Martensitic precipitation hardened stainless steel consisting of 16–19% by weight of Cr, 5–10% by weight of Ni, 0.15–3% by weight of Nb, 0.1–1.5% by weight of Al, not more than 0.1% by weight of C, not more than 1.5% by weight of Mn, not more than 1.4% by weight of Si and the remainder being Fe and unavoidable impurities has a spring bending limit at least 1.5 times as high as that of the conventional 17-7 PH steel, and the stainless steel having 0.3–3% by weight of Nb and 0.1–1.0% by weight of Al particularly among said composition range is very suitable as a spring stainless steel having a good workability.

8 Claims, 3 Drawing Figures
FIG. 1

![Graph showing the relationship between Ni (wt %) and Cr (wt %). The graph includes a shaded area and a curve that decreases as Ni increases.](image)
FIG. 3

- Spring bending limit after treatment
- Hardness after treatment
- Spring bending limit before treatment
- Hardness before treatment

Vickers' hardness (HV)

Spring bending limit (Kb) [kg/mm²]

Amount of Al added (wt%)

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
PRECIPITATION HARDENING STAINLESS STEEL

This is a continuation-in-part of our copending application, Ser. No. 830619 filed on June 5, 1969 now abandoned.

This invention relates to a martensitic precipitation hardening stainless steel, and particularly to a precipitation hardening stainless steel which has a substantially austenitic structure or a considerably large amount of retained austenitic structure at annealing after a solution heat treatment and said structure is capable of being converted to a substantially martensitic structure by applying a predetermined cold work to the annealed stainless steel.

In the present invention, a stainless steel having good characteristics particularly for a spring material is to be obtained.

Precipitation hardening stainless steel is a stainless steel recently developed by adding Al, Ti, Cu, Mo and the like metals to a 17Cr - 7Ni stainless steel, which has been heretofore known as a strong stainless steel capable of being used directly after the cold working, to impart a precipitation hardenability to the stainless steel as well as to produce properties suitable for a wide range of application fields.

The precipitation hardening stainless steels can be classified into the following three types according to the structure and the heat treatability.

1. Martensite type

A blending composition of components, which tends to effect transformation from austenite to martensite, is selected, and a precipitate, which is soluble in austenite structure but insoluble in martensite structure after the transformation, is precipitated in the martensitic matrix.

It is known that there are two kinds of the martensite type stainless steel, that is, the stainless steel (17Cr - 4Ni stainless steel, usually called "17-4 PH"), in which the transformation from the austenite structure to the martensite structure takes place immediately during a cooling step after the solution heat treatment and in which the precipitation hardening can be effected by applying one heat treatment to the transformed stainless steel, and the stainless steel (17Cr - 7Ni stainless steel, usually called "17-7 PH"), in which all or the most of the structure remain austenitic even after the steel is cooled only by the solution heat treatment. This austenitic structure can be transformed to the martensitic structure only by applying an intermediate heat treatment to the steel or by cold working, and the precipitation hardening is capable of being effected by applying a heat treatment to the steel.

2. Austenitic type

A stainless steel in which the hardening is effected by precipitating compounds rarely solid-soluble in the austenitic structure. A 17Cr - 10Ni stainless steel, that is, a stainless steel usually called "17-10P," is known.

3. Austenite-ferritic type

A stainless steel having a two-phase structure, that is, austenite and ferrite, in which compounds solid-soluble in the austenite but solid-insoluble in the ferrite are precipitated from the ferrite phase.

Among these precipitation-hardening stainless steels, both 17-7 PH and 17-4 PH are most widely used, but a 17-7 PH steel which has a high spring bending limit is particularly excellent as a spring material.

The term "spring bending limit" used in the present invention is defined as a surface stress of a sheet metal beam, whose span length (l) is given by an equation \( l = 8,000 \cdot h \) or \( l = 4,000 \cdot h \), wherein \( h \) is a thickness of the beam, when the residual strain at the center of the beam reaches 0.05 or 0.025 mm.

Said "spring bending limit" represents a degree of resistance to the so-called "relaxation" of the spring. The 17-7 PH steel having a nominal chemical composition (C < 0.09% by weight; Si < 1.0% by weight; Mn < 1.0% by weight; P < 0.04% by weight; S < 0.03% by weight; Ni: 6.50–7.75% by weight; Cr: 16–18% by weight; Al: 0.75–1.5% by weight; and Fe: the balance) has, when precipitation-hardened at a 50% reduction, a spring bending limit of about 120 kg/mm².

Further, a 17-7 PH stainless steel having said nominal chemical composition, to which very small amounts of Ti, Zr, U and the like are added to improve the weldability of said 17-7 PH steel, or a 17-7 stainless steel, in which 4% by weight or less of Cr is replaced with the same proportion of Mo to increase the high temperature strength, are known.

The amounts of Ni and Cr in the Ni-Al compound precipitation type stainless steel are selected from wide range compositions, depending on the service purpose, and the ranges which will ensure such excellent precipitation hardenability are 5–10% by weight of Ni and 16–19% by weight of Cr.

An object of the present invention is to obtain a stainless steel having a much higher spring bending limit by improving the conventional 17-7 PH stainless steel as a base.

Another object of the present invention is to obtain a stainless steel having a good workability and a high spring bending limit.

The stainless steel of the present invention consists of 16–19% by weight of Cr, 5–10% by weight of Ni, 0.15–3% by weight of Nb, 0.1–1.5% by weight of Al, and the balance being Fe and unavoidable impurities.

Further, it is not objectionable to replace a portion of Cr with Mo and a portion of Nb with Ti.

The present invention will be hereunder explained in detail with reference to the accompanying drawings and Examples.

FIG. 1 is a graph showing a range for a preferable mixing proportion of Cr and Ni according to the present invention;

FIG. 2 shows a block diagram of precipitation hardening treatment steps of the present stainless steel; and

FIG. 3 shows a graph of characteristic curves of the hardness and spring bending limit of one embodiment of the present stainless steel.

The present stainless steel has an austenitic structure or a considerable amount of retained austenitic structures when the steel is subjected to a solution heat treatment and then cooled directly as it is, as explained above, and has a properly selected, specific mixing proportion of Cr and Ni so that such a structure may be converted to substantially martensitic structure by applying thereto a cold working at a predetermined degree of cold working.

FIG. 1 shows a correlation of mixing proportions of Cr and Ni which are effective for carrying out the present invention within said range. The hatched area in FIG. 1 is the most effective zone. In the zone where the amounts of Cr and Ni are larger than in the hatched zone, the hardening action by the precipitation hardening treatment becomes weak due to an excessive stabi-
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3. As a method for the precipitation hardening treatment of 17-7 PH steel as in the present invention, three procedures, that is, TH procedure, RH (subzero) procedure and CH procedure, are known according to the manner for transforming the structure of steel after the solution heat treatment to the martensitic structure.

FIG 2 shows a typical block diagram when the precipitation hardening treatment is effected according to said three procedures. Among these, the CH procedure is most excellent, the RH procedure and the TH procedure are excellent in this order from the viewpoint of obtaining a stainless steel having a high spring bending limit.

Besides these three procedures, a procedure which comprises working a solution heat treated steel at a low temperature of less than 0°C has also been known as a "transformation treating step" means a step of transforming the solution heat treated austenit steel structure in accordance with any one of the above-mentioned various procedures into martensite structure.

Accordingly, the characteristics of the present stainless steel is explained in the following on the basis of the hardening treatment according to the CH procedure.

The Nb to be added to the present stainless steel has a function to lower the hardness of the steel before the final heat treatment, as compared with the stainless steel having no Nb, and at the same time it has a function to enhance the spring bending limit after the final heat treatment.

A preferable range of Nb to be added is 0.15-3% by weight, but about 1% by weight of Nb is most satisfactory in particular, because, firstly, less than 0.15% by weight of Nb does not lower the hardness of a cold-rolled steel before the final heat treatment and thus is not satisfactory; secondly the effect of Nb addition upon enhancing the spring bending limit becomes saturated at about 1.4% by weight of Nb; and thirdly the addition of 3% by weight or more of Nb will not enhance the spring bending limit effectively contrary to the expectation of such an increased proportion of Nb and the steel itself becomes expensive and the fatigue strength of the steel is lowered. Thus, these disadvantages are often encountered in such cases.

Ti has a function almost equal to that of Nb, and thus, it is possible to replace a portion of said Nb with Ti. In that case, it is desirable that the amount of Ti is one half of the amount of Nb to be replaced.

The Al of the present stainless steel has a function of enhancing a hardness and a spring bending limit after the final heat treatment without excessively enhancing the hardness before said heat treatment, if added in a proper range.

A preferable range of Al is 0.1-1.5% by weight, because in the case that 0.1-0.3% by weight of Al is added to the steel, the spring bending limit after the final heat treatment can be 10 or more % enhanced, and even if more Al is added, the effect has a tendency of saturation, and addition of 1.5% or more by weight of Al has no more significance, but the addition of an increased amount of Al increases a dirtiness of the molten steel, and the solution heat treatment of the steel itself is difficult. The hardness of steel before the final heat treatment tends to be abruptly enhanced if the amount of Al to be added exceed 1% by weight. Thus, it is preferable that Al to be added be within a range of not more than 1.0% by weight in the case that the workability must be taken into consideration.

Free carbon has a strong action to stabilize the austenitic structure and an action to make worse the corrosion resistance. Such actions can be somewhat reduced with Nb or Ti to be added in the present invention, because Nb or Ti reacts with said free carbon to fix it in the forms of such compounds as NbC, TiC, etc. However, it is difficult to convert the free carbon completely to the form of fixed carbon, and thus it is rather desirable that the amount of carbon to be added be 0.1% or less by weight.

The amount of Si to be added is not so severely restricted as the amount of carbon, but it is desirable that the amount of Si be 1.4% or less by weight, because even the addition of 1.4% or more by weight of Si will rarely help to enhance the spring bending limit of the steel at the precipitation hardening treatment, but even an almost undetectable amount of Si can enhance the spring bending limit more sufficiently according to the present invention, than that of the conventional steel.

The present stainless steel contains Mn or unavoidable impurities such as S and P, usually contained in the ordinary stainless steel, in addition to said components.

The amount of said Mn is enough in a range usually used in the ordinary stainless steel to be added to improve its workability, that is, 1.5% or less by weight, and it is needless to say that it is more desirable that the amount of other unavoidable impurities is rather less.

Table 1 shows compositions and spring bending limits after the final heat treatment of the present stainless steel (Examples 1 to 7) and the conventional 17-7 PH steel (Reference Examples 1 to 3) of the standard compositions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (wt. %)</th>
<th>Spring bending limit After final heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Si</td>
</tr>
<tr>
<td>Ref. Ex. 1</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>Ref. Ex. 2</td>
<td>0.09</td>
<td>0.23</td>
</tr>
<tr>
<td>Ref. Ex. 3</td>
<td>0.09</td>
<td>0.43</td>
</tr>
</tbody>
</table>
In said respective Examples and Reference Examples, cold rolling is effected at a 50% degree of working after the solution heat treatment, and the coldrolled steels are heat-treated at 480°-500°C for 60 minutes as the final heat treatment, and in Examples 1 to 5, the amount of Al is somewhat made smaller than that of the standard composition of the 17-7 PH steel.

As is obvious from the Table, addition of about 0.15% by weight of Nb to the 17-7 PH steel having a standard composition can increase the spring bending limit over 160 kg/mm², and the spring bending limit tends to be enhanced according to an increase in the amount of Nb to be added.

Example 6 shows a case where a portion of Nb is replaced with Ti. In this case, the increase in the spring bending limit is particularly remarkable, and a stainless steel having a spring bending limit exceeding 180 kg/mm² can be obtained by adding a mixture of about 0.1% by weight of Nb and not more than 0.1% by weight of Ti.

Example 7 shows an example where 1.04% by weight of Nb is added to a 17-7 PH steel having the standard composition in which the amount of Al is relatively increased, and an example where only about 0.1% of Nb is added thereto, together with the spring bending limits of the steels, to which the same precipitation hardening treatment as in examples of Table 1 is applied.

When the workability of the 17-7 PH steel must be taken into consideration, a hardness at the shaping naturally becomes important. That is, it can be said that the workability of a steel becomes better, if the hardness is lower before the final heat treatment according to the CH procedure.

FIG. 3 is a graph showing relations among the amount of Al, Vickers' hardness and spring bending limit of the present stainless steel.

The composition of the stainless steel used in the Examples is Cr: 17.0% by weight, Ni: 7.0% by weight, Nb: 1.0% by weight, Si: 0.6% by weight, Mn: 0.4% by weight, Al being selected in a range of 0.05% to 1.4% by weight, and the balance being Fe.

Further, it can be said that the hardness before the final heat treatment has a tendency to rapidly increase around a point over 1.0% by weight of Al to be added. Thus, it can be seen that, in order to obtain a stainless steel having a high spring bending limit and a good workability, a preferable amount of Al to be added is within a range of 0.3 to 1% by weight.

Table 3 shows comparison of several examples of the present invention with several reference examples.
The stainless steels used in the Examples and Reference Examples shown in Table 3 were sheet materials cold-rolled at a 50% degree of working after the solution heat treatment and subjected to the final heat treatment.

As the final heat treatment, a heat treatment was applied at 600°C for 60 minutes in Reference Example 16, and at 480°-500°C for 45 minutes in other Examples and Reference Examples.

In Reference Example 14, a kind of well-known stainless steels for spring purpose, which have an unstable austenitic structure after the solution heat treatment, but are of non-precipitation hardening material, though a martensitic structure is developed by cold working. The steel of this Reference Example has also a difficulty that the hardness after the cold rolling is very high, and has not so high spring bending limit after the heat treatment as that of the present stainless steel.

The stainless steels of Reference Examples 16 and 17 have the conventional stable austenitic structure. In these cases, the hardness of cold-rolled steel can be lowered to some degree, but the spring bending limit after the precipitation hardening treatment cannot be made excessively higher.

Example 21 shows a case where the amount of Al is relatively increased among the examples of the present invention. In this case, the hardness of the steel before the precipitation hardening treatment is considerably high.

Reference Example 18 shows a case where no Al is added at all. In this case, the hardness of the steel before the final heat treatment is not too high, but the spring bending limit cannot be made high.

In the examples of the present invention shown in Table 3, a stainless steel having a Vickers' hardness of 350 after the 50% cold-rolling and a spring bending limit of 180 kg/mm² after the final heat treatment can be readily obtained.

As shown in Examples 18 and 20, the stainless steel, a portion of whose Cr is replaced with Mo, has also a high spring bending limit. By replacing a portion of Cr with Mo in this way, a stainless steel having a high high temperature strength, though its hardness is somewhat enhanced, can be obtained.

As explained above, it has been found, as shown in the examples, that a stainless steel having a low hardness before the final heat treatment, a ready workability and a very high spring bending limit after the final heat treatment can be obtained by selecting specific ranges of Nb and Al to be added. These improved properties can bring about a very good effect when the present stainless steel is used as various spring materials.

For example, a spring material for the holder of a shadow mask in a color television set can be mentioned. The spring is classified into two cases according to the method for holding the shadow mask. That is, the one is a case where a material of a low thermal expansion is required, and the other is a case where a material having a coefficient of thermal expansion close to that of the material constituting the shadow mask (usually pure iron is used) is required.

It is the latter case that the present stainless steel is used as a spring for said holding purpose. In the latter spring case, a material having an austenitic structure is not appropriate, because it is an excessively high coefficient of thermal expansion, and a material having a martensitic structure, as in the present stainless steel, is required.

In order to avoid an occurrence of a displacement of the shadow mask position due to a vibration or shock, it is necessary to use a spring having a high resistance to the so-called "relaxation." In this regard, the present stainless steel having a high spring bending limit can perform an excellent service.

Further, it is required in mass production of springs to conduct shaping readily by means of press punching and save a loss of press die. In this regard, the present stainless steel is excellent, because the hardness at the shaping, that is, before the precipitation hardening treatment is low.

What is claimed is:

1. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by cold working which consists essentially of

   6.50 - 7.75% by weight of Ni,
   16-18% by weight of Cr,
   0.15-1.5% by weight of Nb,
   0.1-1.0% by weight of Al,
   not more than 0.1% by weight of C,
   not more than 1.4% by weight of Si,
   not more than 1.5% by weight of Mn,
   and the balance being unavoidable impurities and Fe.
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the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment, and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

2. The martensitic precipitation-hardening stainless steel according to claim 1, wherein the amount of Si is in the range of 0.02-1% by weight.

3. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by cold working which consists of

6.50 - 7.75% by weight of Ni,
16 - 18% by weight of Cr,
0.15 - 1.5% by weight of Nb,
0.1 - 1.0% by weight of Al,
not more than 0.1% by weight of C,
not more than 1.4% by weight of Si,
not more than 1.5% by weight of Mn,
and the balance being unavoidable impurities and Fe, the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment, and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

4. The martensitic precipitation-hardening stainless steel according to claim 3, wherein the amount of Si is in the range of 0.02-1% by weight.

5. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by a cold working which consists essentially of 6.50 - 7.75% by weight of Ni, 16 - 18% by weight of Cr, 0.15 - 1.5% by weight of Nb, 0.1 - 1.0% by weight of Al, not more than 0.1% by weight of C, not more than 1.4% by weight of Si, not more than 1.5% by weight of Mn, and the balance being unavoidable impurities and Fe, with a portion of Nb being replaced with one-half of the portion of Ti, and the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment, and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

6. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by a cold working which consists essentially of 6.50 - 7.75% by weight of Ni, 16 - 18% by weight of Cr, 0.15 - 1.5% by weight of Nb, 0.1 - 1.0% by weight of Al, not more than 0.1% by weight of C, not more than 1.4% by weight of Si, not more than 1.5% by weight of Mn, the balance being unavoidable impurities and Fe, with a portion of Cr being replaced with the same amount of Mo, and the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

7. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by a cold working which consists of 6.50 - 7.75% by weight of Ni, 16 - 18% by weight of Cr, 0.15 - 1.5% by weight of Nb, 0.1 - 1.0% by weight of Al, not more than 0.1% by weight of C, not more than 1.4% by weight of Si, not more than 1.5% by weight of Mn, and the balance being unavoidable impurities and Fe, with a portion of Nb being replaced with one-half of the portion of Ti, and the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment, and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

8. A martensitic precipitation-hardening stainless steel capable of being transformed to a substantially martensitic structure by a cold working which consists of 6.50 - 7.75% by weight of Ni, 16 - 18% by weight of Cr, 0.15 - 1.5% by weight of Nb, 0.1 - 1.0% by weight of Al, not more than 0.1% by weight of C, not more than 1.4% by weight of Si, not more than 1.5% by weight of Mn, and the balance being unavoidable impurities and Fe, with a portion of Cr being replaced with the same amount of Mo, and the proportions of Ni and Cr being so selected and arranged that a substantially transformable austenitic structure or a considerable amount of retained austenitic structure prevails after solution heat treatment and said austenitic structure is transformed to said substantially martensitic structure when a cold working is applied thereto.

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