June 11, 1957 T. ANGEL ET AL 2,795,519

METHOD OF MAKING CORROSION RESISTANT SPRING STEEL AND PRODUCT THEREOF

Filed March 25, 1955

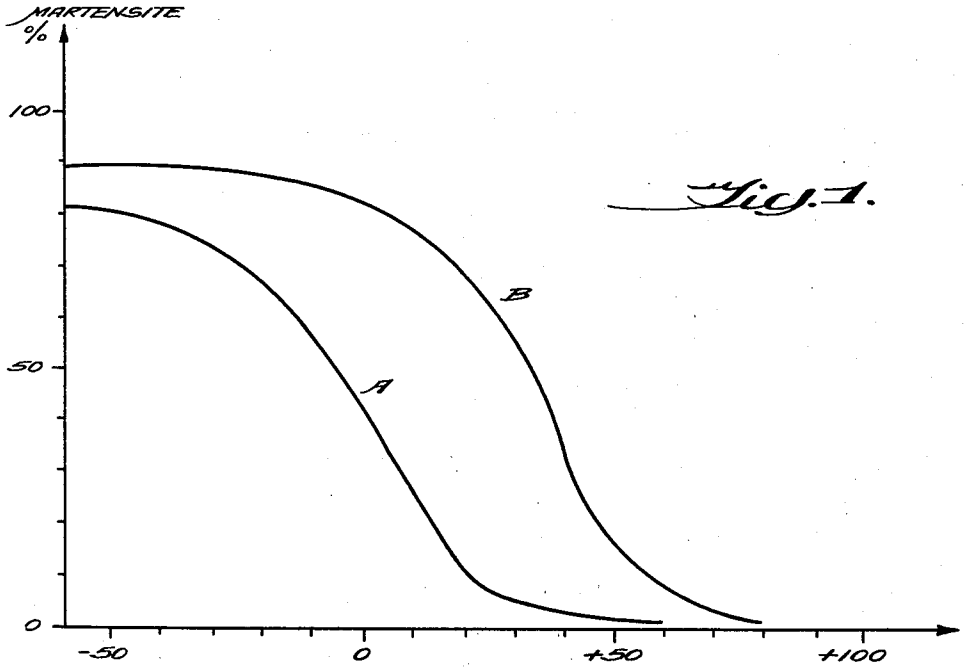


Fig. 1.

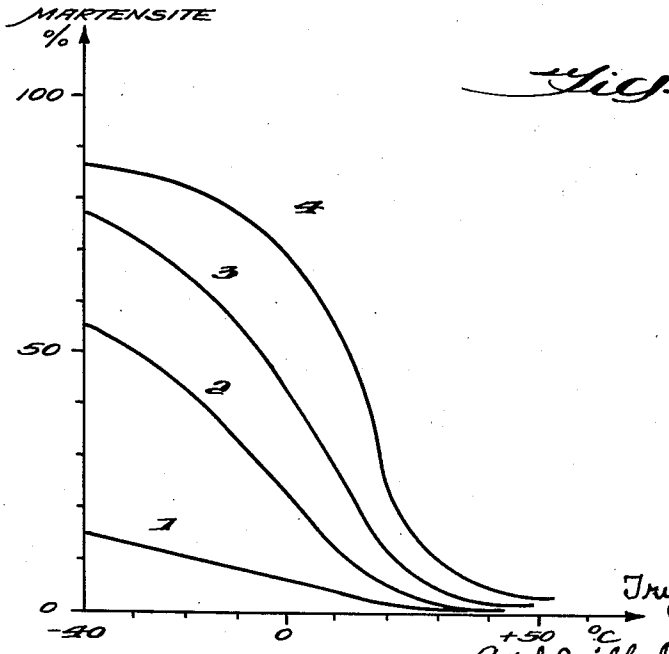


Fig. 2.

INVENTORS
Tryggve Angel
Axel Wilhelm Bernstein
BY Pierce, Scheffler & Parker
ATTORNEYS

United States Patent Office 2,795,519
Patented June 11, 1957

2,795,519

METHOD OF MAKING CORROSION RESISTANT SPRING STEEL AND PRODUCT THEREOF

Tryggve Angel and Axel Wilhelm Bernstein, Sandviken, Sweden, assignors to Sandvikens Jernverks Aktiebolag, Sandviken, Sweden, a corporation of Sweden

Application March 25, 1955, Serial No. 496,904

Claims priority, application Sweden March 27, 1954

6 Claims. (Cl. 148—12)

The present invention relates to alloy steel springs and spring material having not only excellent spring properties such as high values of modulus of elasticity, ultimate strength and fatigue limit at low, normal and elevated temperatures but also good corrosion resistance.

Heretofore, in order to secure this combination of properties, highly alloyed and expensive steels containing alloying elements which interfere with the hot and cold working thereof have been used. Also carbon steel provided with permanent corrosion preventing coatings has been used. Such corrosion preventing coatings are however not always permanently effective and are costly and difficult to apply and may cause hydrogen embrittlement of the steel.

For a long time the need has existed for a product having good spring properties made from the well known austenitic stainless steel compositions. Such compositions cannot however have their strength increased by heat treatment in the usual way because they retain their austenitic structure down to and below room temperature and therefore cannot have their strength increased by transformation of the soft austenite into hard martensite. A hardening, which is not generally desirable, and which is due to a certain transformation of austenite into martensite has been observed as a result of cold working of such austenitic alloys.

Earlier attempts to reduce the cross sectional area 25–60% by cold rolling of austenitic chromium nickel steels, followed by heat treating at a relatively low temperature, for example between 74–200° C. has given a certain increase in strength, which, however, is not sufficient when high strength and elastic properties, as for instance in spring steels for use in watches and instruments are required. Material treated in this way is not suitable for springs which have to withstand elevated temperatures, for example 300–500° C.

It has further been proposed to use certain metastable austenitic steels, which have been subjected to a very considerable decrease in cross sectional area preferably about 90%, by cold working followed by tempering. It is true that these steels, which are the subject of application Serial No. 260,856, filed on December 12, 1951, in the name of Axel Wilhelm Bernstein have given springs with excellent elastic properties, but a severe disadvantage thereof is the extreme degree of reduction, which gives rise to difficulties in their manufacture and necessitates very expensive equipment. With modern cold rolling mills it has not been possible to reduce a rough, relatively thick material as much as 90% and thus the limit of the thickness for the finished spring steel material has been restricted to about 0.5 mm.

We have found through extensive investigations that by choosing a suitable composition of the austenitic steel very excellent elastic properties may be obtained, even at a relatively low degree of reduction. The composition should be so chosen that the finished product after a reduction of the cross sectional area which may not be less than 50% and which should not exceed 75% should contain between 25 and 60%, preferably about 50% of martensite.

The rate of transformation from austenite to martensite is dependent partly on the stability of the austenite, i. e. its greater or less tendency to transform and partly on the degree of deformation. For a certain amount of cold working the quantity of martensite formed increases with decreasing stability of the austenite. Inversely, it can be said that for a certain stability of the austenite, the quantity of martensite formed is increased with the degree of cold working. Any desired quantity of martensite may be obtained in the steel. The resulting strength will depend upon this transformation. The stability of the austenite depends partly on the percentages of the alloying elements and partly on the working temperature. Different alloying elements have different effects upon the stability. By lowering the temperature the stability of the austenite is decreased. Thus the working temperature affords a further means of controlling the transformation.

Our experiments have shown that relatively insignificant changes in the percentages of the alloying elements, may cause a considerable change in the stability of the austenite. Thus many closely related materials, as to composition, show quite different elastic properties. On this account it is essential to characterize alloys suitable for the invention on a different basis than the composition alone. We have therefore chosen to characterize the alloy with reference to its stability. The particular measure which we have chosen for the stability of the austenite, we will call M_{d30} analogical to the symbol M_s which latter represents the characteristic temperature for ordinary steels, where the austenite spontaneously starts to transform into martensite. M_{d30} can be determined by a tensile test and can be defined as the characteristic temperature at which 50% of martensite is formed under tension at a true strain of 0.30 (30%). True strain is defined as

$$\epsilon = ln\frac{l}{l_o}$$

in distinction from the conventional strain

$$e = \frac{l - l_o}{l_o}$$

where l_o=the original measured length of the test bar and l=the length after the elongation. We have further found that the effect of the most important alloying elements on the stability measured as M_{d30}, may be determined by the following equation:

$$M_{d30} = 413 - 462\,(\%\ C + \%\ N) - 9.2\,(\%\ Si) - 8.1\,(\%\ Mn) - 13.7\,(\%\ Cr) - 10.0\,(\%\ Ni) - 18.5\,(\%\ Mo)$$

The terms within parenthesis signify the weight percentages of the various elements. M_{d30} should, according to our investigations, be chosen between 20° C. and −20° C., preferably between 10° C. and −10° C. in order to obtain the results characteristic for the invention. Through the above equation a further and closer definition of those austenitic alloys that are suitable for the invention is obtained. The said equation may of course be completed with further alloying elements.

According to the invention the specimens are made from alloys which after quench-annealing are austenitic and have such a stability that the deformation temperature at which 50% martensite is formed from the austenite, after the material has been deformed in tension, corresponding to a true strain of 30%, will lie between 20° C. and −20° C., preferably between 10° C. and −10° C. and which after quench-annealing and reduc-

tion of cross sectional area through cold-working more than 50% below 75% will contain between 30% and 60% of martensite, preferably between 40 and 60%.

Of great importance for the elastic properties is the amount of martensite in the finished specimens. With a percentage of martensite outside the above mentioned range excellent elastic properties will not be obtained. As a rule the best results have been obtained when the percentages of austenite and martensite are about equal.

The cold working is carried out in several steps without intermediate heat-treatment and the reduction of the cross sectional area may not be less than 50%. Usually it should be between 50% and 70%, but in certain instances it has been necessary to proceed to 75%. The quench-annealing that precedes the cold working necessitates a heating to high temperature, usually within the interval 950–1200° C. with subsequent rapid cooling. The carbides usually present in the austenitic steels after air cooling are thereby brought into solution, which gives the steels the properties necessary for the subsequent cold working.

The working temperature is another factor, that has great influence on the result. A lowering of this temperature below that normally used for cold working will give a greater percentage of martensite at the same degree of working or will require a lower degree of working for obtaining the same percentage of martensite. It has been shown that such a lowering of the working temperature with a simultaneous decrease of the degree of reduction will not cause any change in the excellent elastic properties that are obtained with the austenitic alloys covered by the invention. This means great advantages from the point of view of manufacturing. By keeping the degree of reduction low—it must not be less than 50%—several reduction steps are saved and at the same time the dimensional range for finished spring material may be considerably increased without going beyond the permissible roll pressure of the modern rolling mills.

The working temperature which is the easily measured temperature of the material immediately before entering the rolling mill may thus advantageously be below room temperature. The temperature range between −10 and 15° C. has proved to be particularly suitable for this purpose.

A further improvement in the elastic properties of the specimens, according to the invention, may be obtained by tempering after cold working within the temperature range of 350–550° C. for a time, which due to several factors such as the tempering temperature and the shape of the specimen may suitably be chosen within the range from a few minutes up to several days. Within the range 400–550° C. which has proved to be advantageous, the tempering time may advantageously be within the range from 2 to 8 hours. Considerably longer times have in some instances proved to be advantageous, but are as a rule not necessary and would naturally increase the cost, which should be avoided.

In the accompanying drawings we have shown the relationship between the percentage of martensite, deformation temperature and true strain in the case of two different austenitic alloys after quench-annealing.

In Fig. 1 are shown two alloys A and B, the former of which falls within the scope of the invention, while the latter obviously lies outside the scope of the invention. Both alloys have been subjected to a true strain of 30%, but only alloy A has the defined stability at which 50% martensite is formed within the temperature range from 20° to −20° C. For alloy A this characteristic temperature is about −5° C., while for alloy B the characteristic temperature is about 33° C.

Fig. 2 shows the percentage of martensite for alloy A as a function of the deformation temperature and as a function of the true strain. The curves **1**, **2**, **3**, and **4** represent a true strain of 10, 20, 30, and 50% respectively. From this it is plainly shown how the transformation proceeds with increasing degrees of deformation and also the considerable influence of the working temperature.

It should be pointed out, that the curves in the drawings represent actual experiments. Thus the alloys A and B have the following compositions in percent of weight:

	A	B
Carbon	0.11	0.06
Silicon	1.03	0.39
Manganese	1.15	0.33
Chromium	17.5	18.4
Nickel	8.3	8.6
Molybdenum	0.88	0.06
Nitrogen	0.025	0.024

The remainder iron with usual impurities.

The alloy B differs as seen principally from alloy A in that it has somewhat lower percentages of carbon, silicon, manganese, and molybdenum. The M_{d30} values for the alloys A and B determined by the previously mentioned equation are −7.5° C. and +33° C. respectively, and thus only the first mentioned alloy satisfies the definition for alloys according to the invention.

The properties of the alloys A and B after quench-annealing about 1050° C. with subsequent rapid cooling were as follows:

	A	B
Tensile strength kg./mm.²	65	65
Elastic limit $\sigma_{0.01}$ kg./mm.²	15	15
Martensite percent	0	0

After cold rooling at room temperature of the quench-annealed alloys in a plurality of steps without intermediate annealing and with a cross-sectional area reduction of 60% the following properties were obtained.

	A	B
Tensile strength kg./mm.²	180	115
Elastic limit $\sigma_{0.01}$ kg./mm.²	110	60
Martensite percent	50	25

A further rise in tensile strength and elastic limit was gained by a subsequent tempering at 425° C. for 4 hours.

	A	B
Tensile strength kg./mm.²	200	125
Elastic limit $\sigma_{0.01}$ kg./mm.²	125	75
Martensite percent	about 52	about 27

As earlier mentioned, the alloys should, after quench-annealing, be fully austenitic, that is free from δ-ferrite. This has a favourable influence on the corrosion resistance. The requirement for corrosion resistance means that the percentage of chromium must not be less than 13%. In order that δ-ferrite shall not be present, it is essential that the so-called ferrite forming elements, such as chromium, silicon and molybdenum are balanced against the austenite forming elements, such as nickel, manganese, carbon and nitrogen.

It has been shown that alloys best suitable for the purpose in mind, should contain elements within following limits: 0.07–0.20% carbon; 0–0.1% nitrogen; 14–20% chromium; 7–12% nickel; 0.2–2% silicon; 0.4–2% manganese; 0–4% molybdenum and 0–10% cobalt or 0.07–0.20% carbon; 0–0.1% nitrogen; 14–20% chromium, 3–7% nickel; 0.2–2% silicon; 4–12% manganese; 0–4% molybdenum and 0–10 cobalt. Besides one or more other alloying elements may be added, such as

tungsten, titanium, columbium, tantalum, or aluminum in percentages up to 1%. Other elements in relatively small amounts may be present but the remainder consists substantially of iron.

Particularly suitable are alloys within the following closer limits: 0.08–0.20% carbon; 0.005–0.075% nitrogen; 16–18% chromium; 7–10% nickel; 0.8–1.5% silicon; 0.8–1.5% manganese; 0–2% molybdenum; 0–5% cobalt; 0–1% titanium; 0–1% columbium and/or tantalum; 0–2% tungsten; 0–1% vanadium and the remainder iron with usual impurities. A preferred range of analysis for steels at this type is: 0.10–0.15% carbon; 0.015–0.035% nitrogen; 17–18% chromium; 7.5–9% nickel; 0.9–1.20% silicon; 0.9–1.2% manganese and 0.5–1.5% molybdenum.

It is of great importance in obtaining excellent elastic or spring properties that the percentage of carbon shall be kept at a relatively high value for austenitic steels. It should not be lower than 0.07% and most suitably between 0.10 and 0.15%. Thus the increase in the mechanical strength due to a certain amount of martensite obtained in cold working is proportional to the carbon content. As an increase in the mechanical properties results in a corresponding increase in the spring properties it is easily understood that a proper choice of carbon content is of great importance.

The invention is in the first place concerned with springs of all types, for example watch springs, but other objects, in which excellent elastic properties are necessary, fall within the scope of the invention. There is no difficulty in producing springs according to the invention with thicknesses of up to at least 2 to 3 mm. with excellent spring properties and good corrosion resistance, at normal as well as at elevated temperatures for example 500° C. In comparison with carbon steel springs, the springs produced according to the invention, possess considerably better fatigue properties and are at the same time corrosion resistant.

We claim:

1. Method of making a steel object having good corrosion resistance and excellent spring properties which comprises quench-annealing a steel alloy from a temperature within the range from 950° C. to 1200° C., cold working the quench-annealed alloy in a plurality of steps without intermediate annealing with a cross-sectional area reduction within the range from 50% to 75% at a temperature within the range from —20° C. to 20° C. to a martensite content of 40% to 60% and tempering the resulting cold worked alloy within the temperature range from 350° C. to 550° C., said alloy having a composition within the limits 0.07% to 0.20% carbon, 0% to 0.1% nitrogen, 14% to 20% chromium, 7% to 12% nickel, 0.2% to 2% silicon, 0.4% to 2% manganese, 0% to 4% molybdenum, 0% to 10% cobalt and less than 1% of any one of the metals of the group consisting of tungsten, titanium, columbium, tantalum and aluminum with the remainder consisting substantially of iron, said alloy after said quench-annealing being fully austenitic and having such a stability that about 50% of martensite will be formed from the austenite when the quench-annealed alloy is deformed at a tension corresponding to a true tension of 30% at a temperature within the range from —20° C. to 20° C.

2. Method of making steel objects as defined in claim 1 in which the quench-annealed alloy has such a stability that about 50% of martensite will be formed from the austenite when said quench-annealed alloy is deformed at a tension corresponding to a true tension of 30% at a temperature within the range from —10° C. to 10° C.

3. Method of making steel objects as defined in claim 2 in which the alloy is tempered at a temperature within the range from 400° C. to 550° C.

4. Method of making steel objects as defined in claim 3 in which the cold working is carried out at a temperature within the range from —10° C. to 15° C.

5. Method of making steel objects as defined in claim 1 in which the alloy is cold worked to a reduction in cross-sectional area within the range from 50% to 70%.

6. A steel object having good corrosion resistance and excellent spring properties made by the method defined in claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,044,743	Bain et al.	June 16, 1936
2,080,368	Ffield	May 11, 1937
2,527,287	Ziegler	Oct. 24, 1950
2,590,074	Bloom	Mar. 25, 1952
2,696,450	Breeler	Dec. 7, 1954

OTHER REFERENCES

Transactions of the American Society for Metals, vol. 39, 1947. Pages 869–888.

Steel Processing, vol. XXXVII, Issue 1, January 1951, page 24.