

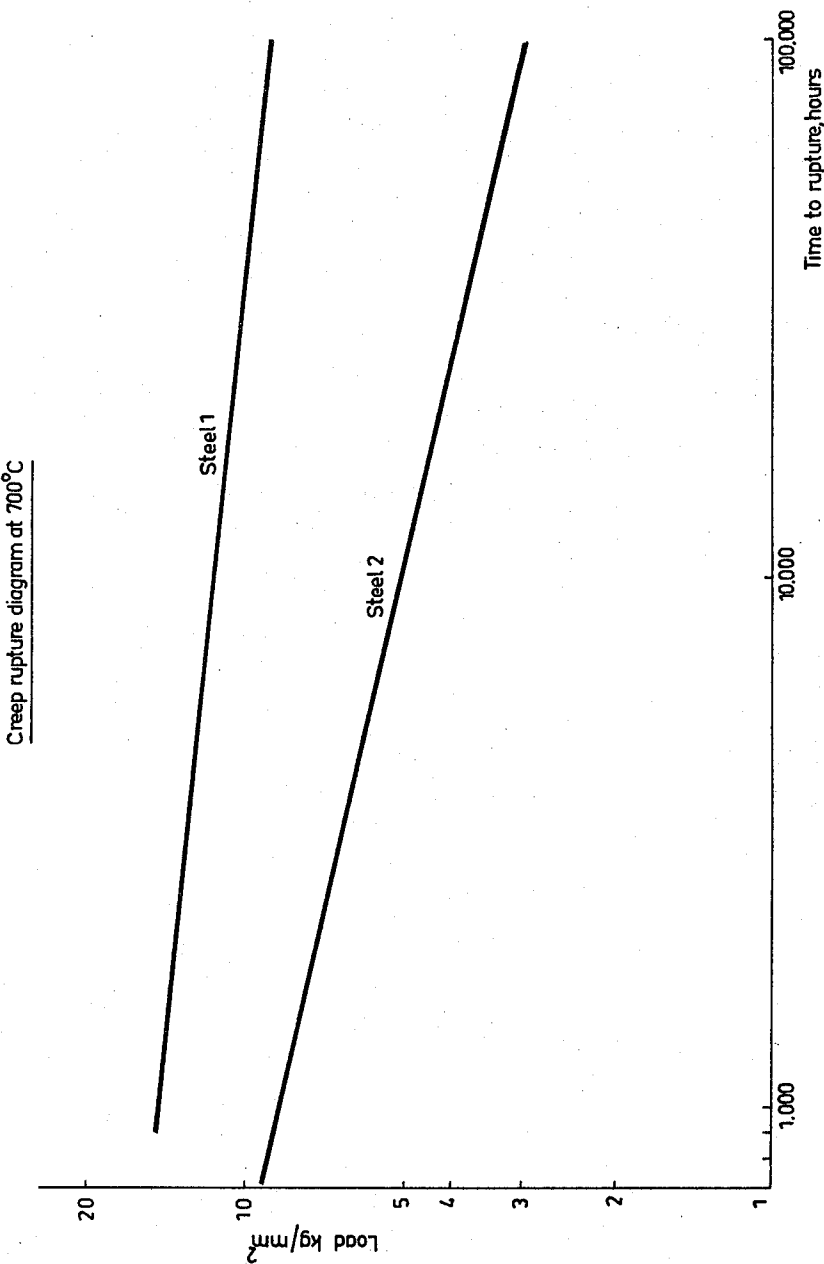
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ALLOY STEEL AND METHOD OF MAKING SAME

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ALLOY STEEL AND METHOD OF MAKING SAME

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12 Claims. (Cl. 75—128)

ABSTRACT OF THE DISCLOSURE

An austenitic chromium-nickel steel having very high creep strength at high temperatures under prolonged conditions of heavy loading comprises 0.03–0.20% carbon, up to 1.0% silicon, up to 4.0% manganese, 13.0–20.0% chromium, 10.0–35.0% nickel, 0.3–0.8% titanium, 0.2–1.7% molybdenum, at least 0.002 but not more than 0.020% boron, not more than 0.018% nitrogen, not more than a total of 1.0% of metals selected from a first group consisting of vanadium, tungsten, columbium and tantalum, up to 1.0% cobalt, up to 0.5% copper, up to 0.2% of each of a metal selected from a second group consisting of cerium and zirconium, and iron the balance save for insignificant quantities of impurities.

The desired properties of this alloy composition are realized by carrying out a steel-making procedure involving either vacuum melting or vacuum casting or both and subsequent hot working, annealing and cold working steps.

The present invention relates to alloy steels and articles made therefrom.

Due to rapid development, for example in steam boilers and nuclear reactors, the need has increased for heat resistant steel alloys with good hot working properties together with substantially improved creep strength at high temperatures particularly under prolonged conditions of heavy loading. Such heavy loading is, for example, present in steam boiler tubes subjected to high internal pressures of steam superheated to high temperatures. The austenitic chromium-nickel steels, which, in comparison with ferritic steels, have superior creep strength, have been of great interest for such uses, and a large number of such steel alloys have been proposed. It has, however, been found that austenitic chromium-nickel steels have not necessarily fulfilled the desired high quality requirements. In general the strength over very long loading periods at high temperatures, e.g. between 650–750° C., has been found insufficient, although the short load-time strength of the steel has been high. Another disadvantage of these prior alloys has been insufficiently good hot working properties due to unsuitable choice of alloying elements, unsuitable relative proportions between the alloying elements and/or too high a content of alloying elements relative chromium and nickel. Still another disadvantage in the earlier proposed steels of the above type has often been an insufficient rupture elongation, which, for safety reasons, has rendered them unsuitable for the intended use.

One of the principal objects of the present invention is to provide austenitic chromium-nickel steels in which the above disadvantages are substantially eliminated or minimized.

Further objects of the invention are to provide such steels and articles manufactured therefrom which under load for long periods of time e.g. 15,000 hours or more and at temperatures up to at least 750° C. have a very high long time creep strength, i.e. the articles will with-

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stand heavy loading over very long time periods without substantial deformation or rupture. The articles of the invention have a good corrosion and oxidation resistance at the working temperatures, a large elongation immediately before rupture and excellent hot working properties resulting in easier and cheaper manufacture. The invention makes it possible for instance to improve the service conditions for superheated steam boiler tubes with regard to pressure, temperature and service time.

According to the invention there is provided an austenitic chromium-nickel steel which under long-time stresses, for example, 15,000 hours or more at temperatures up to at least 750° C., has a very high long-time strength and in addition good resistance to corrosion and oxidation and a great elongation before rupture. The steel contains, besides iron with insignificant quantities of impurities such as sulphur and phosphorus, 0.03–0.20% carbon, up to 1% silicon, up to 4% manganese, 13–20% chromium, 10–35% nickel, 0.3–0.8% titanium, 0.2–1.7% molybdenum, 0.002–0.02% boron and up to 0.018% nitrogen and optionally a total of up to 1% of vanadium, tungsten, columbium and/or tantalum, up to 1% cobalt, up to 0.5% copper and up to 0.2% each of cerium and/or zirconium.

The invention also includes a method for the manufacture of the said articles. The articles of the invention, include tubes, wires, rods, strips and plates which may be particularly useful, for example, for superheater tubes and tubes for steam boilers, nuclear reactors and the like, welding rods and turbine blades and rotors.

A composition of steel according to the invention and preferred for many purposes is the following: 0.06–0.14% carbon, up to 0.50% silicon, 0.3–3% manganese, 14–17% chromium, 13–20% nickel, 0.5–1.7% molybdenum, 0.3–0.8% titanium, 0.004–0.02% boron, up to 0.015% nitrogen, the balance being in the main iron with insignificant quantities of impurities, the contents of sulphur and phosphorus each being preferably less than 0.020% and 0.030% respectively.

The alloying elements are balanced in relation to each other within relatively narrow limits, and moreover titanium should always be present together with molybdenum and boron. Furthermore it is necessary that the content of nitrogen is held as low as possible, and the steel is therefore preferably manufactured by a vacuum melting and/or vacuum casting process.

The high strength under elevated temperature conditions of steels according to the invention is illustrated in the accompanying drawing in which the single figure is a diagram showing the creep rupture curve of a steel 1 within the scope of the invention in comparison with the creep rupture curve of another steel 2, outside the scope of the invention. The diagram clearly shows the very good long-time strength of steel 1, which is illustrated by the small inclination of the creep rupture curve, characteristic for this steel. By this favorable property the steel is suitable for use under high temperatures and stresses for a substantially longer time than hitherto has been common and possible.

The steel has further such a composition that it is not embrittled under long-time use within the service temperature range by formation of sigma-phase. This ensures that the toughness at lower temperatures will be satisfactory, which is important in connection with temporary cessation of high-temperature conditions. Due to the low alloy content, in addition to chromium and nickel, and the choice of alloying elements, very good hot working properties are obtained, resulting in a relatively simple manufacturing procedure in comparison with earlier known steel alloys, and at the same time, costs can be kept at a reasonable level. Moreover the steels according to the invention have, with regard to the high long-time

creep strength, a very good plasticity or elongation before creep rupture, which is of a great significance, since the risk of sudden and unexpected ruptures after only a more or less insignificant preceding deformation is eliminated.

To obtain the high long-time creep strength, the alloying elements have been selected and their quantities have been balanced in relation to each other with special regard to precipitation of carbides, the strength and stability of the matrix of the steel and the influence of impurities especially upon the grain boundaries at elevated temperatures.

As well as titanium, columbium has been previously used as a carbide former in austenitic steels for elevated temperature service. It has, however, been found that titanium gives far better properties to the steel. The necessary content of titanium in the steel has been found to lie in the range 0.3–0.8%. A higher content of titanium is for several reasons not desirable as it, inter alia, lowers the workability and the plasticity of the steel.

Unexpectedly, it has further been found that the long-time creep strength of the steel is remarkably increased if the content of nitrogen dissolved in the steel is held as low as possible. The use of titanium is, in this respect, advantageous, because, in addition to its disposition to form carbide precipitation, it also pronouncedly lowers the content of nitrogen dissolved in the steel. Normal nitrogen content, e.g. 0.020% and more, has not previously been considered to be deleterious in heat resistant steels, and nitrogen has, in fact, often been added in order to increase heat resistance. In steel according to the invention it is, however, necessary that the nitrogen content is held low in order to obtain the desired properties. Thus the nitrogen content must not exceed 0.018% and preferably not above 0.015%. Sometimes it is desirable to have a still lower upper limit for nitrogen content, for example 0.012% or even as low as 0.010%. In order to obtain a low nitrogen content the manufacturing procedure for the steel should include a suitable treatment step for removal of nitrogen. This is preferably performed by vacuum treatment of the molten steel, for example by re-melting in a vacuum arc furnace.

The carbon content of the steel should be in the range 0.03–0.20% and should further be related to the quantity of titanium to aid in the desired removal of nitrogen and the desired carbide precipitation. A suitable range for the carbon content is 0.06–0.14%, and often 0.08–0.12%. For the relation between the titanium, carbon and nitrogen contents of the steel the following formula can be used:

$$\frac{\text{Ti}-3 \times \text{C}}{\text{N}} > 1$$

From this formula it can be appreciated that the content of titanium should exceed a certain minimum determined by the content of carbon and nitrogen in the steel. The content of dissolved nitrogen can then be reduced by binding part of the nitrogen to titanium as nitride.

It is of great importance that the matrix of the steel has a sufficient thermodynamic stability. The degree of stability is in the first place determined by the content of chromium, nickel and molybdenum, the content of nickel having particular influence upon the stability of the matrix structure.

The resistance of the steel against corrosion and oxidation is in the first place determined by the content of chromium. In the mention range of 13–20% of chromium, the lower limit is determined by the condition that a sufficient resistance against corrosion must be obtained, the upper limit being determined by the fact that the structural stability rapidly decreases with rising chromium content. Preferably, the steel should contain at the most 18% and preferably at least 14% chromium. The range 14.5–17% chromium has been found especially advantageous.

The content of nickel must, with regard to the stability of the steel, not be lower than 10% and preferably not lower than 12.5%. In those cases where very high resistance against corrosion is required, a nickel content of up to 35% may occur. Normally the nickel content is chosen within the range of 13–30%, and often 13–20%, but for most purposes the range 13–17% nickel is suitable. As an example of the chromium and nickel contents in steels for use at temperatures up to 750° C., 14.5–15.5% chromium and 14.5–15.5% nickel, have been found optimal.

The silicon content should be held low and must not exceed 1%. Usually it should be below 0.5%. A variation of the content of manganese can be permitted within the limits 0–4%, having regard to the fact that too high a quantity of manganese can result in difficulty in shaping the steel, at the same time as manganese can contribute to an increased solubility of carbides in connection with the normal solution heat treatment, by which the heat resistance can be promoted. Normally the manganese content should, however, be chosen within 0.3–3%. A content of 0.5–2.5% and often 1–2% has for many purposes been found particularly suitable.

The simultaneous occurrence of both molybdenum and boron in the steel is very important. Molybdenum has two effects, opposed to each other, upon the heat resistance of the steel. It has thus been found that an increased molybdenum content in the first place raises the short-time strength of the matrix and also the long-time strength increases distinctly with the molybdenum content up to an optimal limit. If the optimal content of molybdenum is exceeded this results in a lowered long-time strength, which means that the creep rupture curve in a double-logarithmic diagram has a relatively steep inclination, and also other desired properties are impaired. With the aid of small additions of boron it is, however, possible to raise the optimal content of molybdenum, and thus to obtain a substantial increase in long-time strength. The addition of boron also has other advantages e.g., the precipitation of carbide is speeded up, thus effectively lowering the deformation speed. The content of molybdenum is selected within the range 0.2–2.1% and the boron content within the range 0.002–0.2%. Preferably the content of molybdenum should, however, not exceed 1.7%, while the boron content as a rule should be at the most 0.020% and suitably at least 0.004%. Quantities of 0.7–1.5% molybdenum and 0.005–0.012% boron have been found particularly suitable.

Apart from nitrogen, other impurities normally present in steel must occur only in insignificant quantities. It has thus, inter alia, been found that at least a low content of sulphur has a favorable influence upon the inclination of the creep rupture curve. For instance the sulphur content should not exceed 0.020%, and preferably not exceed 0.015% while the content of phosphorus should not exceed 0.030%, and preferably not exceed 0.020%, said maximum values being lower than the ones normally specified for heat resistant steels.

Besides the above described alloying elements, others which do not have an unfavorable effect upon the desired properties, can be added to the steel. Thus the steel can contain at the most 1% vanadium, tungsten, columbium and/or tantalum, at the most 1% cobalt, at the most 0.5% copper and at the most 0.2% of each of cerium and/or zirconium. The content of vanadium, tungsten and columbium and/or tantalum respectively should, however, in general not exceed 0.5%.

The following table clearly illustrates the improvement in long-time creep strength obtained in steels according to the invention particularly by the prescribed proportions of molybdenum and boron as well as the negative influence of a too high nitrogen content. Of the steels in the table, steel A lies within the scope of the invention and steels B, C and D lie outside of the scope of the invention.

TABLE

[Time in hours for creep rupture of austenitic chromium-nickel steels under a load of 10 kg./mm.² at 700° C. The steels have been annealed at 1,150° C.]

	A	B	C	D
Percent:				
C	0.09	0.09	0.08	0.10
Si	0.30	0.38	0.22	0.24
Mn	1.52	1.36	1.65	1.76
P	0.009	0.015	0.013	0.007
S	0.006	0.014	0.007	0.008
Cr	14.7	14.9	15.0	14.9
Ni	14.8	15.0	14.9	14.7
Mo	0.93	0.88	-----	0.89
Ti	0.33	0.58	0.29	0.22
B	0.0075	-----	-----	0.012
N	0.012	0.010	0.016	0.023
Time to rupture in hours	>25,000	3,200	2,500	1,500

The steels in the table contained besides the mentioned alloying elements only iron with insignificant quantities of impurities. Of these steels A, B and C had been vacuum refined by re-melting in a vacuum arc furnace. It should be noted that for steel A, containing molybdenum as well as boron, the time period to rupture is about eight times the time period to rupture for steel B, which contains no boron, and steel C, which contains neither molybdenum nor boron. The influence of an excessive amount of nitrogen and a too low Ti/C ratio can be clearly perceived from the test result with steel D.

The very favorable effect upon the long-time creep resistance of the steels according to the invention appears clearly from the previously mentioned diagram in the accompanying drawing. Steel 1 in the diagram, which is within the scope of the invention, had the following composition: 0.09% carbon, 0.3% silicon, 1.5% manganese, 14.7% chromium, 14.8% nickel, 0.93% molybdenum, 0.33% titanium, 0.008% boron, 0.012% nitrogen, the balance being iron with usual impurities. The compared steel 2 not within the scope of the invention had a composition typical for earlier heat-resistant austenitic chromium-nickel steels. The approximate composition thereof was the following: 0.06% carbon, 0.6% silicon, 1.5% manganese, 17.5% chromium, 11.5% nickel, 0.4% titanium, the balance being iron with usual impurities. By choice of alloy elements and a suitable balancing of their quantities in relation to each other and in different other respects inter alia by maintaining a low impurity content the creep rupture curve of steel 1 has a very favorable, small inclination, making the steel suitable for use during very long time periods at substantially higher temperatures than earlier has been possible for similar steel types. Also other properties of the steel are important in this connection such as the great rupture elongation, the good hot working properties and the resistance against corrosion and oxidation. As above mentioned it has been found that the steel in order to have the said small inclination of the creep rupture curve should be thermodynamically stable. Molybdenum has a favorable strength increasing effect upon the matrix of the steel but may, if the quantity thereof exceeds a certain optimal value, cause a certain instability, said optimal value being dependent especially on the content of nickel. The relation of molybdenum content to nickel content should therefore not exceed 0.1.

As can be seen from the diagram the small inclination of the creep rupture curve for steel 1, having a composition according to the invention, results in a very high creep rupture limit at 700° C. as well as for 10,000 hours and substantially longer periods of time. Usually the creep rupture limit substantially exceeds 10 kg./mm.² at said temperature and 10,000 hours.

Further it can be pointed out that the creep rupture curve at 700° C. in a double-logarithmic diagram for the time period between 500 and 15,000 hours lies above a straight line through the points 16 kg./mm.² at 500 hours and 0.5 kg./mm.² at 15,000 hours, the creep rupture curve having in addition thereto an inclination which is not greater than the inclination of said straight line.

A further characteristic of the steels according to the invention is that they have, relative to the high long-time creep strength, a very great elongation before creep rupture, the material thus being able to endure a very great deformation without rupturing. Under normal service conditions the actual steels should have as small elongation as possible but in case the steel should approach rupture the elongation should be as great as possible before failure occurs in order to avoid surprise failure and in order to lessen the deleterious consequences thereof. It is therefore important to fulfill the twofold condition of a small elongation under normal service when no risk of rupture is present but a great creep rupture elongation when the conditions approach rupture. The steels of the invention fulfill this twofold condition in a more pronounced way than was the case with known prior steels. After annealing the steel between 1000–1250° C., the usual heat treatment before taking into service, creep rupture elongations up to 40 to 50% and as a rule not smaller than 30 to 35% are obtained as measured on a specimen length of about 35 mm. As an example the following test results are referred to, which were obtained from tests with steel alloys within the scope of the invention.

Temperature, °C.	Load kg./mm. ²	Time to creep rupture, hr.	Creep rupture elongation, percent
700	11	8,500	39
700	13	3,800	36

The creep rupture elongation for previously known heat resistant alloys is usually not higher than 25% and often only about 15% or less.

The creep strength of the steels of the invention can be further raised by a special cold working and annealing procedure. This procedure lessens the stress rupture elongation but in spite of the extremely high long-time creep strength which then can be attained, the creep rupture elongation will not be less than 10% and often not less than 15%, which corresponds to 3 to 4% in earlier types of steel which have been subjected to a similar treatment.

The invention comprises also a method for manufacture of articles from the steels of the invention. In manufacturing the steel the necessary removal of nitrogen must be effected, and the addition of alloying elements, especially ferrochromium, is effected in such a way that pick-up of nitrogen from the surrounding atmosphere is prevented. A very suitable method for limiting the nitrogen content to the desired low values is vacuum refining as for instance vacuum melting and/or degassing. An additional advantage, especially in vacuum re-melting in an arc furnace, is that a more homogeneous distribution, especially of titanium, can be obtained.

The shaping of the articles made from steels according to the invention may comprise hot and cold working, for example forging, extrusion, rolling and/or drawing. The articles are thereafter normally subjected to heat treatment consisting of annealing at a temperature of 1050–1300° C. preferably 1100–1250° C., by which the high long-time creep strength and good plasticity are obtained.

By a suitable combination of shaping procedures and heat treatment the long-time creep strength can be increased by up to 50% in comparison with the strength obtained by the earlier mentioned shaping and heat treatment procedures. At the same time the plasticity of the steel is lessened but still having at least 10% elongation or more before failure also at the extremely high rupture strength level which can be attained. The said treatment comprises hot working, for instance extrusion of rolling, and thereafter cold working, which means shaping at temperatures up to the recrystallization temperature of the steel, said shaping reducing the cross sectional area of the object by 5–45%. The material after being hot and cold worked in said way is finally subjected to an annealing treatment at 550–850° C. The method described may

omit the manufacturing steps other than cold working and annealing as above described.

I claim:

1. An austenitic chromium-nickel steel which under long-time stresses at temperatures up to at least 750° C. has a very high long-time strength and good resistance to corrosion and oxidation and a great elongation before rupture, said steel having the following composition in weight percents:

Carbon	0.03-0.20.
Silicon	Up to 1.0.
Manganese	Up to 4.0.
Chromium	13.0-20.0.
Nickel	10.0-35.0.
Titanium	0.3-0.8.
Molybdenum	0.2-1.7.
Boron	0.002-0.020.
Nitrogen	<0.018.

A first group consisting of vanadium, tungsten, columbium and tantalum -- Up to a total of 1.0.

Cobalt ----- Up to 1.0.

Copper ----- Up to 0.5.

A second group consisting of cerium and zirconium -- Up to 0.2 each.

Iron ----- Balance save for not more than insignificant quantities of impurities.

2. A steel according to claim 1 containing 14.5-15.5% chromium and 14.5-15.5% nickel.

3. A steel according to claim 1 having a carbon content of 0.06-0.14%.

4. A steel according to claim 1 containing 0.3-3% manganese.

5. A steel according to claim 1 containing less than 0.020% sulphur and less than 0.030% phosphorus.

6. A steel according to claim 1 containing at the most 0.5% vanadium, at the most 0.5% tungsten and at the most 0.5% of a metal selected from the group consisting of columbium and tantalum.

7. A steel according to claim 1 wherein the relation between the constant of titanium, carbon and nitrogen in the steel is determined by the formula:

$$\frac{Ti-3 \times C}{N} > 1$$

8. An austenitic chromium-nickel steel which under long time stresses during 10,000 hours and more at temperatures up to at least 750° C. has a very high long-time strength and good resistance to corrosion and oxidation and a great elongation before rupture, said steel consisting of 0.06-0.14% carbon, up to 1.0 silicon, 0.3-3%

manganese, 14-17% chromium, 13-20% nickel, 0.5-1.7% molybdenum, 0.3-0.8% titanium, 0.004-0.02% boron, less than 0.015% nitrogen the balance being iron with insignificant quantities of impurities, the content of sulphur being less than 0.020% and the content of phosphorus being less than 0.030%.

9. Method for manufacturing steel products from steel having the following composition in weight percents:

Carbon	0.03-0.20.
Silicon	Up to 1.0.
Manganese	Up to 4.0.
Chromium	13.0-20.0.
Nickel	10.0-35.0.
Titanium	0.3-0.8.
Molybdenum	0.2-1.7.
Boron	0.002-0.020.
Nitrogen	<0.018.

A first group consisting of vanadium, tungsten, columbium and tantalum -- Up to a total of 1.0.

Cobalt ----- Up to 1.0.

Copper ----- Up to 0.5.

A second group consisting of cerium and zirconium -- Up to 0.2 each.

Iron ----- Balance save for not more than insignificant quantities of impurities.

which comprises subjecting the steel to vacuum treatment and then to hot working at a temperature above 1000° C. followed by cold working to the desired shape.

10. Method according to claim 9, wherein the steel after the hot and cold working is annealed between 1050-1300° C.

11. Method according to claim 9 wherein the cross sectional area of the steel is reduced 5-45% during the cold working without intermediate annealing steps.

12. Method according to claim 9 wherein the steel is subjected to a finishing stage of annealing between 550-850° C.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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May 21, 1968

Lennart Oskar Egnell

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 43, "constant" should read -- content --.

Signed and sealed this 16th day of September 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents