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[54] **HIGH STRENGTH, CORROSION RESISTANT, AUSTENITE-FERRITE STAINLESS STEEL**

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[58] **Field of Search**...... 75/124, 137, 128 G, 128 W

[56] **References Cited**

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[57] **ABSTRACT**

An aging, austenite-ferritic, stainless steel having very high strength, good ductility and notch-impact resistance as well as excellent resistance to general and intercrystalline corrosion, has the following composition, given in percent, by weight:

C maximum value	0.15	preferably 0.01 – 0.10
Si maximum value	2	preferably a maximum of 1.0
Mn maximum value	5	preferably a maximum of 2.0
Cr	20 – 30	preferably 24 – 27
Ni	4 – 9	preferably 5.5 – 7.5
Mo	1 – 3	preferably 1.3 – 1.8
Nb	0.1 – 2.5	preferably 0.1 – 1.6
Ti maximum value	1.5	preferably a maximum of 1.0
Al	0.1 – 2	preferably 0.5 – 1.0
N maximum value	0.15	preferably a maximum of 0.1

the remainder being made up of iron and the impurities and other material usually present in this type of steel. It is further necessary to weigh out the quantity of niobium and titanium in proportion to the quantity of carbon and nitrogen in such manner that the atomic percentage of niobium plus the atomic percentage of titanium ≥ the atomic percentage of carbon plus the atomic percentage of nitrogen.

6 Claims, No Drawings

HIGH STRENGTH, CORROSION RESISTANT, AUSTENITE-FERRITE STAINLESS STEEL

BACKGROUND OF THE INVENTION

It is a characteristic of an austenite-ferritic steel of high chromium content that the steel possesses excellent corrosion resistance even in highly corrosive environments. One example of such a steel, known as type SIS 2324, contains approximately 0.1% C, 26% Cr, 5% Ni and 1.5% Mo. This steel is used in many applications where the requirements for corrosion resistance are very demanding, and this type of steel also possesses high strength in comparison with regular austenitic, stainless steels. However, there is a definite need for a steel of still greater strength than is possessed by the type SIS 2324 steel, and specifically in combination with good ductility and notch-impact resistance as well as high resistance to corrosion.

A method commonly employed to attain increases in steel strength is age-hardening. This requires a suitable combination of alloy material as well as an appropriate aging treatment in order to attain the fine-dispersed precipitate which is necessary for such increase in strength. The aging treatment, which is usually accomplished at relatively low temperatures, is preceded in most cases by a solution anneal at high temperature. However, in the case of austenite-ferritic steels having a high chromium content, such as the above identified type SIS 2324 steel, it has been found that such age-hardening cannot be accomplished satisfactorily. If the aging treatment is carried out at temperatures between 400°C and 525°C, there will occur the well-known so-called 475°C-embrittlement. Likewise, if the aging treatment is carried out at temperatures between 700°C and 850°C, it results in an embrittlement by σ-phase precipitation. It follows, therefore, that the above-mentioned temperature ranges can never be used to carry out the aging treatment, because the impact strength of the steel then becomes unacceptably low.

An aging treatment at temperatures ranging from 525°C to 700°C is not practical either because it has been found that, in case of a treatment at such temperatures, the susceptibility to intercrystalline corrosion becomes unacceptably great. As described in prior U.S. patent application Ser. No. 823,744 and U.S. Pat. No. 3,717,455 it is possible to reduce substantially the adverse tendency of intercrystalline corrosion in case of steels of this kind by the admixture of niobium and titanium. However, tests conducted with steels of type SIS 2324, employing the admixture of strong carbide-forming substances, for example in the form of niobium or titanium, did not result in any increase in strength when subjected to aging treatment within the specific temperature range from 525°C to 700°C.

The above discussed facts indicate clearly that it is not possible to attain in a conventional manner, by admixture of alloys and age-hardening, and increase in strength for steels of the type SIS 2324 if the requirements for good impact strength and good resistance to intercrystalline corrosion are to be maintained. Such age-hardening would accordingly seem to require an aging treatment at temperatures other than the unsuitable temperature ranges discussed above, i.e., at temperatures either below 400°C or above 850°c. However, at temperatures below 400°C the rate of diffusion of the material is extremely low and, as a result, any precipitation hardening progresses at such slow speed that it can never be carried to completion in practice. On the other hand, if temperatures above 850°C are employed, the rate of diffusion becomes so high that overaging takes place very rapidly, thus making a proper age-hardening practically impossible in the present state of the art. Therefore, it is considered to be definitely impossible to increase the strength characteristics of steels of type SIS 2324 by means of age-hardening, while maintaining at the same time the impact strength and resistance to corrosion of said steel.

SUMMARY OF THE INVENTION

The present invention makes it now feasible in the case of a corrosion-resistant austenite-ferritic steel having high strength, good ductility, impact strength and resistance to intercrystalline corrosion, surprisingly to attain, by means of age-hardening, an increase in its strength and resistance to corrosion while maintaining its impact strength. This is accomplished by combining and adding a powerfully carbide-forming compound, such as niobium and titanium as well as aluminum, to an austenite-ferritic steel having a high content of chromium.

In order to attain the desired strength characteristics, special attention must be paid to the proportion of austenite to ferrite in the steel. Excessive quantities of austenite in the steel will cause a lowering in strength after age-hardening, and tests have shown that the content of austenite must accordingly not exceed 35% by volume. On the other hand, the austenite influences advantageously the impact resistance when the material possesses the desired high strength characteristics, and the content of austenite should therefore not be reduced to a very low level. Thus, the austenite content will be a factor for attaining a fine ferrite grain size by its retarding effect on the growth of the ferrite grains during the solution anneal. Furthermore, the austenite phase has an inhibiting influence on the propagation of cracks, and thus influences advantageously the ductility and the impact resistance of the steel. Tests have shown that, in view of the above discussed factors, the austenite content of the steel must be at least 10% by volume for the purpose of the present invention.

As a result, in order to attain the very advantageous combination of high strength and good ductility, which is a characteristic of this invention, the steel of the present invention must contain between 10% and 35%, and preferably between 10% and 25%, by volume of austenite. In order to assure that the steel has an austenite content within these specified limits, it is necessary to take into consideration the ferrite- or ausenite-stabilizing effect of the alloys contained in the steel, and this can be accomplished roughly with the aid of a so-called Schaeffler diagram.

The invention is further characterized by the fact that the steel has the following composition, given in percent by weight:

C	maximum value 0.15	preferably 0.01 – 0.10
Si	maximum value 2	preferably a maximum of 1.0
Mn	maximum value 5	preferably a maximum of 2.0
Cr	20 – 30	preferably 24 – 27
Ni	4 – 9	preferably 5.5 – 7.5
Mo	1 – 3	preferably 1.3 – 1.8
Nb	0.1 – 2.5	0.1 – 1.6
Ti	maximum value 1.5	preferably a maximum of 1.0
Al	0.1 – 2	preferably 0.5 – 1.0
N	maximum value 0.15	preferably a maximum of 0.1

the remainder being made up of iron and the impurities and other material usually present in this type of steel. It is further necessary to weigh out the quantity of niobium and titanium in proportion to the quantity of carbon and nitrogen in such manner that the atomic percentage of niobium plus the atomic percentage of titanium ≥ the atomic percentage of carbon plus the atomic percentage of nitrogen.

Powerfully carbide-forming substances other than niobium and titanium, for example zirconium and tantalum, can also be part of the alloy and, obviously in this case, should be supplied in sufficient stoichiometric amounts in proportion to carbon and nitrogen. The contents of carbon and nitrogen should be kept so low as possible, and a lowest value of approximately 0.01 percent was found to be proper in practice.

EXAMPLES

The invention will now be further explained by referring to several types of steel, whose chemical compositions are listed in Table 1 below.

All steel types were subjected to a 1-hour solution treatment at 1000°C and an aging treatment with the exception of steel No. 1 (standard steel SIS 2324) which was not subjected to the aging treatment but only to a normal quenching with water cooling. Naturally, the reason for this action is due to the fact, emphasized previously, that an aging treatment for the standard steel SIS 2324 is not feasible without incurring an unacceptable deterioration of the impact strength or the resistance to intercrystalline corosion.

Tables 1 and 2 show that even in case of small admixtures of aluminum, such as 0.1%, significant increases in strength are obtained after the aging treatment. As stated above, tests conducted with corresponding steel types without the aluminum admixture have shown that an increase in strength will not occur after conclusion

Table 1

Steel No.	Chemical Composition in % by Weight								
	C	Si	Mn	Cr	Ni	Mo	Nb	Al	N
1	0.09	0.74	0.97	26.0	5.0	1.45	—	—	0.01
2	0.04	0.59	0.73	24.6	6.7	1.54	1.05	0.10	0.02
3	0.04	0.62	0.75	24.5	6.4	1.49	1.06	0.30	0.02
4	0.09	0.64	0.92	24.7	6.4	1.50	1.13	0.66	0.03
5	0.09	0.64	0.85	24.6	7.1	1.49	1.12	0.64	0.03
6	0.08	0.66	1.60	27.1	7.1	1.53	1.22	0.90	0.02
7	0.05	0.53	0.97	23.9	6.4	1.48	0.95	0.01	0.04
8	0.06	0.53	1.02	26.4	6.4	1.54	—	0.58	0.03

Steel No. 1 in Table 1 above is the type SIS 2324 steel discussed earlier. Steels 7 and 8 are type SIS 2324 with niobium only, or with aluminum only, respectively, added thereto. The other types of steel (Nos. 2–6 inclusive) in Table 1 are examples of the present invention, and the steel types 4, 5 and 6 having aluminum contents ranging from 0.5% to 1.0% are especially characteristic of the invention.

Table 2 (on the following page) lists the mechanical properties of the steel types shown in Table 1, together with hardness and aging treatment.

of the aging treatment. These facts are therefore an indication of either a synergistically unexpected and surprising result of the niobium and aluminum combination, or a likewise unexpected, powerful effect of small admixtures of aluminum. Particularly outstanding are the results of the aging treatment of steel types 4, 5 and 6 with the higher aluminum contents.

The characteristics of the steel of the present invention will be further appreciated by reference to Table 3, below.

Table 2

Tensile Strength, Notch-Impact Resistance, Charpy-U and Hardness After Solution Anneal at 1000°C, One Hour, Water Cooling and Aging as Stated Below

Steel No.	0.2% PS kg/mm²	UTS kg/mm²	Elongation 5 D (Expansion)%	Reduction of Area Contraction %	Notch Impact Strength kgm/cm²	HV	Austenite Content % by Volume	Aging Treatment
1	51.0	64.3	27.0	60.4	9.7	230	26	None
2	66.7	80.6	22.0	56.0	8.4	282	18	575°C lh, water cooling
3	69.6	80.6	19.5	56.0	7.8	290	15	575°C lh, water cooling
4	83.6	92.5	18.0	59.4	7.9	321	13	575°C lh, water cooling
5	76.6	89.5	20.5	56.1	8.2	313	24	575°C lh, water cooling
6	91.5	99.5	14.5	43.8	4.6	356	10	575°C lh, water cooling
7	53.7	68.6	23.0	61.0	8.0	244	23	575°C lh, water cooling
8	85.6	94.5	17.0	47.4	5.5	302	10	575°C lh, water cooling
2	63.7	79.6	22.5	56.0	8.2	268	18	600°C lh, water cooling
3	66.7	81.6	20.5	56.0	7.5	274	15	600°C lh, water cooling
4	75.6	86.6	20.0	61.0	8.2	303	13	600°C lh, water cooling
5	69.6	84.6	21.5	61.0	8.7	280	24	600°C lh, water cooling
6	86.6	97.5	13.5	49.2	6.6	323	10	600°C lh, water cooling
7	52.7	67.6	23.0	61.0	7.6	236	21	600°C lh, water cooling
8	76.6	86.6	19.0	56.1	6.7	274	10	600°C lh, water cooling

Table 3

Temper and Austenite Content After a Mere Annealing In Solution at 1000°C, One Hour, Water Cooling

Steel	HV	Austenite Content (in % by volume)
1	230	26
2	236	18
3	237	15
4	237	13
5	235	24
6	254	10
7	233	21.0
8	224	10.0

A comparison of Tables 2 and 3 proves that the high strength characteristics of the steel types are definitely due to the aging treatment because the tables show that the steel types have a much lower hardness after being subjected only to solution anneal, and that the hardness after a mere solution anneal (as shown by Table 3) is fully comparable with the typical hardness which is obtained for the standard steel SIS 2324. Standard strength for the steel type SIS 2324 is approximately 50 kg/mm^2 0.2% proof stress. It is apparent that it will be necessary to admix aluminum with the steel types, as proposed by the present invention, in order to attain the desired increases in strength after aging treatment because the standard steel SIS 2324 does not show any increase in strength after aging treatment at 575° to 600°C.

It was found that aluminum contents between 0.5 and 1.0% are most suitable for attaining maximum increases in strength by age-hardening. Such aluminum contents, furthermore, have an advantageous influence on the steel's resistance to corrosion, another feature of the invention, an influence which is demonstrated clearly by tables 4 and 5 below.

Table 4

Results of Corrosion Tests (20 Hours in Boiling 1 % NaCl-Water Solution, Saturated with AgCl, and $Ca(OH)_2$). Conditions of Heat Treatment: Solution Anneal (in Solution) at 1000°C, One Hour, Water Cooling and Aging as Stated Below

Steel No.	Loss of Weight in % (Median Value)	Occurrence of Spot Corrosions	Occurrence of Intercrystalline Corrosions	Aging Treatment
2	3.9	throughout	insignificant	575°C lh
3	0.2	in spots	none	water
4	0.00	none	none	cooling
5	0.00	none	none	
6	0.00	none	none	
7	3.9	throughout	in spots	
8	0.4	in spots	in spots	
4	0.00	none	none	600°C lh
5	0.00	none	none	water
6	0.00	none	none	cooling
7	4.4	throughout	in spots	
8	1.5	in spots	in spots	

Table 5

Results of Corrosion Tests for a Steel No. 1 (SIS 2324) (20 Hours in a Boiling 1% NaCl-Water Solution, Saturated With AgCl, and $Ca(OH)_2$) Conditions of Heat Treatment: Quenching at 1000°C for one Hour, Water Cooling and Aging as Stated Below.

Steel No.	Aging Treatment	Loss of Weight In Percentage (Median Value)	Occurrence of Spot Corrosions	Occurrence of Intercrystalline Corrosion
1	None	0.00	None	None
1	600°C, 5 minutes, water cooling	9.5	throughout	throughout
1	600°C, 15 minutes, water cooling	10.9	throughout	throughout
1	600°C, 1 hour, water cooling	12.0	throughout	throughout

According to Table 5 the standard steel SIS 2324 shows a substantial loss of weight after the aging treatment (at 600°C, for 1 hour, with water cooling), while steel No. 8 (SIS 2324 + aluminum) shows a much lesser loss after an identical aging treatment according to Table 4. Steels 4, 5 and 6, also listed in Table 4, prove definitely that a combination of aluminum with niobium in steel SIS 2324 will eliminate completely the susceptibility to corrosion.

As previously emphasized, the standard steel SIS 2324 becomes susceptible to intercrystalline corrosion after aging treatments at temperatures ranging approximately from 500°C to 750°C. This is the case even after short periods of aging, and it is especially quick at a temperature around 600°C. Obviously, such susceptibility to intercrystalline corrosion is particularly troublesome and definitely unacceptable for many important fields of application, for example in centrifugal separators. Susceptibility to intercrystalline corrosion was examined for the steel types listed in Table 1, with the tests being carried out under the high strength conditions shown by Table 3, i.e., a 1-hour heat solution treatment at 1000°C, followed by water cooling, and then followed by an aging treatment at 575°C for 1 hour and water cooling, or followed by an aging treatment at 600°C for 1 hour and water cooling respectively. Corrosion tests were then conducted by using disks (3 × 20 mm diameter) which were subjected for 20 hours to a boiling 1% solution of sodium chloride, saturated with finely powdered silver chloride and calcium hydroxide. This method was found to be very effective to detect any susceptibility to intercrystalline corrosion in chlorinated media in the case of steels of type SIS 2324.

The corrosion test results are listed in Table 4 above. Steel No. 2 suffered some loss of weight but the corrosions were primarily spot corrosions, and intercrystalline corrosions were rare. The loss of weight was substantially lower for steel No. 3 than in the case of steel No. 2, and spot corrosions occurred only in isolated cases. Steels 4, 5 and 6 did not suffer any measurable loss of weight, and no corrosions were found at all.

The results of similar tests, conducted with standard steel SIS 2324, are listed in Table 5 above. When this standard steel SIS 2324 was tested by the above described method, aging treatments were conducted over various periods of time at approxiamately 600°C prior to the corrosion treatment. Even short-time aging treatments, such as 5 minutes, caused a very large loss of weight, e.g., almost 10%, and the loss became greater still when the time of treatment was lengthened. Furthermore, when the standard steel SIS 2324 was subjected to aging treatments, spot corrosions and very extensive intercrystalline corrosions occurred abundantly. However, if solution treatment at 1000°C for 1 hour, followed by water cooling, was used solely, steel type SIS 2324 did not suffer any measurable loss of weight and there was no corrosion at all.

The above tests demonstrate that steels composed in accordance with the present invention become, in spite of being aged to increase their strength characterisics, very resistant to general as well as intercrystalline corrosion. The corrosion resistance is fully comparable to the corrosion resistance of standard SIS 2324 steel in its merely quenched state, after the standard steel has been cooled down effectively from the solution temperature. If, however, the standard steel SIS 2324 is used in large dimensions, as is often the case, the rate of cooling throughout the critical temperature range will become so slow that the steel becomes susceptible to intercrystalline corrosion even after quenching. The steels of this invention are completely indifferent to this slow cooling-off process, and retain their resistance to intercrystalline corrosion even if these steels are employed in large dimensions.

The above test results demonstrate that the present invention makes it now feasible to produce a stainless, ferrite-austenitic steel of very high strength, good ductility and notch-impact resistance and excellent resistance to general as well as intercrystalline corrosion. This combination of characteristics was impossible to attain heretofore for steels of the kind here involved.

The steel of the present invention is particularly suitable for use in centrifugal separators and other rotating machine units which operate in hot chloride solutions or which come occasionally in contact with such solutions. Other fields of application are, for example, pump shafts, gear shafts, drive shafts for boat-engines, bolts, stirring equipment, and transport devices for the chemical industry and the cellulose industry, as well as any other parts which are subjected to high stresses in corrosive surroundings, especially if there is a danger of intercrystalline corrosion.

We claim:

1. A corrosion-resistant, austenite-ferritic steel which contains 10% to 35% by volume of austenite, said steel being adapted to attain an increase in strength by age-hardening, while retaining good ductility and notch-impact resistance as well as excellent resistance to intercrystalline corrosion, said steel consisting essentially of the following composition by weight:

C, a maximum of 0.15%
Si, a maximum of 2%
Mn, a maximum of 5%
Cr, from 20% to 30%
Ni, from 4% to 9%
Mo, from 1% to 3%
Nb, from 0.1% to 2.5%
Ti, a maximum of 1.5%
Al, from 0.1% to 2%, and
N, a maximum of 0.15%,

the remainder of said composition constituting iron and impurities, the atomic percentage of Nb plus the

atomic percentage of Ti in said steel composition being equal to or greater than the atomic percentage of C plus the atomic percentage of N.

2. The steel of claim **1** wherein the volume of austenite in said steel is between 10% and 25%.

3. The steel of claim **1** wherein the composition of said steel, given in percent by weight, consists essentially of:

C, a maximum of 0.10%
Si, a maximum of 1.0%
Mn, a maximum of 2.0%
Cr, from 22% to 28%
Ni, from 5% to 8%
Mo, from 1% to 2%
Nb, from 0.1% to 2.5%
Ti, a maximum of 1.5%
Al, from 0.1% to 2%, and
N, a maximum of 0.1%

and the remainder as previously recited.

4. The steel of claim **1** wherein the composition of said steel, given in percent by weight, consists essentially of:

C, a maximum of 0.10%
Si, a maximum of 1.0%
Mn, a maximum of 2.0%
Cr, from 24% to 27%
Ni, from 5.5% to 7.5%
Mo, from 1.3% to 1.8%
Nb, from 0.1% to 2.5%
Ti, a maximum of 1.5%
Al, from 0.1% to 2%, and
N, a maximum of 0.1%

and the remainder as previously recited.

5. The steel of claim **1** wherein the composition of said steel, given in percent by weight, consists essentially of:

C, a maximum of 0.10%
Si, a maximum of 1.0%
Mn, a maximum of 2.0%
Cr, from 24% to 27%
Ni, from 5.5% to 7.5%
Mo, from 1.3% to 1.8%
Nb, from 0.1% to 2.5%
Ti, a maximum of 1.5%
Al, from 0.5% to 1.0%, and
N, a maximum of 0.1%

and the remainder as previously recited.

6. The steel of claim **1** wherein the composition of said steel, given in percent by weight, consists essentially of:

C, from 0.01% to 0.10%
Si, a maximum of 1.0%
Mn, a maximum of 2.0%
Cr, from 24% to 27%
Ni, from 5.5% to 7.5%
Mo, from 1.3% to 1.8%
Nb, from 0.1% to 1.6%
Ti, a maximum of 1.0%
Al, from 0.5% to 1.0%, and
N, a maximum of 0.1%

and the remainder as previously recited.

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