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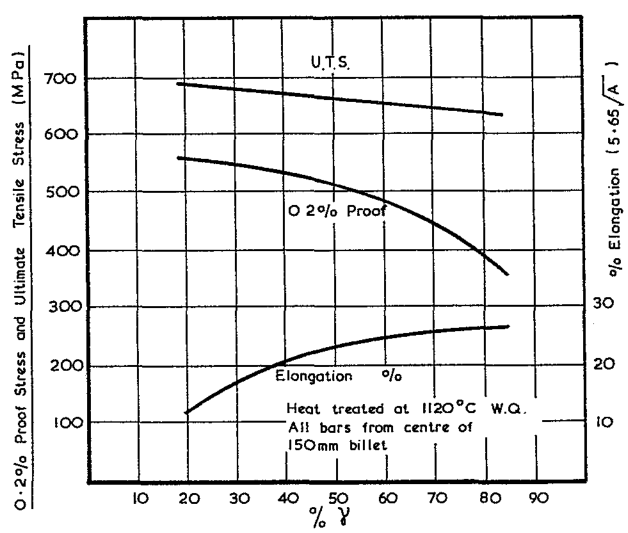
(54) Stainless steel alloy.

(57) A stainless steel alloy has the following composition

	Wt. %
Chromium	23.0 - 26.0
Nickel	5.0 - 8.0
Manganese	3.5 - 5.0
Silicon	max 1.5
Molybdenum	1.75- 3.0
Carbon	max 0.06
Nitrogen	0.15- 0.30
Alloying additions	0- 2.5
Iron & impurities	balance,

The alloy has a duplex microstructure of austentie and ferrite and has good corrosion resistance.



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STAINLESS STEEL ALLOY

The present invention relates to stainless steel alloys.

Duplex stainless steel alloys of the ferritic austenitic type have been developed over recent years for their combination of mechanical properties, high resistance to localized corrosion and their resistance to stress corrosion cracking in a sea-water environment. Such steels are described for example in U.K. Patent No. 1,158,614 and U.S. Patent No. 3,065,119 and are available under the designations CD4MCu and Ferralium.

A typical composition of such an alloy is as follows:

TABLE I

	% by weight
Chromium	23.5-25.0
Nickel	5.0- 8.0
Molybdenum	1.75-3.0
Silicon	max 1.5
Manganese	max 1.5
Carbon	0.02-0.05
Nitrogen	0.05-0.15
Iron	Balance (excluding unavoidable impurities).

The compositional levels of the elements promoting either austenite or ferrite in the micro-structure are controlled to produce a structure which is balanced and which contains a minimum of

65% austenite. This microstructural control provides an alloy which has a good combination of toughness and corrosion resistance in thick section castings when adopting air cooling from solution heat treatment temperatures.

However austenite levels of 65% and above result in an overall reduction in tensile strength since the latter is sensitive to changes in the austenite/ferrite balance.

There is a need for stainless steel alloys which have an improved tensile strength as compared to the above alloys and which still have a good combination of toughness and corrosion resistance.

It is known that the addition of carbon and nitrogen as interstitial solid solution strengthening elements is the most effective way of strengthening in both ferrite and austenite (see for example K.J. Irvine, et al, J. Iron Steel Inst. 1961, Vol 199, p 153 and K.J. Irvine et al, ibid, 1963, Vol 201, p 944).

However increased carbon in a stainless steel is undesirable as it has an adverse effect on corrosion resistance.

Nitrogen is used in amounts up to 0.5% in austenitic stainless steels of the A.I.S.I. 200 series to impart high strength levels. However the solubility of nitrogen in the conventional duplex 25 Cr/5Ni steels reaches a maximum of approximately

0.2% (J.F. Elliot et al Thermochemistry for Steelmaking, Vol II, Adison and Wesley Publishers, 1963). The inclusion of amounts of nitrogen in excess of 0.2% in the conventional duplex 25Cr/5Ni steels results in severe gassing problems in castings.

It is known that manganese additions are effective in several ferrous alloys in promoting nitrogen solubility. However manganese has been shown adversly to effect localised corrosion resistance in austenitic stainless steels (R.J. Brigham and E.W. Tozer, Corrosion N.A.C.E., Vol 30, No. 5, May 1974, p 161) and also to promote formation of the embrittling sigma phase.

It is also clear from the second K.J. Irvine et al reference quoted above that an increase in the austenite content in the microstructure will increase nitrogen solubility. However this results in a net decrease in mechanical properties arising from a loss of dispersion strengthening reflected in the sensitivity of the proof stress value with ferrite volume fraction at higher austenite contents.

It is an object of the present invention to provide a stainless steel alloy which has an improved combination of mechanical properties, resistance to localised corrosion, and resistance to stress corrosion cracking in a sea water environment than the conventional duplex alloys.

According to the present invention there is provided a stainless steel alloy having the following composition

	Wt. %
Chromium	23.0 - 26.0
Nickel	5.0 - 8.0
Manganese	3.5 - 5.0
Silicon	max 1.5
Molybdenum	1.75- 3.0
Carbon	max 0.06
Nitrogen	0.15- 0.30
Alloying additions	0- 2.5
Iron&impurities	balance,

said alloy having a duplex microstructure of austenite and ferrite.

Preferably the alloy is of the following composition

	Wt. %
Chromium	23.5 - 25.0
Nickel	5.0 - 6.5
Manganese	4.0 - 5.0
Silicon	1.0 max
Molybdenum	1.75- 3.0
Carbon	0.02- 0.06
Nitrogen	0.15- 0.3
Alloying additions	0- 2.5
Iron&impurities	balance,

Preferably the alloy has a microstructure comprising at least 60% and more preferably at least 65% austenite

The inclusion of 0.15 - 0.3 % N_2 in the alloy provides an increase in tensile and proof stresses as well as in localised corrosion performance. Amounts of nitrogen less than 0.15% do not give the required properties for the alloy whereas amounts greater than 0.3% cannot be obtained due to its limited solubility. Amounts of manganese less than 3.5% do not give the required N_2 solubility whereas amounts greater than 5.0 % lead to excessive formation of sigma phase.

The alloy may be prepared from a melt containing the various components in the required amount by casting of the melt and subsequent heat treatment in the manner known for the production of duplex alloys of the austenite ferrite type. The nitrogen for the alloy may be provided by high nitrogen ferrochrome.

The invention will be further described by way of example only with reference to the accompanying drawings, in which;

Fig. 1 is a graph showing the effect on Ultimate Tensile Stress, 0.2% Proof Stress and Elongation of increasing the austenite content of a conventional duplex stainless steel alloy of the ferritic,austenitic type;

Fig. 2 is a TTT curve illustrating the rate of formation of sigma phase in various alloys of differing manganese content;

Fig. 3 is a graph showing the effect on corrosion properties of increasing the manganese content of a stainless steel alloy at various fixed nitrogen contents; and

Fig. 4 shows the effect on corrosion properties of increasing the nitrogen content in a stainless steel alloy of fixed manganese content.

Fig. 1 illustrates the variation in Ultimate Tensile Stress (UTS), 0.2% Proof Stress (PS) and Elongation with increasing austenite content in a duplex alloy of nominally 25% Cr obtained by heat treatment at 1120°C with quenching. The variation in austenite content is obtained by varying the nickel content of the alloy.

It will be seen from Fig. 1 that the alloy with above 60% austenite content has a tensile strength of 650 MPa or less and a 0.2% Proof Strength of 490 MPa or less.

In order to improve the properties of the known alloy it was decided to investigate whether a level of manganese addition could be found which would aid nitrogen solubility without loss of toughness or corrosion performance thereby resulting in improved mechanical properties.

Initially a series of ferritic austenitic alloys were cast which contained nominally 25% Cr, 6-7% Ni, 2% Mo, 0.05% N_2, amounts of manganese from 1 to 15%, and a balance of iron plus unavoidable impurities.

A study was then made on the effects on microstructure, and tensile and hardness properties.

Additions of manganese up to 8% were found not to effect the austenite/ferrite phase balance. Proof stress and ultimate tensile strengths were found not to be affected up to a level of 12% Mn.

A progressive increase in hardness was recorded at manganese levels of 5% and above in the solution treated and air cooled condition and was attributable to hard, brittle sigma phase.

Fig. 2 illustrates this formation of sigma phase and is a Time Temperature Transformation curve showing the rate of sigma phase formation in a conventional duplex base alloy (nominally 25Cr/5Ni) (curve A), an alloy containing 3% Mn (curve B), and one containing 5% Mn (curve C). Superimposed on Fig. 2 is a continuous cooling path typical of the cooling rate 'seen' at the centre of a 6" diameter billet.

It will be seen from Fig. 2 that rate of formation of sigma phase increases with increasing manganese content, and above 5% Mn the ferritic microstructure at the centre of a 6" billet will transform partially or wholly to sigma phase upon cooling from the solution heat treatment temperature of 1100^{o}C.

By way of example, Fig. 2 also shows the TTT curve showing rate of formation of sigma phase in Uranus 50, a typical duplex stainless steel alloy with a 50/50 austenite/ferrite microstructure.

From the above discussion it will be appreciated that amounts of manganese of less than 5% should be used in the alloys of the invention to ensure that undesirable amounts of sigma phase are not formed.

In order to study the effect of manganese addition on nitrogen solubility, two series of duplex alloys (nominally 25Cr/5Ni) were prepared. One series of alloys contained a nominal 1% Mn and the other contained 4.5% Mn. The alloys of each series were prepared with nitrogen levels of between 0.2 and 0.35%.

On visual examination it was evident that the alloys containing 1% Mn had gassed severely once a level of 0.15 N_2 was exceeded, whereas the higher manganese alloys showed good soundness up to 0.3% N_2.

Tests were conducted to determine the effect of manganese and nitrogen additions on the critical crevice and pitting temperatures of the alloys.

Fig. 3 is a graph showing the relationship of increasing manganese content on the critical crevice and pitting temperatures in artificial seawater of two nominally 25Cr/5Ni duplex alloys, one containing 0.1% N_2 and the other 0.23% N_2. In Fig. 3, the solid curves represent pitting temperatures and the dashed lines represent crevice temperatures.

It will be seen from Fig. 3 that the alloy with the higher nitrogen content has the higher values of critical pitting tmmperature and critical crevice temperature; the alloy with 0.23% nitrogen maintains a critical pitting temperature of over 60°C up to a manganese addition of 5% and also shows a rise in critical crevice temperature for manganese additions of 3 to 4%.

Fig. 4 is a graph showing the relationship of increasing levels of nitrogen on the pitting and crevice temperatures of a series of duplex alloys (nominally 25Cr/5Ni) containing 4.5% Mn. The alloys were subjected to cyclic anodic polarisation measurement in artificial seawater to determine their localised corrosion performance.

It will be seen from Fig. 4 that increasing the nitrogen content to 0.3% improves the critical pitting and crevicing temperatures by more than 20°C as compared to an alloy containing only 0.1% N_2.

The inclusion of amounts of manganese of from 3.5 to 5% and amounts of nitrogen of from 0.15 to 0.3% in the alloys of the invention results in numerous advantageous tensile properties for the alloys of the invention as will be appreciated from the following.

The tensile properties of an alloy of the invention and containing 0.28% N_2 and 4.5% Mn were compared with those of a conventional duplex alloy of the type set out in Table I above. The comparison for the two alloys for the solution heat treated and water quenched conditions is given in Table II below.

TABLE II

	0.2% P.S. (MPa)	U.T.S. (MPa)	%Elongation.
Conventional alloy	430	700	30
Invention	540	730	32.

It will be seen from Table II that the properties of the alloy are much improved as compared to the conventional alloy. In particular the increase in proof stress, in excess of 100 MPa is totally due to the increased nitrogen addition held in solid solution in the austenite.

It should be appreciated that a number of modifications may be made to the composition of the alloy of the invention.

The addition of copper will have a beneficial effect on corrosion resistance. Thus, for example, the alloy may include copper in an amount up to 1% by weight. If greater than 0.5% by weight of copper is added, the active dissolution rate of a duplex alloy in boiling hydrochloric acid and the crevice corrosion loss in a chloride solution is also decreased.

Tungsten upto 1% by weight increases the immunity potentials to crevice corrosion of a duplex alloy in high temperature chloride solutions above which crevice corrosive starts.

Tin and antimony in amounts upto 0.10% and 0.2% by weight respectively improve the stress corrosion cracking and pitting corrosion in environments containing significant concentrations of H_2S.

Such modified alloys are also within the scope of the invention.

CLAIMS:

1. A stainless steel alloy having the following composition

	Wt. %
Chromium	23.0 - 26.0
Nickel	5.0 - 8.0
Manganese	3.5 - 5.0
Silicon	max 1.5
Molybdenum	1.75- 3.0
Carbon	max 0.06
Nitrogen	0.15- 0.30
Alloying additions	0- 2.5
Iron&impurities	balance

said alloy having a duplex microstructure of austenite and ferrite.

2. An alloy as claimed in claim 1 and having the following composition

	Wt. %
Chromium	23.5 - 25.0
Nickel	5.0 - 6.5
Manganese	4.0 - 5.0
Silicon	1.0 max
Molybdenum	1.75- 3.0
Carbon	0.02- 0.06
Nitrogen	0.15- 0.3
Alloying additions	0- 2.5
Iron&impurities	balance.

3. An alloy as claimed in claim 1 or 2 and having a microstructure comprising at least 60% austenite.

4. An alloy as claimed in claim 3 and having a microstructure comprising at least 65% austenite.

5. A stainless steel alloy as claimed in any one of claims 1 to 4 including copper as an alloying addition in an amount of greater than 0.5% by weight.

6. A stainless steel alloy as claimed in any one of claims 1 to 4 including tungsten as an alloying addition in an amount of up to 1% by weight.

7. A stainless steel alloy as claimed in any one of claims 1 to 4 including tin as an alloying addition in an amount of up to 0.10% by weight.

8. A stainless steel alloy as claimed in any one of claims 1 to 4 including antimony as an alloying additions in an amount of up to 0.2% by weight.

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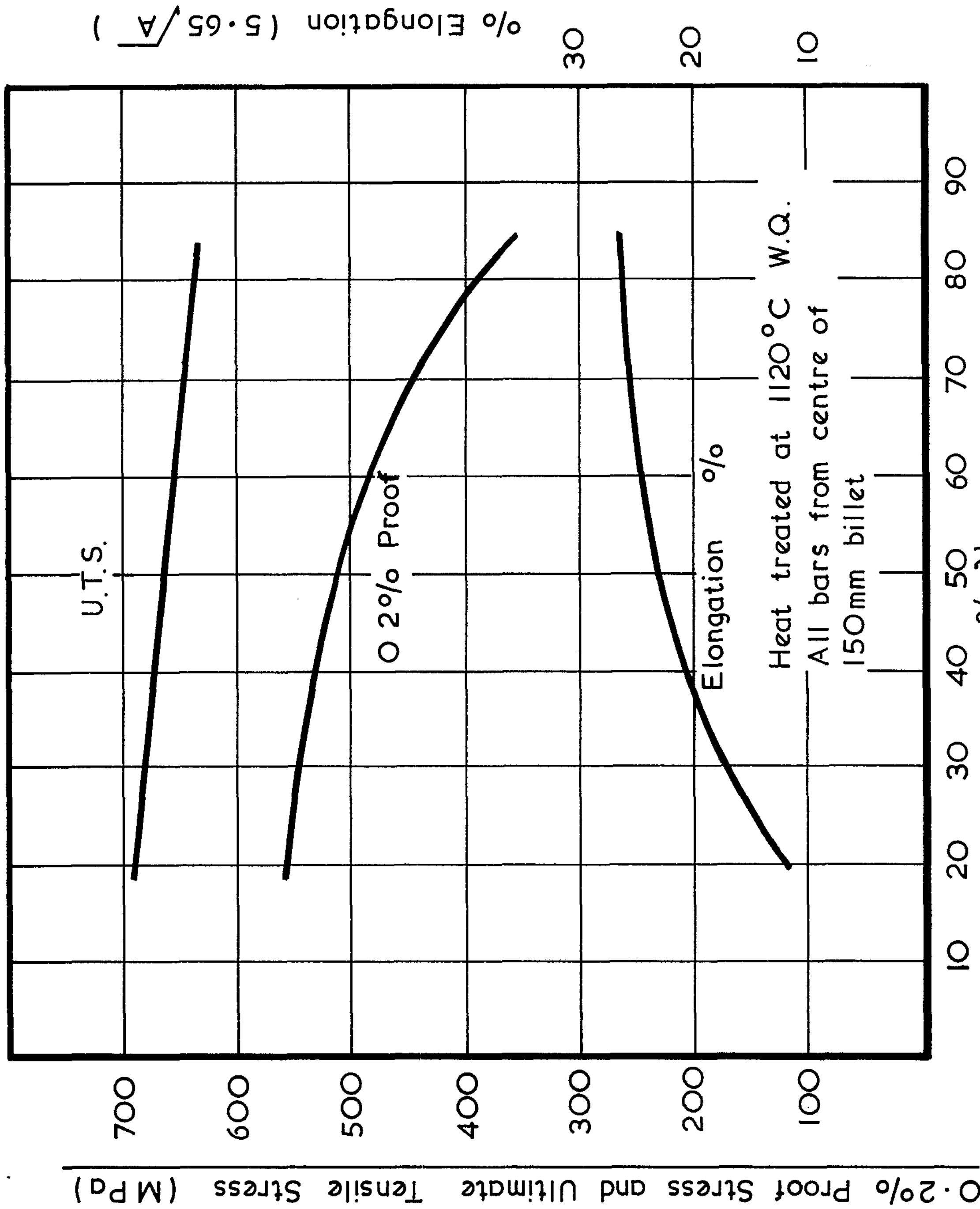

FIG. 1

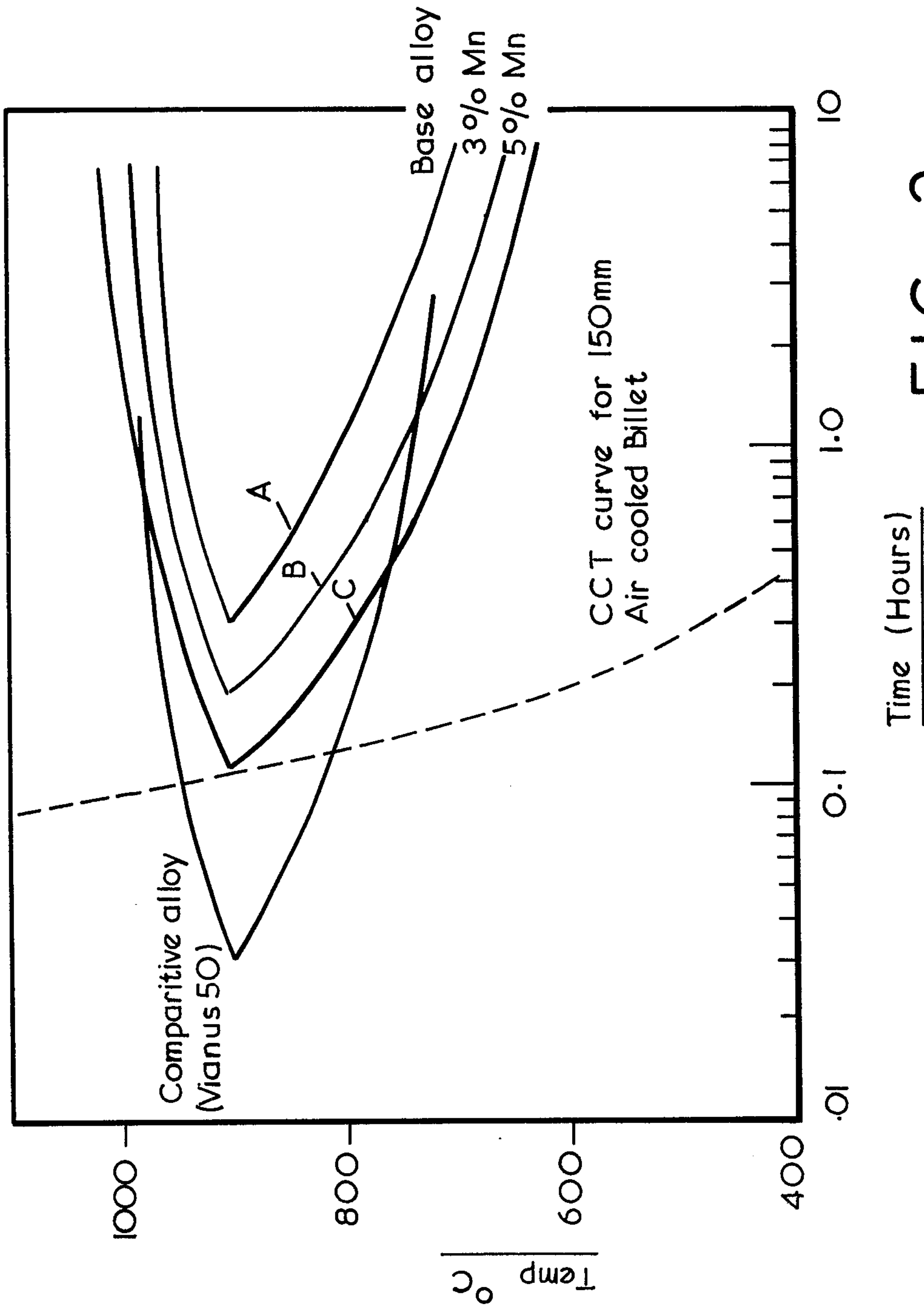
Temp °C
1000
800
600
400
Time (Hours)
.01
0.1
1.0
10
Base alloy
3% Mn
5% Mn
A
B
C
CCT curve for 150mm
Air cooled Billet
Comparitive alloy
(Vianus 50)

FIG. 2

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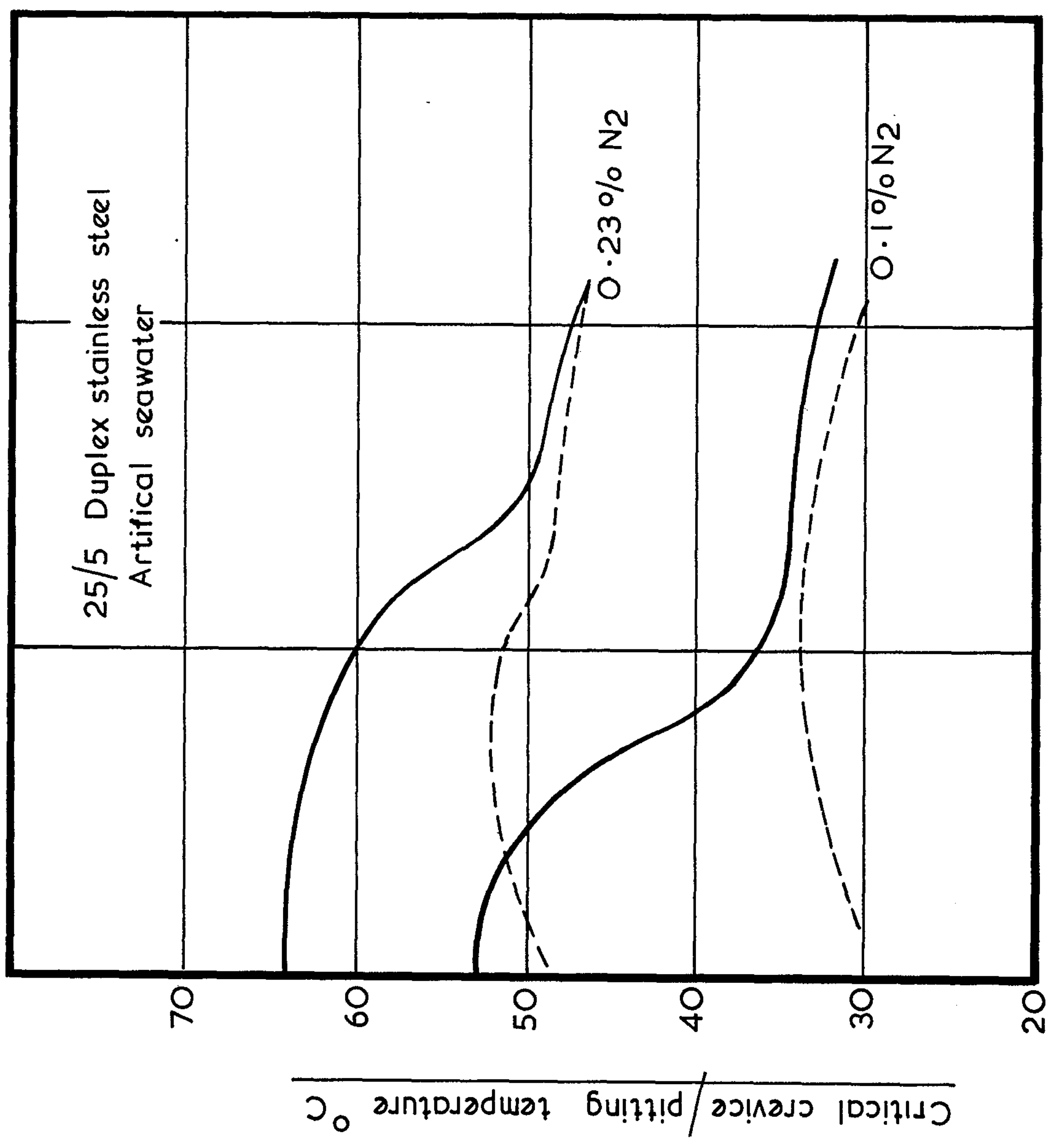

FIG. 3

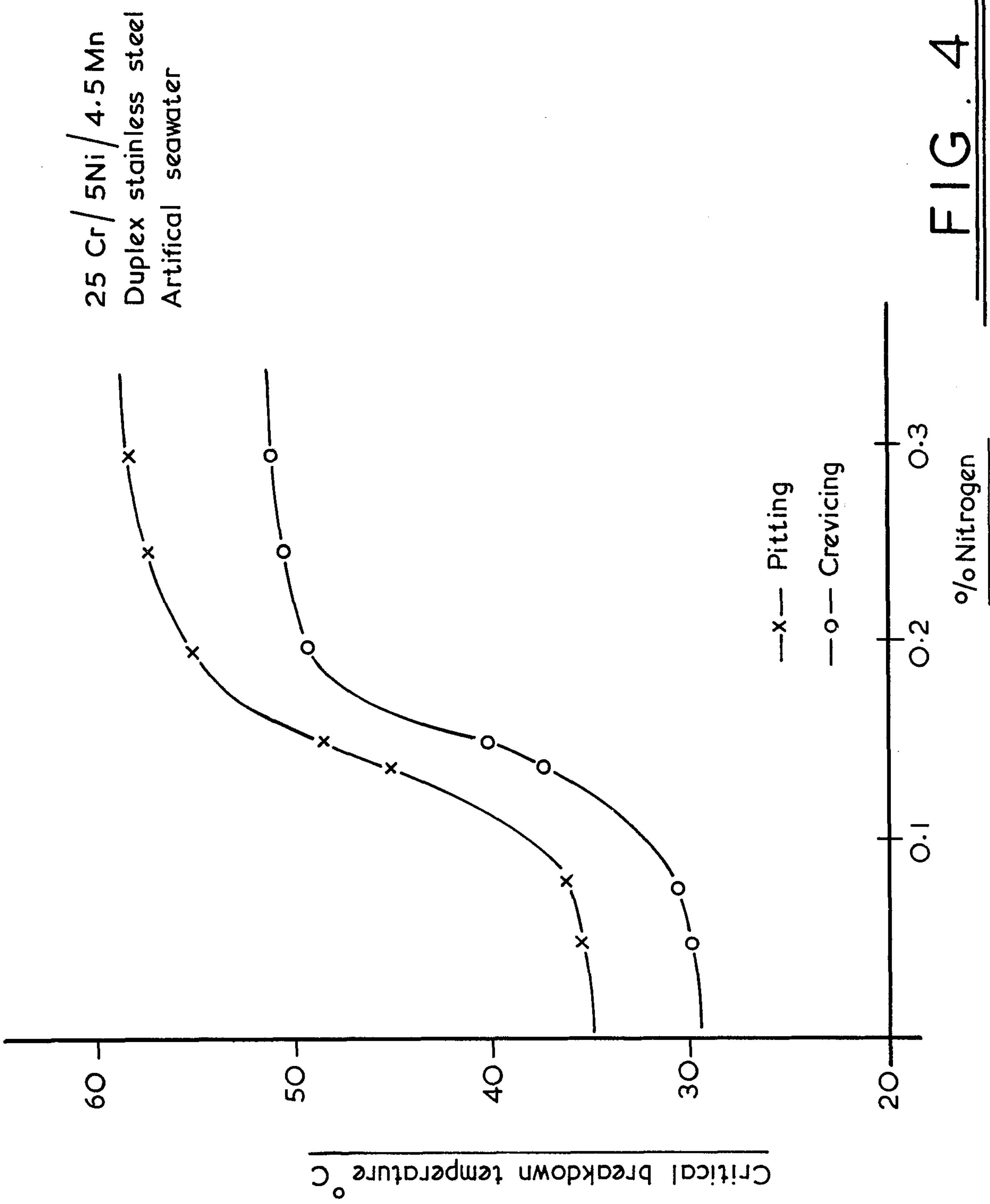
25 Cr/5Ni/4.5 Mn
Duplex stainless steel
Artifical seawater
—x— Pitting
—o— Crevicing
%Nitrogen
0.1
0.2
0.3
20
30
40
50
60
Critical breakdown temperature °C

FIG. 4

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EUROPEAN SEARCH REPORT

Application number

EP 83 30 6395

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	FR-A-2 007 566 (ARMCO STEEL CORPORATION) * Claims 1-3; page 7, lines 20-35 *	1,2	C 22 C 38/58
X	* Page 20, line 6 - page 22, line 23; table IVb *	3,4	

X	EP-A-0 060 577 (BROWN, BOVERI & CIE.). * Claims 1-3,6,7,9; page 10, examples 5,6 *	1,2,5	

Y	US-A-2 229 065 (FRANKS) * Claim 3 *	1,2,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
Y	* Page 1, right-hand column, lines 18-20 *	5	C 22 C 38

Y	DE-A-2 457 089 (SCHOELLER-BLECKMANN STAHLWERKE AG) * Claims 1-3 *	1-3	

Y	DE-B-1 214 005 (STAHLWERKE SÜDWESTFALEN AG) * Claims 1,4-6 *	1,2,5	
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30-01-1984	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

Application number

EP 83 30 6395

Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	FR-A-1 444 807 (COMPAGNIE DES ATELIERS ET FORGES DE LA LOIRE) * Abstract no. 1 * ---	1,2	
A	FR-A-2 045 584 (UGINE-KUHLMANN) * Claim 1 * -----	1,3	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30-01-1984	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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