18% to 32% nickel;

0% to 4% copper; and,

5 the balance iron.

29. A method for making a workable metallic alloy which is resistant to corrosion by sulfuric acid, the method comprising:

- 10 a) alloying at least 22% chromium, at least 6% silicon, at least 20% nickel, up to 4% copper, and iron; and,
- b) heat treating the resulting alloy at a temperature sufficient to cause the alloy to become ductile and to have a duplex structure consisting of a mixture of ferrite and austenite.

15 30. The method of claim 29 wherein the heat treating is performed at a temperature in the range of 1100°C to 1200°C.

20 31. The method of claim 29 or 30 wherein, after heat treatment the alloy has a duplex microstructure characterized by 24% to 30% by volume ferrite and the balance austenite.

32. A heat-treatable duplex stainless steel alloy comprising 8 to 12% by weight of silicon.

25 33. The alloy of claim 32 comprising 16 to 35% by weight of chromium.

34. The alloy claims 32 or 33 wherein the relative amounts by weight of silicon and chromium are expressed by the formula $W_{si} \geq (0.33 \pm 0.06) \times W_{cr}$ wherein W_{si} is the percentage of silicon and W_{cr} is the percentage of chromium.

30

35. The alloy of claim 32 wherein the ratio by weight of silicon to chromium is in the range of 0.2 to 0.7.

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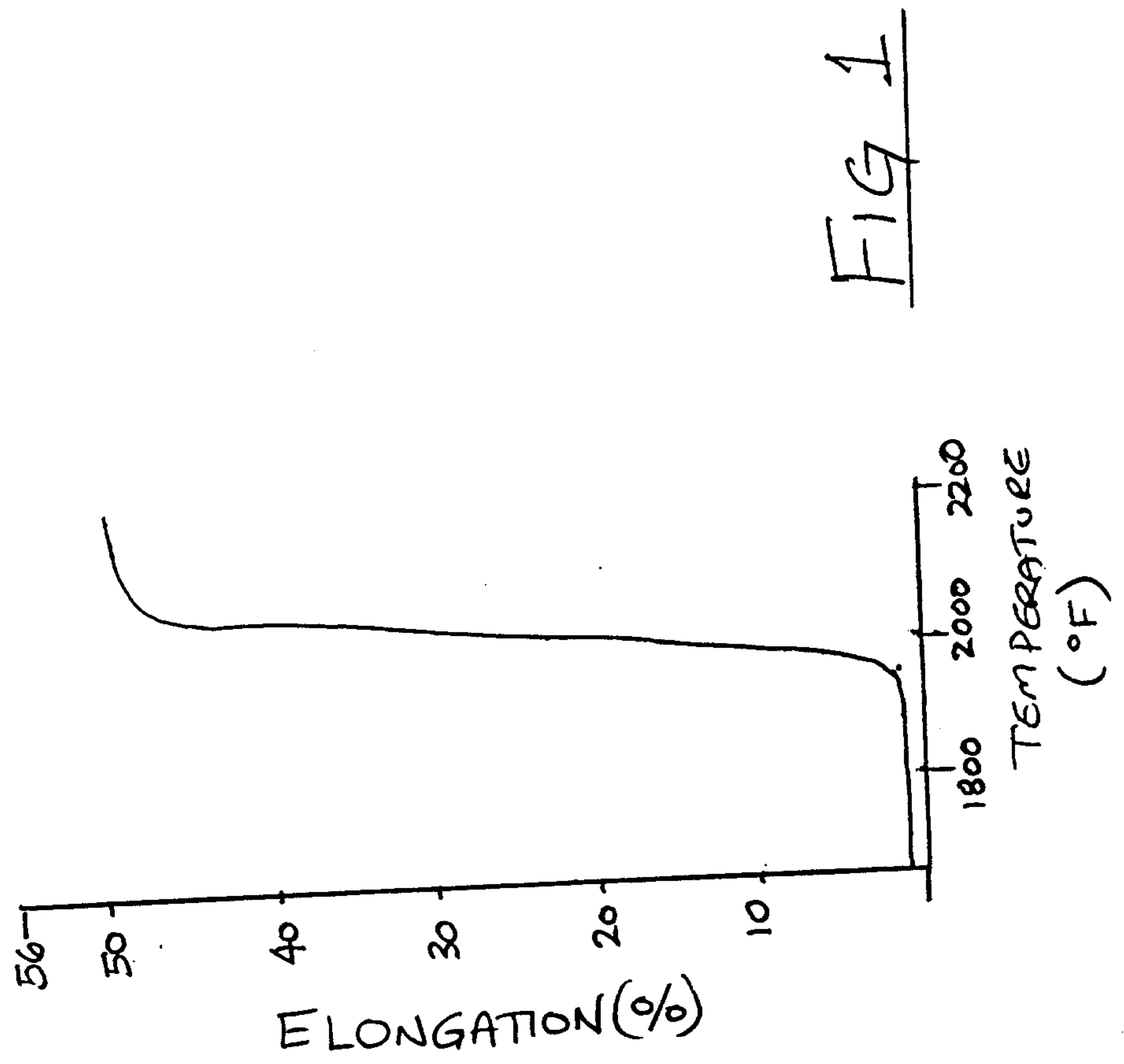
36. The alloy of any one of claims 32-36 comprising 1 to 2% by weight of copper.
37. The alloy of any of claims 32-36 wherein the structure consists of at least 15% by volume of ferrite phase and the balance austenite phase.
- 5 38. An alloy comprising
16 to 35% chromium
8 to 12% silicon
0.5 to 6% of an alloying element selected from the group consisting of up to 4%
10 copper, molybdenum, and a mixture of up to 4% copper and molybdenum;
0.05% to 0.45% nitrogen; and
deoxidizing alloys, grain modifiers and minor additions; and
the balance iron and nickel.
- 15 39. The alloy of claim 38 comprising chromium in an amount greater than 16% by weight.
40. An alloy of claim 39 wherein the relative amounts of silicon and chromium are expressed by the formula: $W_{si} \geq (0.33 \pm 0.06) \times W_{cr}$ wherein W_{si} is the percentage
20 of silicon and W_{cr} is the percentage of chromium.
41. The alloy of claim 40 wherein the ratio of silicon to chromium is in the range of 0.2 to 0.7.
- 25 42. The alloy of any one of claims 38-41 comprising approximately 10% by weight of silicon and approximately 20% by weight percentage of chromium.
43. A stainless steel alloy consisting essentially of:
20% chromium;
30 10% silicon;
20% nickel; and

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less than 10% of one or more of copper, molybdenum, tungsten, vanadium, cerium, niobium, titanium, zirconium, tantalum, palladium and aluminum; and the balance iron.

- 5 44. A stainless steel alloy consisting essentially of:
 22 to 36% chromium;
 6 to 8% silicon;
 18 to 32% nickel;
 0 to 4% copper; and
10 the balance iron.
45. The alloy of claim 43 or 44 wherein, after heat treatment, the alloy has a duplex microstructure characterized by at least 15% by volume of ferrite phase and the balance austenite phase.

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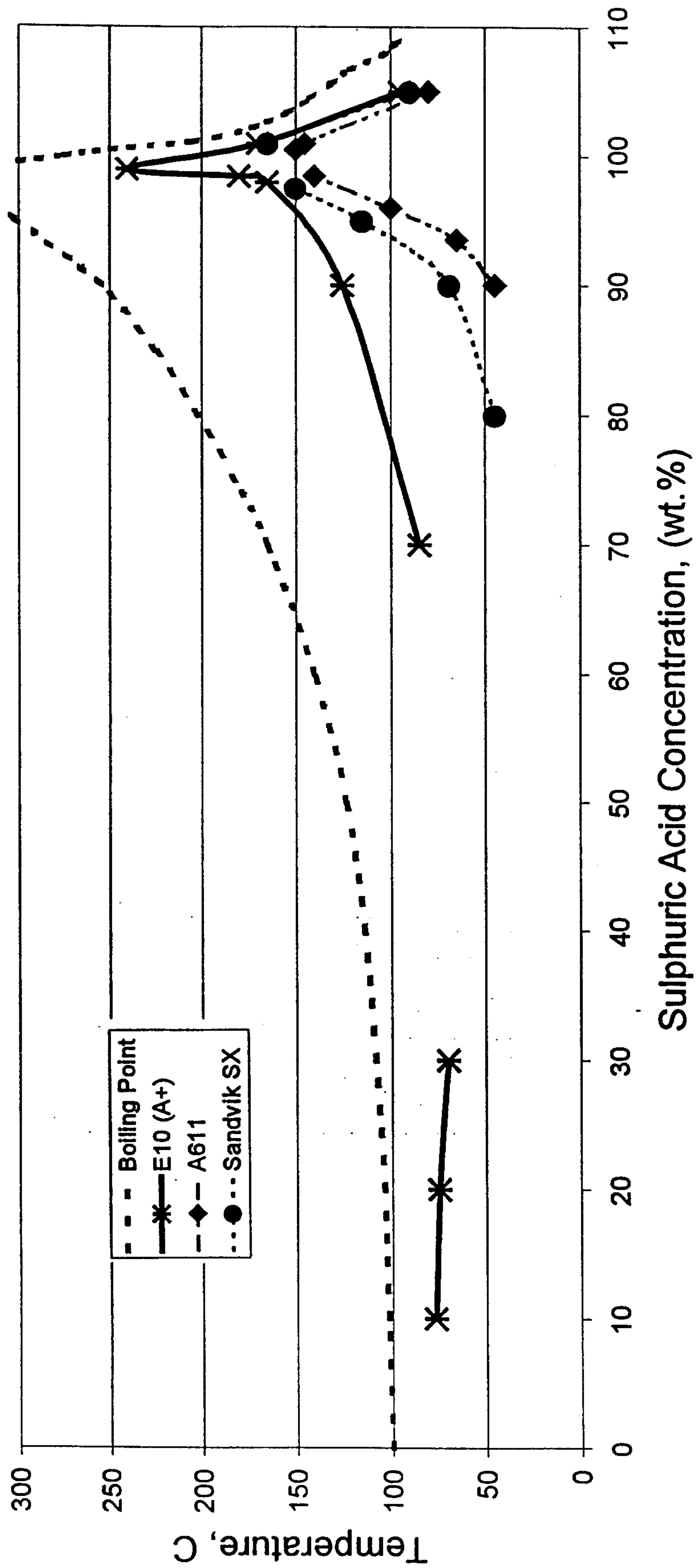


Fig. 2

E10
Sandvik SX
Hastelloy D205
Lewmet 66
Carpenter 20 Cb-3
Hastelloy D
Alloy 59
A611
Haynes 25
Haynes 230
Hastelloy C-276
Alloy 33
645SMO
Zeron 100
RA 85H
2509-7Si

A B C D E F G H I J K L M N O P

FIG. 3A

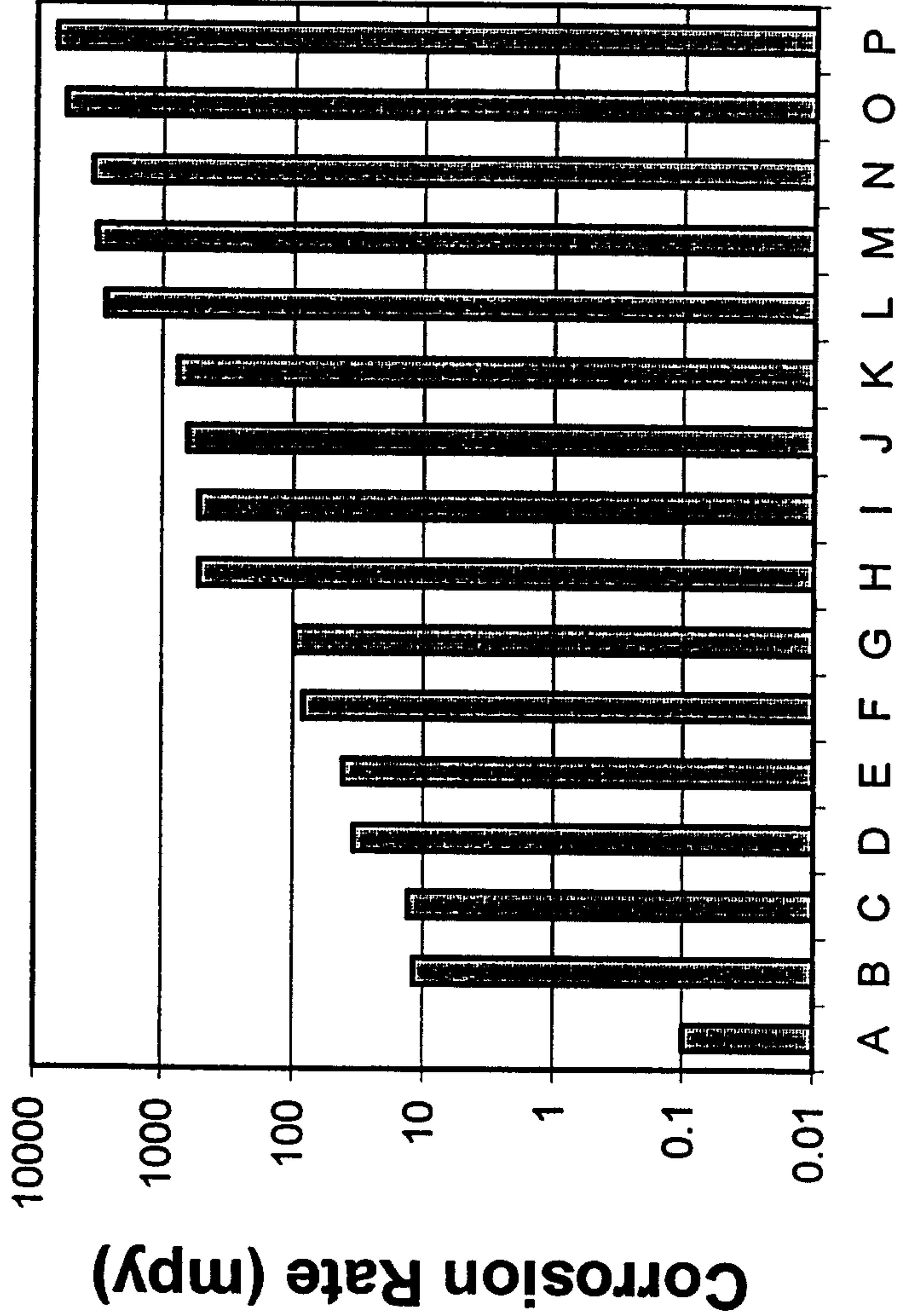


Fig. 3B

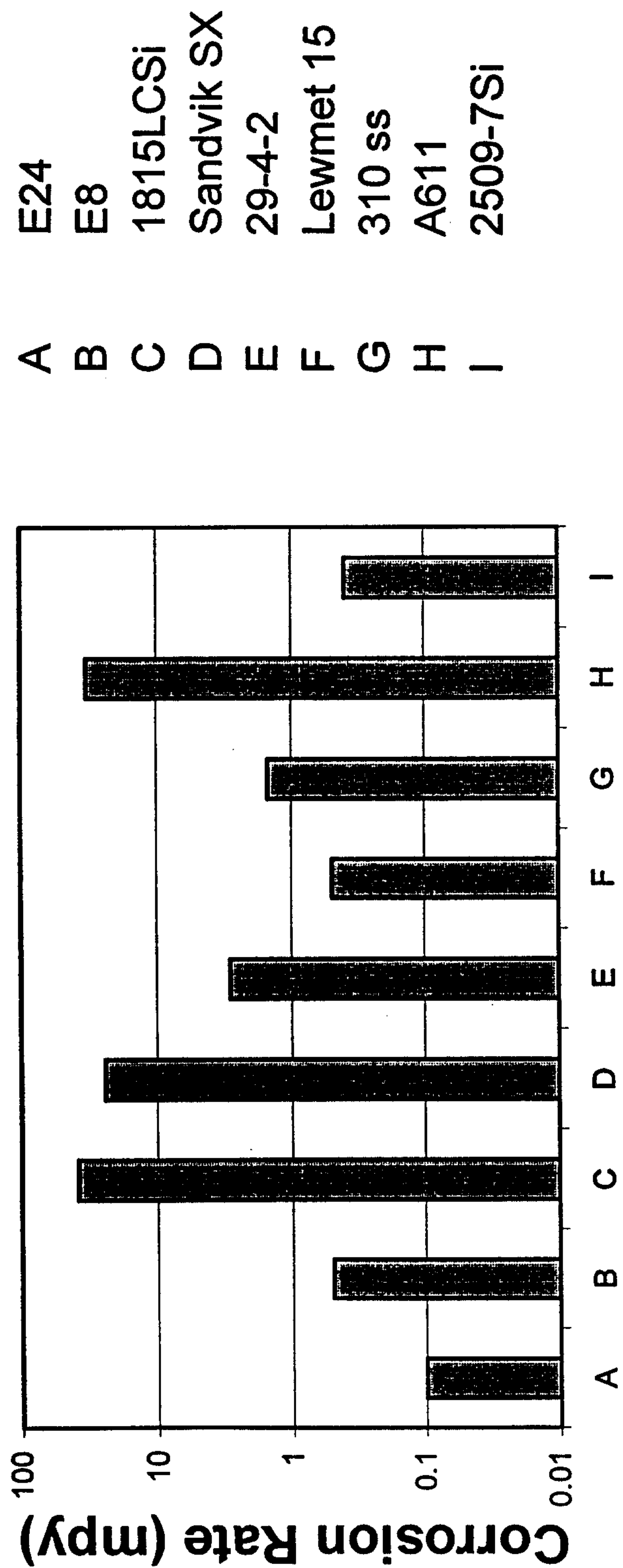


Fig. 3C

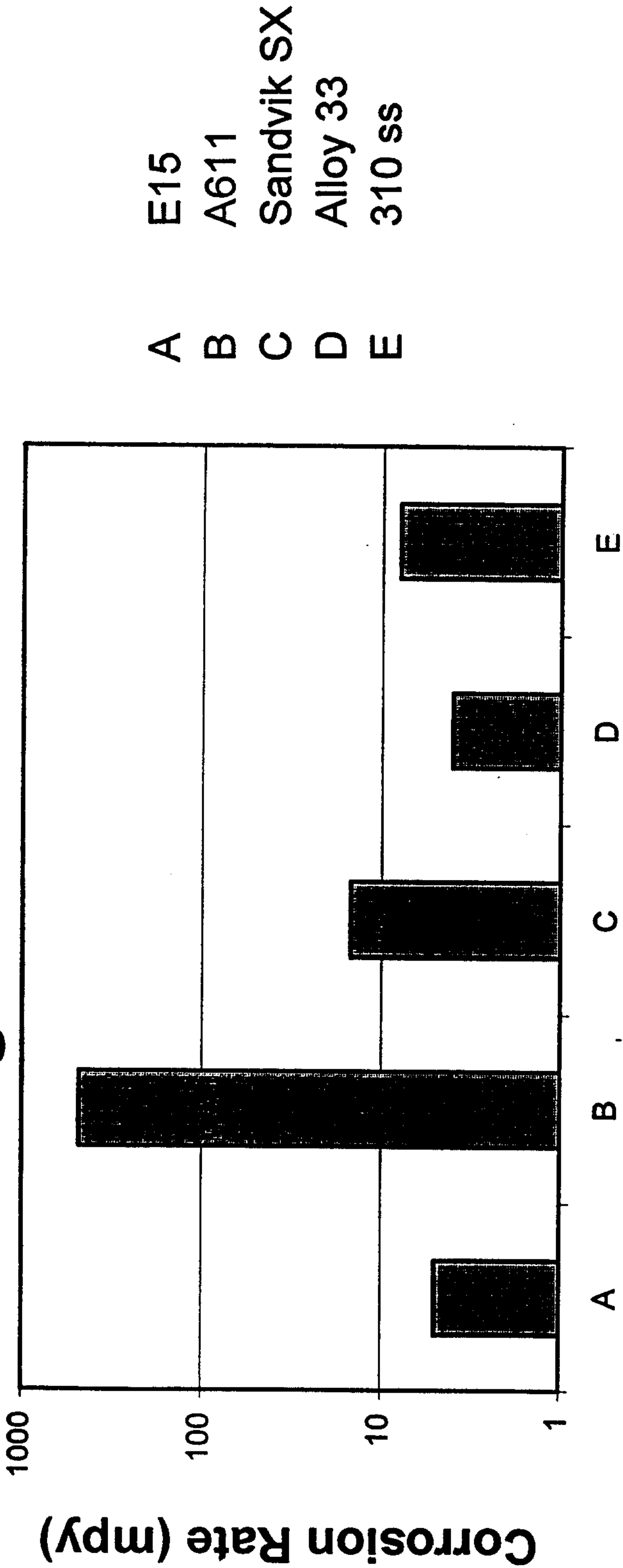
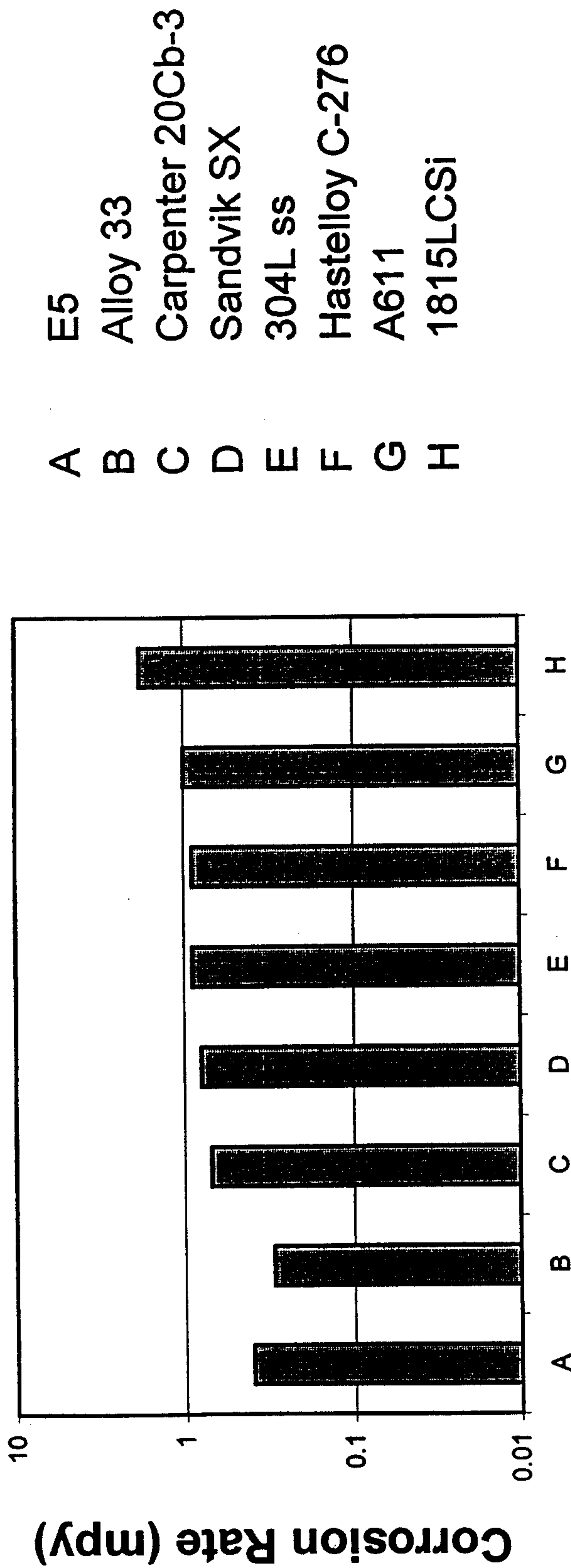


Fig. 3D



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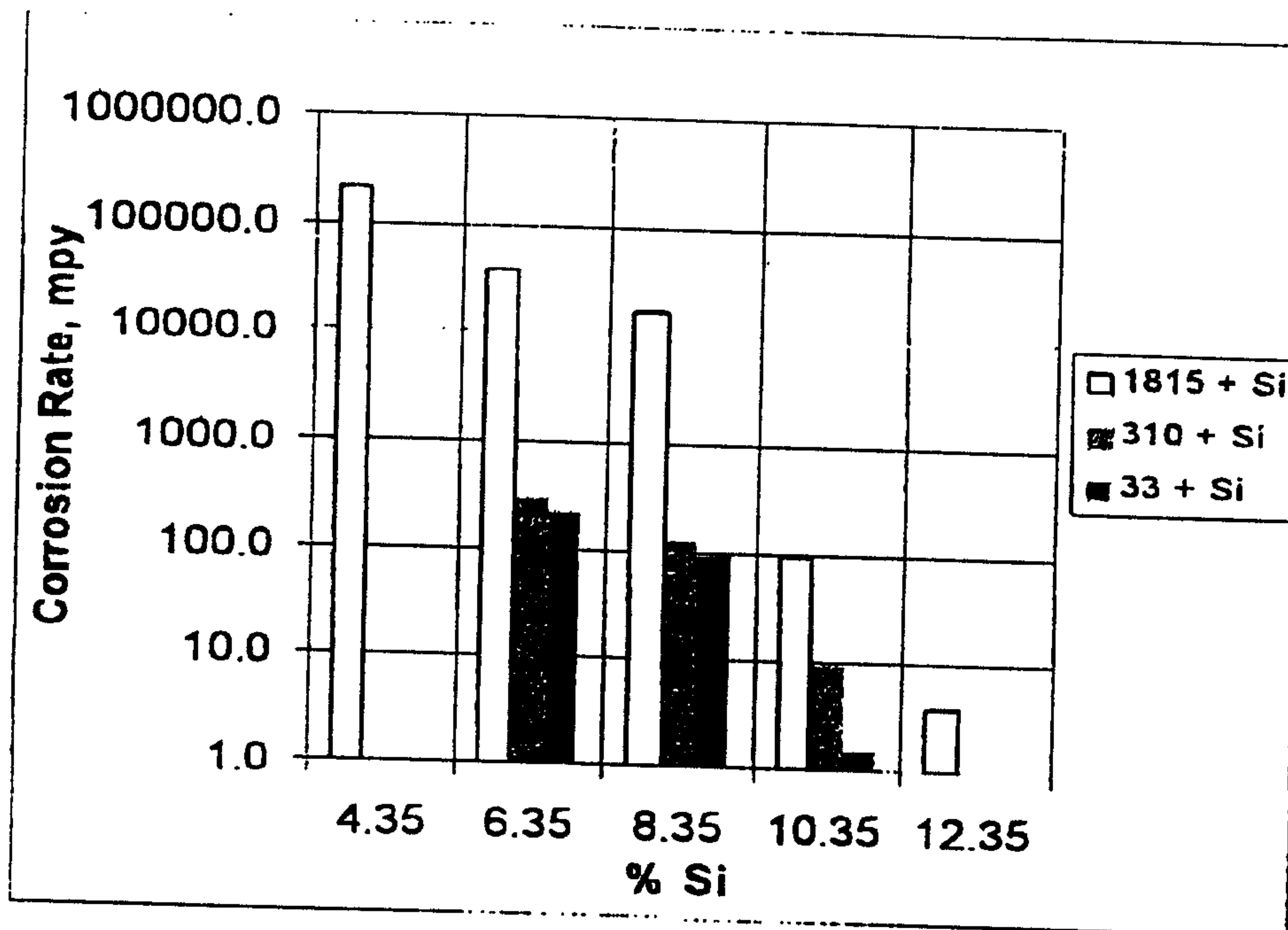


Fig. 4

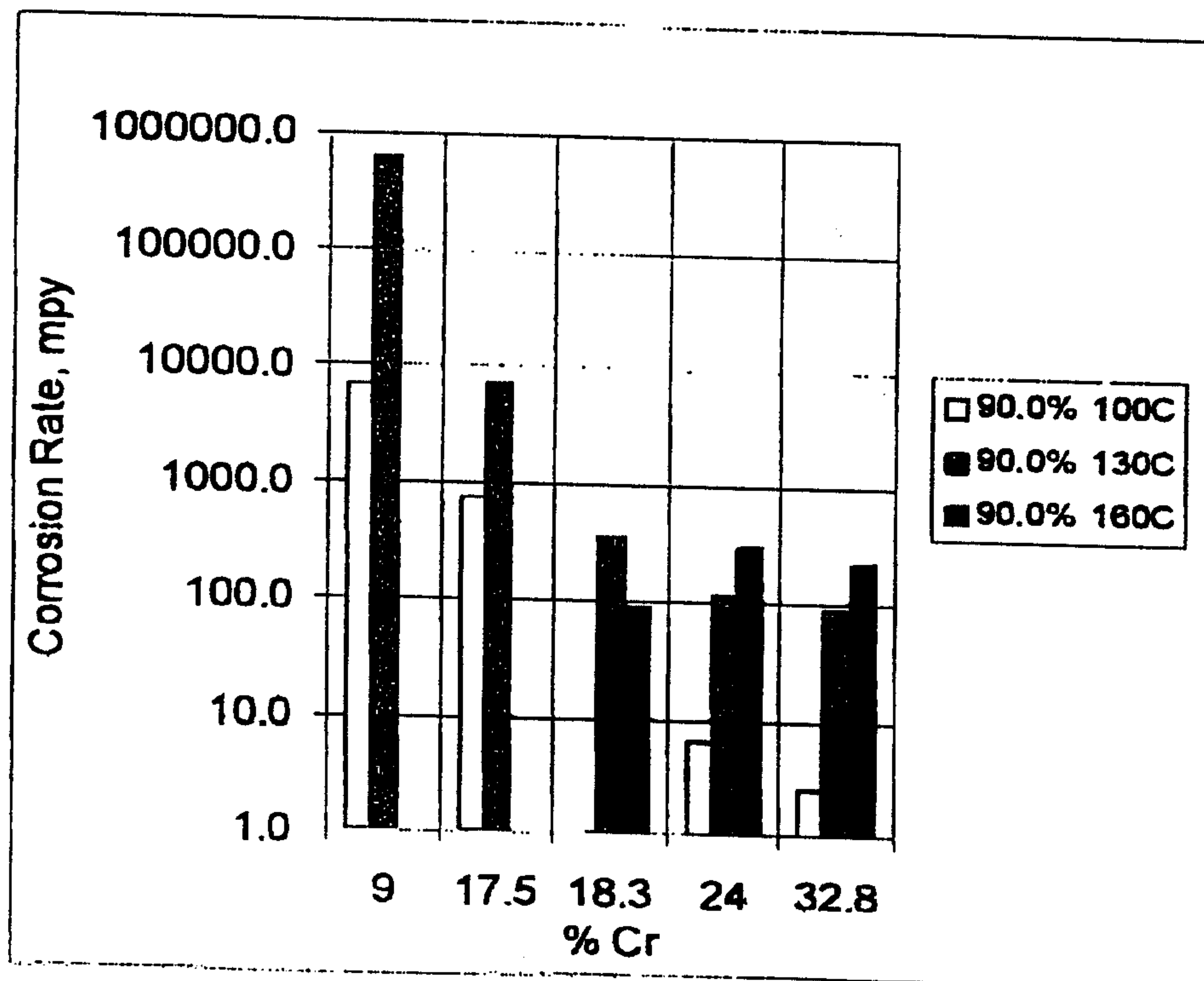


Fig. 5

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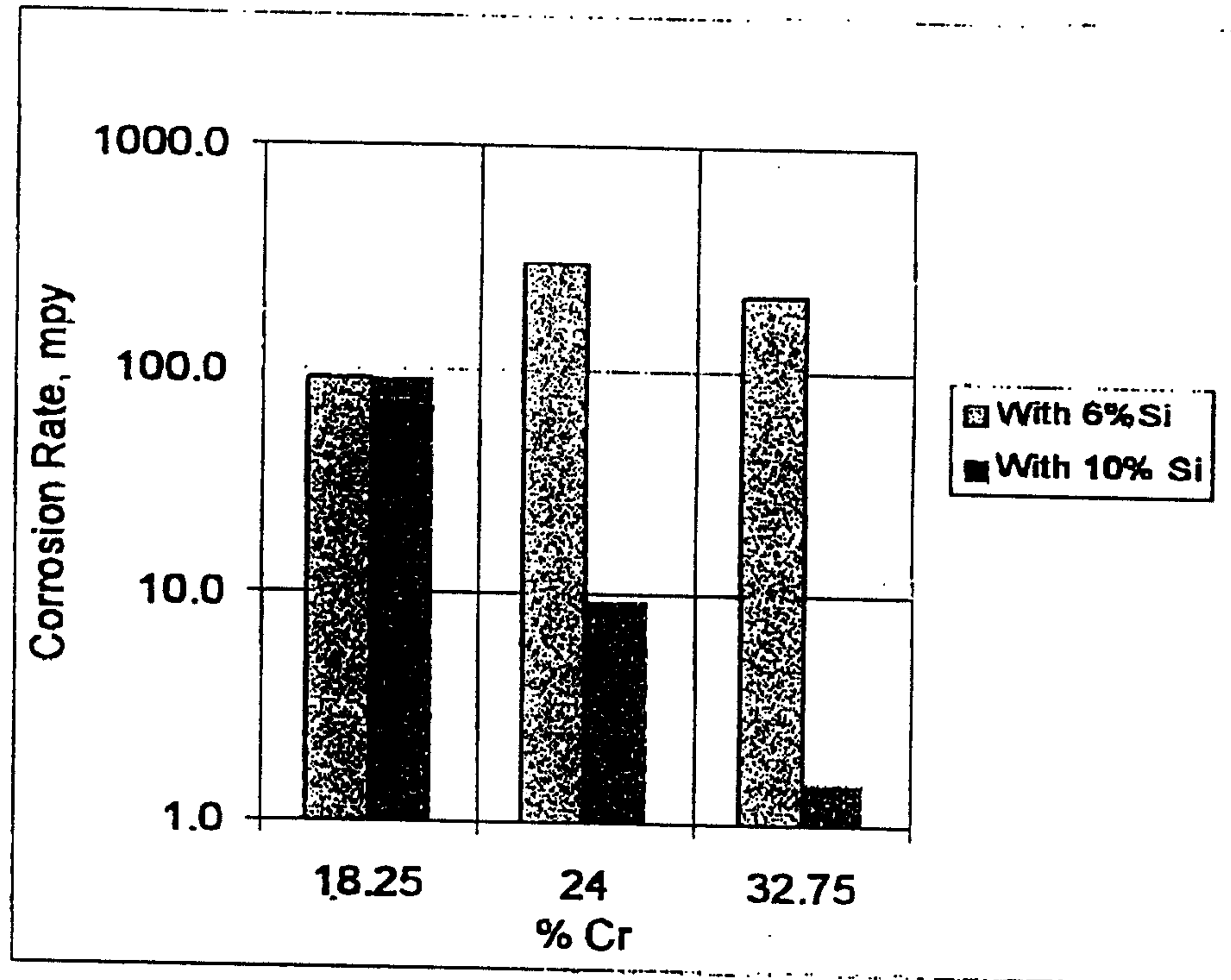


Fig. 6

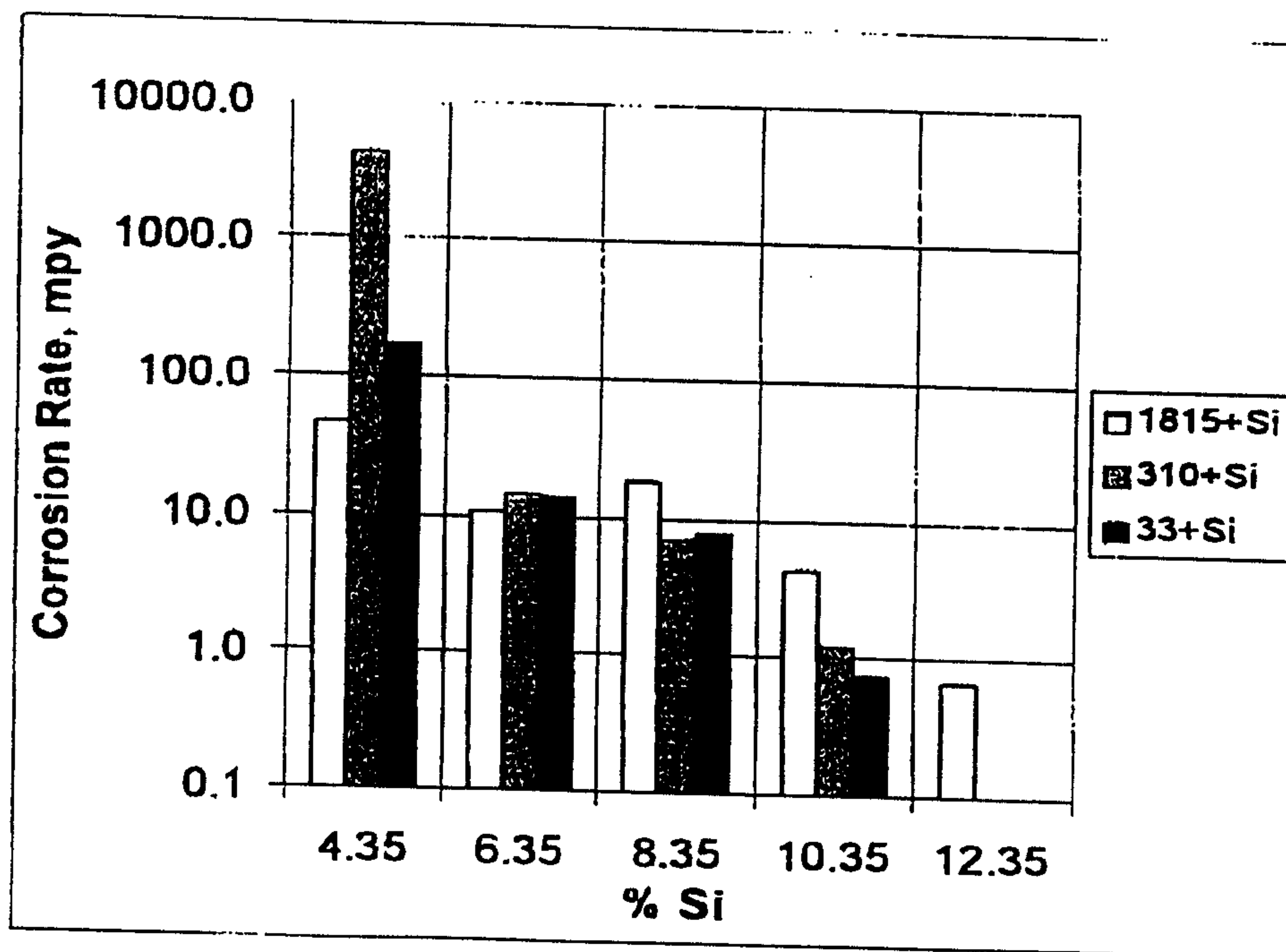
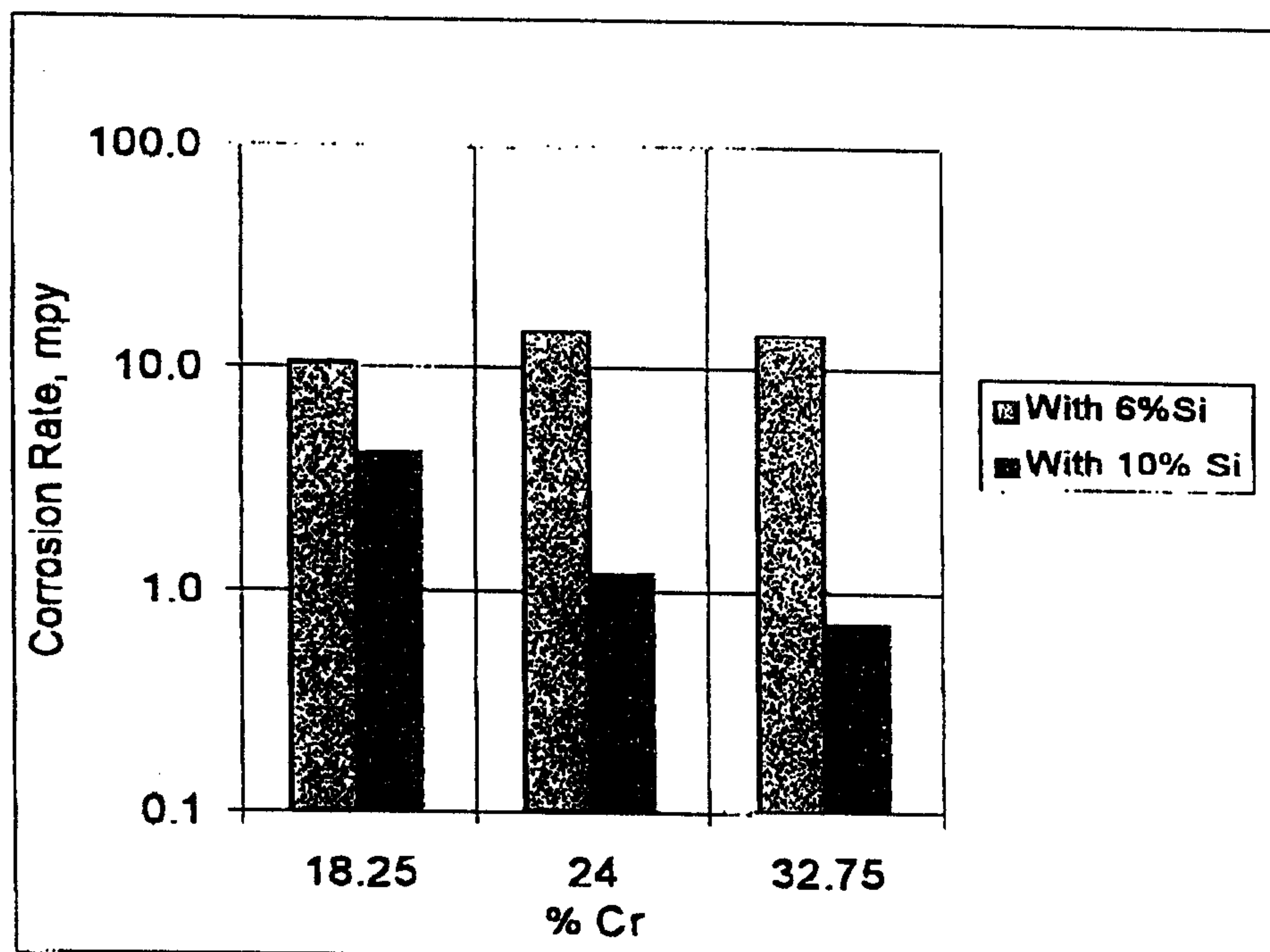


Fig. 7

**Fig. 8**

