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㉔ **Low interstitial, corrosion resistant, weldable ferritic stainless steel and process for the manufacture thereof.**

㉕ A low interstitial, corrosion resistant, weldable ferritic stainless steel has an addition of between 0.05 and 0.50% by weight columbium and/or titanium to give the steel improved toughness when the maximum achievable cooling rate is limited. The steel consists of the following composition by weight percent: between 25.0 and 35% chromium, between 3.6 and 5.6% molybdenum, between 0.05 and 0.50% of columbium and/or titanium, less than 3.0% nickel, less than 2.0% manganese, less than 2.0% silicon, less than 0.5% aluminium, less than 0.5% copper, less than 0.050% phosphorous, less than 0.050% sulfur, less than 0.01% carbon, less than 0.02% nitrogen, the carbon plus nitrogen content being less than 0.025%, and the balance iron. A process is also disclosed which comprises air-cooling a steel having the above composition from the annealing temperature before cold rolling.

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LOW INTERSTITIAL CORROSION RESISTANT WELDABLE
FERRITIC STAINLESS STEEL AND PROCESS FOR THE
MANUFACTURE THEREOF

The present invention relates to a low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness and to a process for the manufacture thereof. More specifically, the present invention is directed to a low interstitial, corrosion resistant, weldable ferritic stainless steel with a small addition of either columbium or titanium to improve the toughness when the maximum achievable cooling rate is limited.

A ferritic stainless steel must have superior pitting and crevice corrosion resistance in order to be used in certain chemical environments as for example in power plants exposed to sea water, and pulp and paper process equipment. Stainless steel containing 29% chromium and 4% molybdenum are highly resistant to crevice corrosion. These steels require a low level of interstitials, for example a total carbon plus nitrogen content of less than 0.025% by weight, to have good post-welding ductility and intergranular

corrosion resistance.

The applications mentioned above often require heavy gauge supporting products such as plate, as well as light gauge welded tubing such as condenser tubing. This equipment is often assembled through a welding process. The shape and size of the assembled equipment usually prevents the use of a final heat treatment or, if capable of a final heat treatment, the shape and size often severely limit the ability of the assembled equipment to cool rapidly from the heat treating temperature. Moreover, the toughness of the alloy decreases as the thickness increases and as the cooling rate decreases. This is illustrated in Figure 12 in a paper by H.E. Deverall entitled "Toughness Properties of Vacuum Induction Melted High-Chromium Ferritic Stainless Steels", published in ASTM STP 706, Toughness of Ferritic Stainless Steels, R.A. Lula, Ed., American Society for Testing and Materials, 1980. The decrease in toughness decreases weldability such that the plate, which in some instances may be incapable of being water-quenched because of its size, might exhibit cracking during welding. Or, if the plate is water-quenched, the cooling rate because of the thickness of the plate may not be rapid enough to achieve suitable toughness such that the plate may exhibit cracking during welding. Therefore, better toughness must be achieved by some other means where water-quenching is impractical or where water-quenching does not achieve suitable toughness to improve the weldability of the various components comprising the final assembled structure.

Even if the final product is to be of light gauge, the

conventional production methods require the cooling of thicker slabs and bands during processing. The cooling rates of these heavier section sizes is slow. Water-quenching would speed up the cooling process, however water-quenching is often impossible or impractical due to shape and size.

As the thickness of the product section increases, the toughness as measured by Charpy impact transition temperature decreases. Toughness is the ability of a metal to absorb energy by deforming plastically before fracturing. The transition temperature is the temperature at which the fracture which occurs from the impact is 50 percent shear (ductile) and 50 percent cleavage (brittle).

The toughness of the 29% chromium - 4% molybdenum alloy is low compared to substantially lower chromium alloys of an equivalent carbon and nitrogen content because of the high alloy content. The toughness of the 29% chromium - 4% molybdenum alloy is improved by water-quenching to speed up the cooling process instead of the slower air-cooling. However, in many cases the water-quenching process is not possible or practical to use, so a method is needed to improve the toughness of the steel in those situations where the maximum cooling rate is limited.

A 29% chromium - 4% molybdenum ferritic stainless steel with a maximum carbon plus nitrogen content of 0.025% is disclosed in United States Patent No. 3,929,473. United States Patent No. 3,932,174 is a modification to which small amounts of other elements are added to achieve the same range of corrosion properties as United States Patent No. 3,929,473. However these patents do not teach the use of columbium or titanium.

United States Patent No. 3,807,991 teaches the addition of between 13 and 29 times the amount of nitrogen or between 0.065% and 0.363% columbium to a steel of 1% molybdenum for improved toughness and intergranular corrosion resistance in the air-cooled condition. United States Patent 3,957,544 discusses the addition of titanium and columbium according to the equation $\%Ti/6 + \%CB/8 = (\%C + \%N)$. The molybdenum content of the steels in these patents is lower than that of the present invention.

The presence of titanium and columbium in the steel reduces the susceptibility of a steel to intergranular attack, but the weldability of the steel is poor unless the level of interstitials is low. Molybdenum improves pitting and crevice corrosion resistance, but according to United States Patent 4,119,765 if molybdenum is present in an amount of over 3.5% and is combined with chromium, titanium, silicon or columbium, the notch toughness is reduced, especially in the as-welded condition. United States Patent 4,119,765 adds from 2% - 4.75% nickel to improve the weldability of the steel. The amount of nickel must be regulated carefully so as to improve notch toughness and acid corrosion resistance without interfering with other properties.

A final reference is a paper entitled "Ferritic Stainless Steel Corrosion Resistance and Economy" by Remus A. Lula. The paper appeared on pages 24-29 of the July 1976 issue of Metal progress. This reference does not disclose the ferritic stainless steel of the present invention.

For the reasons noted hereinabove, the present invention is distinguishable from the references referred to.

An object of the present invention is to provide a low interstitial, corrosion resistant, weldable ferritic stainless steel with a high molybdenum content which exhibits improved toughness in heavier section thickness when the maximum achievable cooling rate is limited.

A further object of the present invention is to provide a low interstitial, corrosion resistant, weldable ferritic stainless steel with a high molybdenum content which exhibits improved toughness due to a small addition of either columbium or titanium.

In particular, this invention provides a low interstitial ferritic stainless steel which is corrosion resistant and weldable at room temperature. The improvement of the present invention being an addition of a small critical amount of columbium and/or titanium to improve the toughness of the steel in situations where water quenching is impossible or impractical.

The present invention provides a low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness characterized in that it consists of, by weight percent: 25.0%-35.0% chromium, 3.6%-5.6% molybdenum, less than 3% nickel, less than 2% manganese, less than 2.0% silicon, less than 0.5% aluminum, less than 0.50% copper, less than 0.050% phosphorus, less than 0.05% sulfur, less than 0.01% carbon, less than 0.02% nitrogen, the sum of the carbon and nitrogen being less than 0.025%, 0.05-0.50% of columbium and/or titanium, and the balance of iron.

The present invention further provides a process for the manufacture of ferritic stainless steel of improved toughness

wherein said steel is hot rolled, annealed and cold-rolled to strip thickness, characterized in that the process comprises air-cooling from the annealing temperature before cold rolling a ferritic stainless steel consisting essentially of, by weight per cent: 25.0% - 35.0% chromium, 3.6% - 5.6% molybdenum, less than 3.0% nickel, less than 2.0% manganese, less than 2.0% silicon, less than 0.5% aluminum, less than 0.5% copper, less than 0.5% phosphorus, less than 0.05% sulfur, less than 0.01% carbon, less than 0.02% nitrogen, the sum of the carbon and nitrogen being less than 0.025%, 0.05% - 0.50% of columbium and/or titanium, and the balance iron, so as to produce a steel with a Charpy impact transition temperature of below -17.8°C (0°F) as cold-rolled to a thickness of 1.575mm (0.062 inches).

Chromium and molybdenum are preferably present in respective amounts of 28.5% to 30.5% and 3.75% to 4.75%. Columbium and/or titanium is present preferably in the amount of 0.05% to 0.20%. Manganese and silicon are each usually present in amounts of less than 1%. Aluminum, copper, phosphorous, and sulfur are present usually in amounts of less than 0.1%. Carbon and nitrogen are present preferably in amounts of less than 0.008% and 0.016% respectively.

The advantages of the steel of this invention will be apparent from the following description which is illustrative of several aspects of the invention. This invention relates to a low interstitial ferritic stainless steel having a chromium content of between 25.0% and 35.0% and a molybdenum content of between 3.6% and 5.6%. A small amount of columbium or titanium of between 0.05% and 0.20% is added to the steel

composition to improve its toughness when the maximum achievable cooling rate is limited.

Ingots from four heats were vacuum-induction melted to the compositions given in Table I.

Table I

		Chemical Composition (wt. %)											
Heat	Al	C	Cb	Cr	Cu	Fe	Mn	Mo	N	Ni	P	S	Si
A	0.012	0.0077	0.01	28.72	0.020	bal.	0.015	3.82	0.016	0.10	0.006	0.023	0.055
B	0.020	0.0046	0.09	28.80	0.010	bal.	0.026	3.99	0.015	0.10	0.006	0.015	0.054
C	0.024	0.0078	0.11	28.94	0.015	bal.	0.01	4.12	0.016	0.10	0.007	0.013	0.030
D	0.028	0.0051	0.16	29.00	0.020	bal.	0.023	3.98	0.016	0.10	0.006	0.013	0.032

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The ingots were conditioned, heated to a temperature of 1121°C (2050°F) and hot rolled to a strip about 3.556mm (0.140 in.) thick. The hot rolled band was annealed at a temperature of 1010°C (1850°F), and water-quenched and cold rolled to a thickness of 1.575mm (0.062 in.). The strip was then annealed at a temperature of 1010°C (1850°F), water-quenched and TIG welded.

Four sets of transverse Charpy V-notch impact subsize specimens were taken, two from the hot rolled band and the others from the 1.575mm (0.062 in.) thick strips. After annealing the specimens at a temperature of 1010°C (1850°F), the specimens were either water-quenched or air-cooled. The cooled specimens were then tested for toughness characteristics. The results of the tests are shown in Table II.

Table II

Heat	<u>Impact Transition Temperature $^{\circ}\text{C}$ ($^{\circ}\text{F}$)</u>			
	<u>3.556mm (0.140 in.) Thick</u>		<u>1.575mm (0.062 in.) Thick</u>	
	Air-Cooled	Water-Quenched	Air-Cooled	Water-Quenched
A	143 (290)	-40 (-40)	54 (130)	-79 (-110)
B	74 (165)	7 (45)	-43 (-45)	-68 (-90)
C	43 (110)	7 (45)	-29 (-20)	-76 (-105)
D	7 (45)	-29 (-20)	-76 (-105)	-101 (-150)

The transition temperature decreases with increasing columbium content in the air-cooled condition thus indicating that columbium acts against the detrimental effects on toughness of slow cooling. Although the impact

transition temperatures of the air-cooled specimens are higher than those of the water-quenched specimens it can be seen from Table II that the difference in impact transition temperatures of an air-cooled and a water-quenched 1.575mm (0.062 in.) thick steel strip is less than 38°C (100°F). Whereas the difference in impact transition temperature for prior art compositions is 115°C (240°F). However, in situations where water-quenching is impractical or in situations where the cooling rates achieved by water-quenching of heavy thickness sections approach or are slower than those of air cooling lighter thickness sections, the addition of columbium improves the toughness. The impact transition temperature of the 1.575mm (0.062 in.) steel strip of a composition according to the present invention is below -17.8°C (0°F) whereas that of prior art composition A is 54°C (130°F). It is essential that the impact transition temperature of such a steel strip be below room temperature so that the steel strip will not crack upon welding. Steels of prior art compositions had to be water-quenched before cold rolling in order to achieve the necessary toughness characteristics. The composition of this invention enables us to achieve good toughness characteristics by air-cooling the steel before cold-rolling instead.

Corrosion tests were also performed on the 1.575mm (0.062 in.) thick strip in the as welded condition and on the base metal specimens which were heat treated at 1232°C (2250°F) and air-cooled to simulate the heat affected zone upon welding a heavier thickness. The specimens 25.4mm x

50.8mm(1 in. x 2 in.) were exposed to a boiling solution of ferritic sulfate-50% sulfuric acid for 120 hours according to ASTM A262 Practice B for intergranular corrosion testing. The corrosion rates are given in Table III.

Table III

Corrosion Rates in Ferric Sulfate - 50% Sulfuric Acid
Intergranular Corrosion Test (ASTM A262, Practice B)

1.575mm(0.062 in.) TIG Welded 1.575mm(0.062 in.) Base Metal
(Heat Treated at 1232°C(2250°F)-
Air-Cooled)

Heat	mm(inches)/month	mm(inches)/month
A	0.012598(0.000496)	0.014732(0.000580)
B	0.012141(0.000478)	0.008382(0.000330)
C	0.009906(0.000390)	0.010033(0.000395)
D	0.012268(0.000483)	0.014122(0.000556)

The results of additional tests of the mechanical properties of the steel in the welded condition are shown in Table IV.

Table IV.

Welded Mechanical Properties of 1.575mm(0.062 in.) Thick Strip

Heat	0.2% Yield Strength, ksi	Tensile Strength, ksi	% Elongation in 12.7mm(0.5 in). 50.8mm(2.0in)	
A	81.0	92.2	24.0	6.0
B	85.4	98.6	24.0	9.0
C	86.5	100.0	9.0'	15.5'
D	88.8	101.2	23.0	6.0

'fracture in base metal, not in weld.

CLAIMS:

1. A low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness characterized in that it consists of, by weight percent: 25.0%-35.0% chromium, 3.6%-5.6% molybdenum, less than 3.0% nickel, less than 2.0% manganese, less than 2.0% silicon, less than 0.5% aluminum, less than 0.50% copper, less than 0.050% phosphorous, less than 0.05% sulfur, less than 0.01% carbon, less than 0.02% nitrogen, the sum of the carbon and nitrogen being less than 0.025%, 0.05%-0.50% of columbium and/or titanium, and the balance of iron.
2. A low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness according to claim 1 with a chromium content of from 28.5% to 30.5%.
3. A low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness according to claim 1 or 2, with a molybdenum content of from 3.75% to 4.75%
4. A low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness according to claim 1, 2 or 3, with 0.05%-0.20% of columbium and/or titanium.
5. A low, interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness according to any one of the preceding claims with 0.05%-0.20% columbium.
6. A process for the manufacture of ferritic stainless steel of improved toughness wherein said steel is hot rolled, annealed and cold-rolled to strip thickness, characterized in

that the process comprises air-cooling from the annealing temperature before cold rolling a ferritic stainless steel consisting essentially of, by weight per cent: 25.0%-35.0% chromium, 3.6%-5.6% molybdenum, less than 3.0% nickel, less than 2.0% manganese, less than 2.0% silicon, less than 0.5% aluminum, less than 0.5% copper, less than 0.5% phosphorous, less than 0.05% sulfur, less than 0.01% carbon, less than 0.02% nitrogen, the sum of the carbon and nitrogen being less than 0.025%, 0.05% - 0.50% of columbium and/or titanium, and the balance iron, so as to produce a steel with a Charpy impact transition temperature of below $-17.8^{\circ}\text{C}(0^{\circ}\text{F})$ as cold-rolled to a thickness of 1.575mm(0.062 inches).

7. A process for making a low interstitial, corrosion resistant, weldable ferritic stainless steel with improved toughness according to claim 6, with the additional step of welding.

8. A low interstitial, corrosion resistant, weldable, ferritic stainless steel with improved toughness made according to the process of claim 6 or 7.



European Patent
Office

EUROPEAN SEARCH REPORT

0057316

Application number

EP 81 30 5667

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	SU - A - 515 825 (KOLIADA et al.) * The complete document *	1,4	C 22 C 38/22 38/26 38/28
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X	FR - A - 2 158 943 (DEUTSCHE EDEL-STAHLWERKE) * Claims 1,2,10 *	1,4	
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A	US - A - 2 183 715 (FRANKS) * Claim 1; page 1, left-hand column, lines 6-33 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
	--		C 22 C 38/22 38/26 38/28
A	FR - A - 2 180 117 (NYBY BRUK A.B.) * Claims 1,2,7 *	1	
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A	FR - A - 2 377 457 (THYSSEN EDEL-STAHLWERKE) * Claims 1,4,5,6,11 *	1	

			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
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	23-04-1982	LIPPENS	