(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 936 280 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.08.1999 Bulletin 1999/33

(51) Int. Cl.[6]: **C22C 38/22**

(21) Application number: **99103043.8**

(22) Date of filing: **16.02.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **17.02.1998 IT RM980092**

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(54) Improved ferritic stainless steel and articles produced therewith

(57) In the group of AISI 436 LI ferritic stainless steels, a narrow composition is proposed in which specifically selected alloying elements as well as a Ti and Nb stabilisation, consent to obtain a monophasic product apt to a plurality of uses, being provided with high formability and weldability characteristics, good resistance to corrosion, also localised and in acid condenses, good resistance to oxidation at high temperatures, to thermal shock and to thermal fatigue, good polishability and absence of aligned superficial defects.

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Description

Prior Art

[0001] Stainless steels are first classified according to their structure as ferritic, martensitic and austenitic and then, within each of those classes, according to their composition. There are many stainless steel compositions, often with seemingly minimal compositions differences, each aimed at a limited number of uses. For instance, there is a steel, DIN X6Cr13 (having the following composition in percent by weight: C ≤ 0,08, Si ≤ 1,0, Mn ≤ 1,0, P ≤ 0,045, S ≤ 0,030, Cr 12,0-14,0) utilised for parts to be used in wet environment, or in internal architecture. Another steel, DIN X6CrAl13, has the same composition, with an aluminium quantity added of 0,1-0,3 weight percent, utilised in the oil industry or in hydroelectric power plants.

[0002] Rising to 15,6-17% the Cr content (DIN X6Cr17) a steel is obtained easy to polish an with good corrosion resistance even in chlorinated environment, utilised for the production of cookware, cutlery, bumpers, hub caps. Another steel, DIN X10Cr13, the only difference with respect to the previous one is the carbon content, set at 0,08-0,12 %, is utilised in the food industry. Still changing the carbon content to 0,17-0,25 % or to 0,28-0,35 %, other kind of steel are obtained (DIN X20Cr13 and X30Cr13) respectively utilised for high resistance mechanical parts (shafts, pump parts, piston rods and the like) or for screws, bolts and springs. Still another modification of the DINX20Cr13 steel, consisting in the addition of 0,9-1,3 % Mo and of less than 1% Ni gives another steel (DINX20CrMo13) utilised for the production of turbine blades, engine valves, overheated steam valves.

[0003] It is then apparent how an high specialisation exists for stainless steels, requiring a consequently high specialisation of the steel producer who is therefor limited in its possibility to satisfactorily follow the market, or is forced to keep a very diversified, and therefore costly, warehouse.

[0004] Thus, at the moment the state of the art does not contemplate inox steels having different uses.

[0005] As a consequence, the present invention offers a stainless steel composition which, even remaining within a known type, has a large spectrum of different properties, such as: formability, absence of ridging and roping, weldability, hot oxidation resistance, thermal shock and fatigue resistance, resistance to corrosion by acid condensates and anti-ice salts, resistance to localised corrosion (pitting, crevice) and relevant propagation, good immunity to tensiocorrosion, good attitude to polishing, very good surface appearance, absence of defects in the rolling direction.

[0006] The steel according to present invention is, therefor, suitable for instance to the use in the automotive field, in catalysed exhaust systems and in the external exposed parts, in interiors and outdoor architecture, for white goods and ovens, for coins.

Description of the invention

[0007] According to present invention a ferritic, monophasic Cr, Mo, Cu stainless steel, Ti and Nb stabilised, is proposed, having the following weight percent composition: C ≤ 0,025, N ≤ 0,025, Mn 0,1-1,0, Si 0,2-0,7, P ≤ 0,025, S ≤ 0,002, Ni < 0,40, Cu 0,30-0,60, Cr 17-21, Mo 1,0-1,5, Ti 0,10-0,20, Nb 0,20-0,35, (REM + Hf + B) 0,01-0,10, remaining being iron and minor impurities, in which with REM the rare-earth metals are meant.

[0008] Preferably, the steel has the following composition, in weight percent,: C 0,018-0,014, N 0,08-0,014, Si 0,25-0,40, Mn 0,30-0,45, P 0,016-0,025, S 0,008-0,015, Ni 0,07-0,15, Cu 0,35-0,50, Cr 17,50-18,50, Mo 1,10-1,25. Ti 0,12-0,17, Nb 0,22-0,28, B 0,045-0,060, (REM + Hf) 0,020-0,040.

[0009] A typical composition, in weight percent, is: C0,010, N0,010, Si 0,30, Mn 0,40, P 0,022, S 0,001, Ni 0,10, Cu 0,45, Cr 18,30, Mo 1,20, Ti 0,15, Nb 0,25, B 0,0050, (REM + Hf) 0,030.

[0010] In this composition it is preferable that some elements are in mutual relationship according to the following (the data are in weight percent): (C + N) ≤ 0,025; (Ti + N) > 10(C + N); (Ni + Cu) < 0,80; Cr + 3(Mo + Cu) ≥ 22. Moreover, it is still more preferable to observe also the following conditions (the data are in weight percent): B ≤ 0,0060; Hf ≤ 0,04; REM ≤ 0,04; $Nb_{free} = Nb_{total} - 8(C + N) \geq 0,20$.

[0011] It is also advisable to treat the steel, in a way known per se, to maintain the total volumetric fraction of inclusions at or below a value of 0,20%, with no stringers and clusters.

[0012] The chemical composition of the steel according to present invention is chosen to suitably balance the effects of the microalloying elements. Thus, Cu and Mo have a beneficial effect on the resistance to general and localised corrosion, particularly in chloride-containing environments. The rare-earth metals globulise the sulphides, thus improving ductility and hence formability. Ti and Nb improve weldability and enhance the, particularly intergranular, corrosion resistance. Moreover, the above composition relationships contribute, in a not yet clear way, to enhance and uniform the above qualitative levels, for instance limiting the harmful precipitation of carbides in the welded zones.

[0013] A secondary but nevertheless important effect in all the uses in which the appearance of the final product is important, is a specific hue of the steel, warmer than the usual bluish one of the ferritic stainless steels, which impart to the steel a much more appealing look.

[0014] The thermal treatment consists in a continuous annealing at 900-1050 °C, preferably at 950-1000 °C, for a time comprised between 1 and 5 minutes, preferably 2 and 3 minutes.

[0015] The present invention will now be illustrated

with reference to some exemplificative embodiments, not limiting the objects and scope of present invention.

EXAMPLE 1

[0016] A steel having the following weight percent composition; C 0,010, N 0,0011, Si 0,44, Mn 0,16, S 0,001, P 0,014, Cr 18,5, Mo 1,12, Cu 0,51, Ti 0,12, Nb 0,22, B 0,005, (REM + Hf) 0,025, the remaining being iron and minor impurities, was rolled into 1 mm thick strips, having no superficial defects; samples of such material were imparted an isothermal oxidation at temperatures comprised between 900 and 1000 °C for 50-200 hours; the results are shown in Table 1.

Table 1

	900 °C	950 °C	1000 °C
	Weight increase, mg/cm^2		
50 h	0,20	0,35	1,32
100 h	0,27	0,43	1,48
150 h	0,31	0,47	1,83
200 h	0,35	0,51	2,11

[0017] As a reference, the performance of steels qualified for use at high temperatures, such as austenitic AISI 304 and 321, can be cited, which show a weight increase of about 0,5 mg/cm^2 and of 1,5 mg/cm^2 respectively at 900 and 950 °C, for a 100 hours exposure.

[0018] Utilising the above steel according to present invention terminal parts for the car exhaust pipes and parts for stoves were produced, to be exposed to flame or high temperatures. After a prolonged exposition, the parts in steel according to present invention did show a life increase of at least 30%, compared with similar parts in AISI436LI known steel.

EXAMPLE 2

[0019] The steel of Example 1 was laboratory tested for saline corrosion in NaCl 0,05 M at 23 °C; the depassivation pH was 2,1 without crevice, and the pitting potential was 0,6 V with respect to the saturated calomel electrode.

[0020] In the same conditions a known AISI436LI steel did show a pitting potential of about 0,5 V and a depassivation pH of about 3.

[0021] With the same steel were produced internal parts for dish washers, pots and cutlery. The parts did show an excellent level of formability and drawability, and were thereafter exposed to many washing simulating cycles. After 350 cycles, no traces of pitting were found.

[0022] Also car external parts were produced (hub caps, stone fenders and the like), utilised in accelerated practical tests on snow-covered, or in any case salt strewed, traks and roads. After a duration equivalent to 150.000 Km, no evident traces of corrosion were found.

EXAMPLE 3

[0023] The steel of Example 1, 0,4 mm thick, was laboratory tested for corrosion resistance in condensates. The test solution, known per se, comprise the following species, in ppm, Cl^- 1000; $SO_4^=$5000; $CO_3^=$ 3000; $NO_3^=$ 100; NH_4^+ 4600; HCOOH 100.

[0024] The test consists in simulating the condensation of aggressive solutions which happens into the exhaust pipe terminal parts of car mufflers. In the test, the solution pH varied from about 8,5 at the beginning to about 3,5 after evaporation of most of the liquid.

[0025] A test cycle consisted in heating the sample with test solution from 20 to 250 °C in 1 h, then keeping this temperature for 3 h and finally cooling the whole at 20 °C in 6 h.

[0026] After a number of cycles, the sample was washed and dried, and the maximum pitting dept, in μm, measured. The results are shown in Table 2.

TABLE 2

	Number of cycles			
	10	20	30	40
Pit dept, μm	24	50	56	88

[0027] In a control test, a known AISI 436LI steel did show, in the same test conditions, the following pit dept, in μm, 45, 76, 85, 140.

[0028] Terminal parts for exhaust pipes were also produced, tested in the same vehicles utilised for the accelerated tests of previous Example. At the end of the test, said terminal parts did not show any through-holes or extended corrosion.

EXAMPLE 4

[0029] Other steel samples of Example 1 were tested for Erichsen drawing; the Erichsen Index value was about 8,40, compared with a value of 8,10 for a corresponding known steel.

[0030] The steel according to present invention can, thus, be utilised for any use in which at least one of the following characteristics is requested: localised and general corrosion resistance, good drawability and formability, good weldability, resistance to hot oxidation and to thermal shock, resistance to thermal fatigue, no superficial defects.

[0031] The steel can be usefully utilised for the production of goods such as: car exhaust pipes and terminal parts, parts exposed to the flame or otherwise to

high temperatures (formability, weldability, hot oxidation resistance, resistance to acid condensates), parts of stoves and ovens, pots; hub caps and car external trimmings (superficial appearance, drawability, polishing, chloride corrosion resistance); internal parts of dishwashers, cutlery, pots (drawability, superficial appearance, resistance to localised corrosion in chlorinated environment); signs, architectural coverings, internal and external furnishing (formability, drawability, superficial appearance, resistance to generalised corrosion).

Claims

1. Monophasic ferritic Cr, Mo, Cu stainless steel stabilised with Ti and Nb, characterised by the following composition, in % by wt.: C ≤ 0,025, N ≤ 0,025, Mn 0,1-1,0, Si 0,2-0,7, P ≤ 0,025, S ≤ 0,002, Ni < 0,40, Cu 0,30-0,60, Cr 17-21, Mo 1,0-1,5, Ti 0,10-0,20, Nb 0,20-0,35, (REM + Hf + B) 0,01-0,10, remaining being iron and minor impurities.

2. Steel according to claim 1, having the following composition, in weight percent,: C 0,018-0,014, N 0,08-0,014, Si 0,25-0,40, Mn 0,30-0,45, P 0,016-0,025, S 0,008-0,015, Ni 0,07-0,15, Cu 0,35-0,50, Cr 17,50-18,50, Mo 1,10-1,25. Ti 0,12-0,17, Nb 0,22-0,28, B 0,045-0,060, (REM + Hf) 0,020-0,040.

3. Steel according to any one of the preceding claims, having the following composition, in weight percent: C 0,010, N 0,010, Si 0,30, Mn 0,40, P 0,022, S 0,001, Ni 0,10, Cu 0,45, Cr 18,30, Mo 1,20, Ti 0,15, Nb 0,25, B 0,0050, (REM + Hf) 0,030.

4. Steel according to any one of the above claims, in which the following composition relationships are observed (the data are in weight percent): (C + N) ≤ 0,025; (Ti + N) > 10(C + N); (Ni + Cu) < 0,80; Cr + 3(Mo + Cu) ≥ 22.

5. Steel according to any one of the above claims, in which the following conditions are observed (the data are in weight percent): B ≤ 0,0060; Hf ≤ 0,04; REM ≤ 0,04; $Nb_{free} = Nb_{total} - 8(C + N) \geq 0,20$.

6. Steel according to any one of the above claims, in which the total volumetric fraction of inclusions is maintained at or below a value of 0,20%.

7. Steel according to any one of the above claims, continuously annealed at 900-1050 °C, for a time comprised between 1 and 5 minutes.

8. Steel according to claim 7, for which the continuous annealing temperature is comprised between 950-1000 °C, for a time comprised between 2 and 3 minutes.

9. Use of a steel according to any one of the preceding claims in the manufacture of goods for which at least one of the following characteristics is requested: localised and general corrosion resistance, good drawability and formability, good weldability, resistance to hot oxidation and to thermal shock, resistance to thermal fatigue, no superficial defects.

10. Goods produced with a steel according to any one of claims 1 to 8 and having at least one characteristic according to claim 9, such as: car exhaust pipes and terminal parts, parts exposed to the flame or otherwise to high temperatures, parts of stoves and ovens, pots, hub caps and car external trimmings, internal parts of dishwashers, cutlery, signs, architectural coverings, internal and external furnishing.