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PROCESS OF TREATING STAINLESS STEELS

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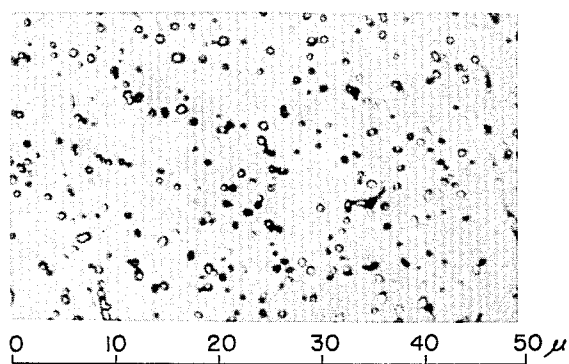


FIG. 1

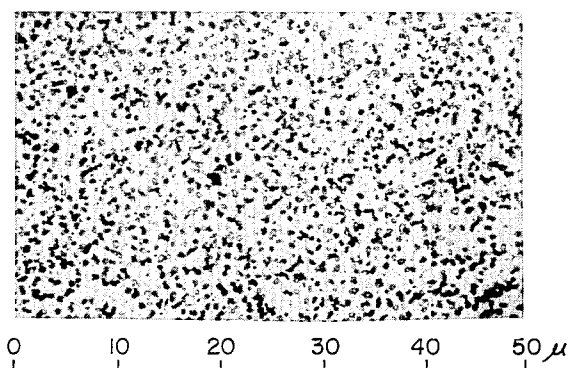


FIG. 2

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PROCESS OF TREATING STAINLESS STEELS

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7 Claims 10

ABSTRACT OF THE DISCLOSURE

Stainless steel of essentially the austenitic structure is cold worked to transform at least a portion of the austenitic structure to the martensitic structure. Then the steel is heated for a period of time at a temperature sufficient to transform the martensitic structure to the sigma phase. The resulting steel has excellent resistance to corrosion and mechanical strength particularly at higher temperatures.

This invention relates in general to a process of treating stainless steels and more particularly to a treating process of imparting heat resistant property to stainless steels of the austenitic structure.

Stainless steels of austenitic structure are generally poor in heat resistant property. At elevated temperatures they not only rapidly increase in corrosion rate and suddenly decrease in mechanical strength but also become brittle. This is primarily caused from the fact that when the stainless steels of austenitic structure are heated at elevated temperatures for long intervals of time, the sigma phase is precipitated at the grain boundaries therein resulting in a decrease in anti-corrosion and in an increase in brittleness. Therefore the existing stainless steels of austenitic structure are forced to be used at relatively low temperatures.

Heretofore it is the prevailing conception that the abovementioned decrease in both anti-corrosion and mechanical strength of the austenitic stainless steels at elevated temperatures cannot be inherently avoided in view of their properties. For this reason, heat resistant nickel base alloys such as expensive Inconel and Hasteloy have been commonly employed at elevated temperatures. It is very desirable and extremely economically advantageous to provide the type of austenitic stainless steels inexpensive and improved in anti-corrosion to allow them to be actually used at elevated temperatures.

Accordingly, it is an object of the invention to provide a new and improved type of stainless steels increased in anti-corrosion and capable of being actually used at higher temperatures than those previously possible by increasing the anti-corrosion of the austenitic stainless steels.

With the above cited object in view, the invention resides in a treating process of imparting heat resistant property to stainless steels of austenitic structure having a composition including, by weight, from 6 to 22% of nickel, from 16 to 35% of chromium, up to 2% of man-

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ganese, up to 1.5% of silicon, up to 0.122% of carbon and the balance being iron except for very small amounts of incident impurities which process comprises the steps of cold working a body of said stainless steel to precipitate the ferritic or martensitic phase therein, and heat treating the said cold worked body at a temperature of from 500° to 800° C. for a period of time sufficient to convert the precipitated ferritic or martensitic phase into the sigma phase.

The invention will become more readily apparent from the following detailed description taken in conjunction with the accompanying drawing in which:

FIGS. 1 and 2 are microphotographs of specimens cut from sheets of stainless steels treated in accordance with the teachings of the invention.

As previously stated, it is well known that if stainless steels of austenitic structure are heated at elevated temperature for long periods of time then the sigma phase is precipitated at the grain boundaries therein with the result that they become brittle and decrease in anti-corrosion. Heretofore this deteriorative effect has prevailingly been considered to be incapable of being inherently avoided in view of the properties of the austenitic stainless steels.

It has now been found that the sigma phase itself has excellent heat resistant and anti-corrosive properties. It has also been discovered that uniform distribution of the fine sigma phase in austenitic stainless steel is not only effective for preventing embrittlement of the steel due to precipitation of the sigma phase at the grain boundaries but also makes it possible to greatly increase the heat resistant and anti-corrosive properties of the stainless steel.

In order to uniformly precipitate the fine sigma phase in a body of austenitic stainless steel in question, the invention contemplates first to cold work the body of stainless steel to uniformly precipitate the fine ferritic phase or the fine martensitic phase or a mixture thereof and then to heat the cold worked body at a temperature of from 500° to 800° C. for a period of time of from several to several hundred hours. This results in stainless steel having fine sigma phase grains in a large amount uniformly distributed therein.

Austenitic stainless steels suitable for treatment according to the process of the invention may have any composition capable of precipitating the ferritic or martensitic phase therein by a cold working operation. However, it has been found that for the best result, the composition of the austenitic stainless steel includes, by weight, from 6 to 22% of nickel, from 16 to 35% of chromium, up to 2% of manganese, up to 1.5% of silicon, up to 0.12% of carbon and the balance being iron except for very small amounts of incident impurities. In order to decrease the total amount of carbides which might be precipitated by heat treatment, austenitic stainless steels low in content of carbon may be preferably used. If desired, austenitic stainless steels suitable for treatment according to the present process may additionally include, by weight, up to 3% of molybdenum, up to 1% of niobium and up to 1% of titanium.

It has been found that the many types of cold working processes, that is, cold swaging cold, rolling and cold reducing processes are performed to a reduction in area of from 10 to 95% with good results. Cold working may

be performed to a magnitude of from 10 to 95% below room temperature with a satisfactory result. Also the austenitic stainless steels may be subject to a shot peening operation until the ferritic or martensitic phase appears in the surface layers thereof alone.

Since an amount of the sigma phase precipitated is approximately proportional to an amount of the ferritic or martensitic phase precipitated in the cold working operation the composition of austenitic stainless steel and the degree of cold working can be appropriately selected to control the amount of ferritic or martensitic phase precipitated thereby to provide stainless steel including the desired sigma phase. It has been found that the particle size and distribution of the precipitated sigma phase grains

distribution of sigma phase grains such as illustrated in FIG. 1 wherein a microphotograph magnified by a factor of 2000 is illustrated for such a specimen as Heat No. 18-10L depleted in the sigma phase precipitated after cold rolling and heat treatment. On the other hand four of the plus signs correspond to the amount and distribution of sigma phase grains such as illustrated in FIG. 2 wherein a microphotograph illustrated for a specimen such as Heat No. 19-9L enriched with the sigma phase precipitated after cold rolling and heat treatment. Two or three plus signs mean the amount and distribution of sigma phase grains intermediate those illustrated in FIGS. 1 and 2 respectively. It has been found that the control sheets included no sigma phase.

TABLE I.—ANTI-CORROSION CHARACTERISTICS OF STAINLESS STEELS

Heat No.	Chemical Composition in wt. percent								Amount of Sigma Phase		Corrosion Weight Gain in mg./dm. ² /1,000 hours	
	C	Si	Mn	Ni	Cr	Mo	Nb	Ti	Invention	Conventional	Invention	Conventional
17-8.....	0.04	0.55	1.05	8.0	17.4				++	—	113	425
18-9.....	0.06	0.84	0.96	8.6	18.3				+++	—	26	251
18-10L.....	0.02	0.77	1.57	10.2	18.4				+	—	135	224
18-11L.....	0.03	0.54	0.81	11.0	17.8				+++	—	38	286
18-13.....	0.05	0.47	1.55	13.1	18.1				+++	—	19	291
19-9L.....	0.03	0.17	0.65	9.3	18.9				+++	—	6	267
19-9.....	0.07	0.59	0.93	9.0	18.9				++	—	67	279
19-10L.....	0.02	0.27	1.26	9.9	18.7				++++	—	12	289
19-10.....	0.05	0.59	1.71	9.9	19.1				+++	—	20	322
19-11L.....	0.03	0.66	0.92	10.6	18.6				++	—	43	261
23-14.....	0.12	0.79	1.36	13.7	22.6				+++	—	10	178
24-21.....	0.12	1.25	1.50	20.7	23.5				+++	—	8	125
17-13-Mo.....	0.06	0.94	1.82	12.5	17.0	2.60			+	—	128	510
18-9-Mo.....	0.06	0.63	1.70	9.3	17.7	2.43			+	—	121	502
19-14-Mo.....	0.03	0.63	1.78	13.8	19.0	2.41			++	—	56	283
18-11-Nb.....	0.06	0.69	1.21	11.0	18.0		0.71		+++	—	30	269
20-9-Ti.....	0.03	0.98	1.84	9.1	21.2			0.24	++++	—	10	150

depend upon the conditions for heat treatment. It has been also found that the lower the heat treating temperature the finer the particle size can be with the necessity of increasing the heating time. In this way, control of the amount and particle size of the sigma phase grains can provide a stainless steel having both the mechanical strength and the anti-corrosive property suitable for practical purposes.

The following examples illustrate the practice of the invention.

EXAMPLE I

Sheets of austenitic stainless steels having different compositions listed in the following Table I were cold rolled to a reduction of 80% at room temperature to transform a part of their austenitic structure to the ferritic or martensitic structure and then heated in a heat treatment furnace at 600° C. for 25 hours. The heated sheets were allowed to cool to room temperature within the furnace. The sheets thus treated were exposed to hot, high pressure steam at 600° C. under a pressure of 100 kgs./cm.² for 1000 hours. Then the sheets were determined in terms of corrosion weight gain in mgs./dm.²/1000 hrs. and the results are listed in Table I.

Also a control series of the same austenitic stainless steels were conducted with the same corrosion test after they were heat treated at 1050° C. for ½ hour followed by water quenching in conventional manner without cold working. The results also are listed in Table I. The amount and distribution of sigma phase grains precipitated in each of the tested specimens by the abovementioned cold rolling and heat treating operation is symbolically designated by the number of plus signs. A minus sign indicates no sigma phase. A single plus sign corresponds to the amount and

From Table I, it will be appreciated that the austenitic stainless steels treated according to the present process are greatly excellent in corrosion resistance as compared with those annealed in the conventional manner. Table I indicates that the higher the amount of the precipitated sigma phase the more the corrosion resistance will be improved. Further it has been proved that the amount of precipitated sigma phase depends upon the amount of the ferritic or martensitic structure transformed from the austenitic structure during the cold rolling of the invention.

EXAMPLE II

AISI Type 304L austenitic stainless steel including by weight, 0.013% of carbon, 0.27% of silicon, 1.07% of manganese, 9.6% of nickel and 18.5% of chromium was made in rods having a diameter of 10 mms. The rods were cold swaged to a reduction of 60% to transformation precipitate several tens percent of the austenitic structure to the ferritic or martensitic structure and then heated at 650° C. for 25 hours to form several tens percent of the sigma phase therein. The heated sheets were allowed to cool to room temperature. Control specimens were heat treated at 1050 C. for ½ hour followed by water quenching in the conventional manner without cold working.

All the rods thus treated were exposed to hot, high pressure steam at 25°, 300°, 400°, 500°, 600°, 700° C. under a pressure of 100 kgs./cm.² for a long interval of time (i.e., 1000 hours) to determine the corrosion resistant characteristics. Also the mechanical properties were measured by using circular test pieces ¼ in. in diameter with a gauge length of 1 in. The measurements were made between room temperature and 700° C. The results are listed in Table II.

TABLE II.—MECHANICAL AND CORROSION PROPERTIES OF STAINLESS STEELS AT ROOM TEMPERATURE AND ELEVATED TEMPERATURES

Specimen Treatments	Test Temper- ature in ° C.	Mechanical Properties				Corrosion Weight Gain in mg./dm. ² / 1,000 hrs.
		0.2% Yield Strength in kg./mm. ²	Ultimate Tensile Strength in kg./mm. ²	Elon- gation in percent	Reduc- tion in Area in percent	
Invention.....	25	50	87	40	40	-----
	300	48	56	27	60	10
	400	45	51	28	60	9
	500	35	42	32	63	8
	600	27	30	45	68	8
	700	20	21	60	75	-----
Conventional.....	25	18	56	75	58	-----
	300	8	38	40	73	10
	400	7	37	38	70	11
	500	7	32	35	66	48
	600	6	28	33	48	464
	700	5	22	42	44	-----

From Table II, it will be appreciated that the products treated in accordance of the process of the invention are far high in strength and good in corrosion resistance as compared with the conventional annealed products. It is noted that the invention provides stainless steels having not only an extremely high 0.2% yield strength but also a high elongation, a high tenacity and excellent corrosion resistant properties at high temperature.

EXAMPLE III

Rods identical to those used with Example II were first cooled in liquid nitrogen and then cold swaged to a reduction of 20% at -196° C. followed by heat treatment at 650° C. for 25 hours. The resulting rods exhibited substantially the same effects as rods cold swaged to a reduction of more than 40% followed by the similar heat treatment. This means that cold working at low temperatures is more effective for transformation of the austenitic to the martensitic structure than a working at room temperature. In other words, a lower temperature permits a working degree to reduce with the same result.

EXAMPLE IV

Pipes of an austenitic stainless steel substantially similar in composition to that used with Example II and having an outside diameter 28 mms. and a wall thickness of 2 mms. were cold worked into pipes 19 mms. in outside diameter and 1 mm. in wall thickness at room temperature by a Cold Pilgar Process and then subject to a heat treatment at 650° C. for 25 hours. The results were substantially similar to those in Table II.

EXAMPLE V

Steel sheets made of Heat No. 19-10L (see Table I) were subject to shot peening to strongly work their surfaces and then to heat at 600° C. for 25 hours. The sheets thus treated had corrosion resistance characteristics substantially similar to those shown in Table I.

The following Table III shows a comparison of AISI Type 304L stainless steel treated in accordance with the present and conventional processes and known nickel alloys in terms of mechanical properties at 25° C. and corrosion resistance to hot steam at 600° C. under a pressure of 100 kgs./cm.². Table III indicates that the stainless steel treated according to the invention is comparable to Inconel and Hasteloy in mechanical strength at room temperature and in corrosion resistance to hot steam.

TABLE III.—MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF STAINLESS STEELS AND NICKEL ALLOYS

Alloy	Mechanical Properties at 25° C.				Corrosion Weight Gain in mg./dm. ² / 1,000 hrs.
	0.2% Yield Strength in kg./mm. ²	Ultimate Tensile Strength in kg./mm. ²	Elon- gation in percent		
25					
30					
Conventional AISI Type 304L Stain- less Steel.....	20	53	78		294
Present AISI Type 304L Stainless Steel.....	50	87	40		8
Inconel.....	24	63	42		7
Inconel X.....	76	121	24		5
35					
Hasteloy B.....	38	87	54		32
Hasteloy C.....	35	76	58		13
Monel.....	18	46	47		133

From the foregoing, it will be appreciated that the present invention provides stainless steels greatly improved in heat resistance and anti-corrosion by the formation of the sigma phase grains uniformly distributed in a large amount therein.

What we claim is:

1. A process for obtaining stainless steel highly corrosion resistant even at elevated temperatures, from stainless steel of austenitic structure having a composition by weight of 6 to 22% of nickel, from 16 to 35% of chromium, up to 2% of manganese, up to 1.5% of silicon, up to 0.12% of carbon, and the balance being iron except for very small amounts of incidental impurities, which comprises cold working at least partly a body of said stainless steel to transform at least part of the austenitic structure to a structure selected from the group consisting of ferrite and martensite and then heating the cold worked body of steel for a period of time at a sufficient temperature to transform the resultant ferritic or martensitic structure into the sigma phase.

2. A process of treating a body of stainless steel of the austenitic structure having a composition including, by weight, from 6 to 22% of nickel, from 16 to 35% of chromium, up to 2% of manganese, up to 1.5% of silicon, up to 0.12% of carbon and the balance being iron except for very small amounts of incident impurities, comprising the steps of cold working at least partly the body of stainless steel to transform at least one part of the austenitic structure to a structure selected from the group consisting of ferrite and martensite and heating the cold worked body at a temperature of about 600° C. to 800° C. for a period of time sufficient to transform the thus obtained ferritic or martensitic structure to the sigma phase.

3. A process as claimed in claim 1, wherein said composition additionally includes up to 3% of molybdenum, up to 1% of niobium and up to 1% titanium.

4. A process as claimed in claim 1, wherein the cold working is performed to a reduction of from 10 to 95%

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and the heating time ranges from a few hours to a few hundred hours.

5. A process as claimed in claim 1, wherein the cold working is one selected from the group consisting of cold rolling, cold drawing, cold reducing and cold swaging.

6. A process as claimed in claim 1, wherein after said body having been cold worked below 0° C., said body is cold worked to a reduction of from 10 to 95% and is then subjected to heat treatment at a temperature of the order of 600° to 800° C. for a few hours to a few hundred hours.

7. A process as claimed in claim 1, wherein said body is subjected to shot peening until the surface thereof has a structure selected from the group consisting of ferrite and martensite.

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