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(72) Inventors KATSUMI YAMAMURA, HIROSHI HARIGAYA, KAZUTOMO KASAI and MICHIO ASAHINA

(54) WATCH CASE

(71) We, KABUSHIKI KAISHA SUWA SEIKOSHA, a Japanese company of 3—4, 4-chome, Ginza, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by he following statement:—

The present invention relates to a watch case formed of an age-hardenable stainless steel as disclosed in the specification of our British Patent No. 1,213,690.

The finest watch cases known in the art are made of gold and they are sometimes even furnished with enamel. These known watch cases are however very expensive and they have, moreover, to be carried with the utmost care since they would immediately be damaged, if they were carried in everyday life for manual labour or sport.

The only way hitherto known in the art for obtaining a watch case resistant to hard conditions of wear was to make it of steel and in particular of stainless steel. However, if such a watch case is repeatedly submitted to frictional engagement with hard objects, its finely polished outer surface portions exposed to contacts with foreign objects will soon be scratched, and the watch case will suffer a substantial damage.

It is therefore an object of the invention to provide a stainless steel which may be used to reinforce the outer area in such a manner that it will not readily be damaged by impacts or frictional engagements with hard foreign objects, will be resistant to the oxidizing agents of the atmosphere, and will have an attractive and durable appearance.

It is well known in the art that age hardening appears by adding Mo to Fe in an amount exceeding 15% by weight. Such alloys, however, can be used only as cast alloys because they cannot be rolled or drawn. Moreover, their resistance to corrosition is insufficient.

According to the present invention, there is provided a watch case formed at least in part of an age hardenable stainless steel having the following percentage composition by weight:—

Cr	6—22%
Mo (+W if present)	4—13% such that $0 \leqslant \frac{W}{Mo + W} \leqslant 0.6$
C	0—0.1%
Si	0—2.5%
Cu	0.35—3%
Nb	0—0.3%
Ti and/or Be (If provided) such that	
Ti only	0.1—4%
Be only	0.05—2%
Ti and Be together	0—4%
Co and/or Ni (If provided) such that	
Ni only	0—5%
Co only	0.5—12%
Co and Ni together	0.5—12% (Ni not exceeding 4.5%)

the balance being iron and impurities.

The steel may contain no tungsten, the molybdenum being present in the range 5—13% by weight.

The chromium content of the steel may be in the range 6 to 20% by weight.

In the alloy according to the invention resistance to corrosion is greatly increased by adding Cr to an Fe—Mo alloy, and the amount of Mo required for age hardening is reduced and sufficient workability can be obtained.

Further it is found that toughness, resistance to heat, and resistance to corrosion may be increased without spoiling the age hardening of the material by adding Co and Ni, singly or together, and that age hardening property is greatly increased by adding W, Be and Ti.

The importance of the various elements in the steel is discussed below, all percentages being by weight.

1. Cr . . . 6 to 22%

Cr stabilizes Fe material, and increases resistance to corrosion of the material. In the alloy according to the invention, too, Cr is added to increase resistance to corrosion, the amount of Mo required in the alloy being decreased by adding Cr. Thus workability for cold rolling and drawing is improved without spoiling age hardenability. With Cr less than 6% in content resistance to corrosion is insufficient, while with Cr over 22% in content the alloy tends to harden and the workability is spoiled.

2. Mo + W . . . 4 to 13% $\left(0 \leqq \frac{W}{Mo + W} \leqq 0.6\right)$

The element Mo in Fe-Mo alloy produces age hardening effect. The alloy according to the invention not only has improved age hardening but also resistance to corrosion against non-oxidising acid. The element W in Fe material, in the same way as Mo, possesses an age hardening property. The effect of W on age hardening property is weaker that that of Mo. However, it shows greater reinforcement for solid solution than Mo, so it strengthens the matrix of this alloy. Too much addition, however, makes the material brittle and deteriorates its workability. After alloys were examined with respect to hardenability, solid solution reinforcement and brittleness of the material, it was found that Mo + W should be 4 to 13%, W being up to 60% of the total Mo + W.

3. Co and Ni

Co only	0.5 to 12%
Ni only	from 0 up to 5% (preferably 0.5 up to 5%)
Co and Ni together	0.5 to 12% (Ni not exceeding 4.5%)

Co and Ni greatly increase the toughness of the steel and improve workability in the case of rolling and drawing. These elements also improve resistance to corrosion. Ni, in particular, improves resistance to corrosion at normal temperature and Co improves acid proofness at high temperature. The amounts added should be as described above. When the amounts added are less than the lower limit there is little effect and when the amount exceeds the upper limit, the material tends to be brittle and workability deteriorates. Ni with more than 5% added, tends to produce a γ phase.

4. Ti and Be

Ti only	0.1 to 4
Be only	0.05 to 2%
Ti and Be together	0 to 4% (preferably 0.05 to 3.5%)

Ti and Be in Fe material stabilize Ferrite. As the temperature lowers, the solubility decreases and age hardening effect appears. The resulting alloy has a body centred, ferrite crystal construction. By means of the elements Ti and Be strength is greatly increased without spoiling the age hardenable property. This effect is due to the fact that the treatment conditions for age hardening of Fe-Mo and that of Fe-Be and Fe-Ti are similar, and that the precipitation compounds which contribute to hardening have completely different phases and do not influence each other. Therefore Ti and Be added together do not spoil the hardening effect. When the amount added is less than 0.05%, hardenability deteriorates, and when the amount of Ti and Be added singly or mixed together is over the upper limit, the material becomes brittle and working becomes difficult.

5. Si . . 0—2.5% (preferably 0—2.0%)

Si deoxidizes melting metal and promotes ageing of Fe-Mo alloy. With Si more than 0.5% in content age hardening appears. However when the amount of Si exceeds 2.5% the material tends to be brittle.

6. Cu . . . . 0.35—3%

Cu improves proofness against non-oxidizing acid. It also shows an age hardening effect. Too much addition, however, reduces workability, especially hot workability, and resistance to corrosion. After various experiments it was found that Cu not exceeding 3% in content is most suitable.

7. Nb . . . 0—0.3%

Nb reacts with C to form stable carbide and improves resistance to corrosion. Particularly in this alloy, Ti, Mo and Cr easily reacts with C and reduces not only resistance to corrosion but also age hardenability. By adding Nb, a carbide of Nb stable at higher temperature is formed, which prevents the reaction with these elements. However, when Nb is added by more than 0.3%, it tends to form compounds with elements other than C, and brittleness of the material increases.

8. C . . . Not exceeding 0.1%

C easily forms carbides with Mo, Ti and Cr, and deteriorates resistance to corrosion and age hardenability. C should be avoided as much as possible, but it is inevitably introduced during the melting operation. Considering the above fact, Nb is preferably added in the present alloy. Nb of less than 0.1% in content is sufficient.

Table 1 below shows typical compositions of a number of alloys (i.e. Alloys Nos 1—23) according to the invention. For comparison, two kinds of age hardening stainless steels on the market (i.e. Alloys 17—4PH and 17—7PH) and that of the known 18—8 stainless steel are also shown.

In Table 1, all alloys No. 1 to 23 were melted in vacuo by a high frequency induction furnace wherein the degree of vacuum during melting was maintained at 3 to 8 $\times 10^{-3}$ mmHg. Such melting materials as electrolytic pure iron, pure Cr, Ferro-Mo, Ferro-W, pure Co, pure Ni, Ferro-Ti, Ferro-Be, Ferro-Nb, Ferro-Si, and electrolytic pure copper were used. They were melted in such a manner that electrolytic pure iron, pure Cr, Ferro-Mo, Ferro-W, pure Co, pure Ni were charged into a high pure alumina crucible and the furnace was made vacuous, the melting operation then being started. Fe-Si was added after the material was melted down in the crucible. The temperature was set to the value 100 to 200°C above the melting temperature when the melting metal became clean. Cu, Ferro-Nb, Ferro-Ti and Ferro-Be were thrown in quickly in this order. One or two minutes after the Ferro-Be was melted, the ingot was cast. The temperature was measured by an optical pyrometer. The surfaces of these ingots were made smooth and band material was formed by hot forging, hot and cold rolling, i.e. hot rolling at 1050 to 900°C, the material being heated up to 1150 to 1200°C and quenched by water to be used as pieces to be tested for strength and resistance to corrosion.

TABLE 1

		Cr	Mo	W	Co	Ni	Ti	Be	Si	Cu	Nb	C	Fe
	1	10.12	9.98	—	—	—	—	—	0.29	2.50	—	0.02	balance
	2	12.06	9.11	—	—	—	—	—	0.31	2.49	0.21	0.03	„
	3	14.96	5.89	—	—	—	—	—	1.33	2.91	—	0.02	„
	4	15.00	8.01	—	—	—	—	—	0.03	1.01	0.12	0.02	„
	5	15.10	9.08	—	—	—	—	—	1.02	1.04	0.11	0.02	„
	6	20.12	7.20	—	—	—	—	—	0.28	2.95	—	0.02	„
	7	6.33	7.21	3.58	—	—	2.74	0.08	0.26	1.04	0.11	0.02	„
alloys	8	8.45	5.08	4.12	—	—	0.23	0.36	0.42	2.01	—	0.02	„
according to the	9	12.58	5.27	4.18	—	—	—	—	1.67	2.85	0.08	0.03	„
invention	10	16.12	6.22	—	—	—	—	1.62	0.34	1.15	0.09	0.02	„
	11	6.36	7.14	3.50	—	2.28	1.42	—	0.34	1.08	—	0.02	„
	12	11.91	8.10	1.23	—	0.83	0.23	0.38	0.22	1.00	0.10	0.02	„
	13	15.11	9.01	—	—	4.23	0.13	0.08	0.91	0.85	—	0.02	„
	14	19.42	8.63	1.37	—	3.25	2.04	0.13	0.38	0.62	—	0.02	„
	15	15.03	9.03	—	—	4.72	—	—	1.08	0.96	0.12	0.03	„
	16	8.55	9.57	1.14	0.92	—	1.23	0.33	0.42	1.16	—	0.02	„
	17	15.01	8.89	—	5.12	—	—	—	1.02	1.00	0.11	0.02	„
	18	18.42	6.03	3.28	7.08	—	0.42	—	0.96	0.85	—	0.02	„
	19	14.96	7.28	1.03	11.01	—	2.18	—	0.34	0.66	—	0.02	„
	20	7.15	10.86	—	6.14	2.03	0.89	—	1.23	1.07	—	0.02	„
	21	15.18	9.02	0.84	9.22	1.05	—	—	0.96	0.88	0.10	0.02	„
	22	17.45	6.03	4.35	1.12	4.36	1.89	0.16	0.14	0.35	—	0.03	„
	23	19.05	4.58	4.72	4.26	2.16	0.43	—	1.19	0.92	—	0.02	„
17—4PH		16.88	—	—	—	4.13	0.21	—	0.62	4.01	Mn 6.81	0.05	„
known alloys 17—7PH		17.00	—	—	—	7.11	—	Al 1.15	0.83	—	Mn 0.67	0.07	„
compared 18—8		18.54	—	—	—	8.91	—	—	0.48	—	Mn 0.96	0.05	„

Table 2 shows hardness, tensile strength and elongation of these alloys. From these results it can be seen that addition of Ni or Co has great influence on toughness of the material. Alloys from No. 11 to 16 have higher elongation than those from No. 1 to 10 which do not include Ni and Co. Alloys including such age hardening elements as Ti or Be, show higher hardness in melting than those which do not include them. These alloys when melting have the same strength as 17—4 PH and 17—7 PH on the market which are known as age hardening stainless steel.

TABLE 2

Strength of melting material

		hardness (Hv)	tensile strength (kg/mm^2)	elongation (%)
	1	250	96	11
	2	266	93	10
	3	242	91	15
	4	248	96	14
	5	246	98	13
	6	255	94	11
	7	302	103	10
	8	310	101	12
	9	268	102	10
	10	306	99	12
	11	322	101	27
	12	286	96	18
	13	291	103	34
	14	334	111	26
	15	280	102	31
	16	301	98	20
	17	287	103	30
	18	298	106	31
	19	311	108	26
	20	294	105	29
	21	301	103	26
	22	311	116	24
	23	298	108	28
alloys to be compared	17—4PH	370	105	12
	17—7PH	183	91	35
	18—8	153	60	50

Table 3 shows hardness and tensile strength of 50% cold rolled material and those when the alloys were aged. Age hardening treatment was performed both on the alloys according to the invention and the materials compared under such a condition that the maximum strength was obtained in the preliminary experiment. All heat treatment was performed in the vacuum furnace in order to avoid oxidation. From the results shown in Table 3, it can be seen that before age hardening treatment there is little difference between the alloys according to the invention and the alloys compared, 17—4 PH, 17—7 PH which have been subjected to heat treatments H900 and CH900 respectively and 18—8 stainless steel, but that there appears great difference between them after ageing, which shows that the ageing property of the alloys according to the invention is excellent.

TABLE 3

		50% rolled material			age hardening material	
		tensile strength (kg/mm²)	hardness (Hv)	ageing condition	tensile strength (kg/mm²)	hardness (Hv)
alloys according to the invention	1	128	391	570°C×7H	195	662
	2	129	389	„	192	641
	3	126	360	„	191	638
	4	116	341	„	196	582
	5	125	347	„	198	685
	6	120	392	„	178	420
	7	152	428	„	237	762
	8	150	419	„	241	723
	9	134	395	„	216	636
	10	142	421	„	223	743
	11	150	431	„	228	758
	12	150	419	„	240	756
	13	137	368	„	209	707
	14	158	449	„	238	752
	15	134	352	„	201	694
	16	148	412	„	202	740
	17	139	371	„	203	694
	18	146	395	„	223	706
	19	160	431	„	229	748
	20	132	385	„	214	695
	21	138	392	„	208	682
	22	143	396	„	224	703
	23	136	389	„	217	701
known alloys compared	17—4PH	120	380	H900	150	430
	17—7PH	140	420	CH900	183	500
	18—8	140	385			

Heat treatments H900 and CH900 referred to in Table 3 are:

H900: After quenching from 1038°C ± 14°C hold in air at 482°C ± 5°C for one hour.

CH900: After quenching from 1066°C ± 14°C, apply cold rolling of 30—50% and then hold in air at 482°C ± 6°C for one hour.

After age hardening treatment the test pieces of Table 3 were immersed in various corrosion liquids for ten days and their degree of corrosion and discoloration was examined. The results are shown in Table 4 below.

The artificial sea water and artificial sweat referred to in Table 4 are sweat and sea water made artificially by mixing chemicals, the components of which are similar to those of natural sweat and sea water.

Their compositions are as follows:—

Composition of artificial sweat

NaCl	0.648 to 0.987%
Na_2S	0.006 to 0.025%
$(NH_2)_2CO$	0.086 to 0.173%
NH_4OH	0.010 to 0.018%
Saccharose	0.006 to 0.022%
Lactic Acid	0.034 to 0.107%

Composition of artificial sea water

NaCl	2.30 to 2.35%
$MgCl_2$	0.45 to 0.49%
Na_2SO_4	0.37 to 0.39%
$CaCl_2$	0.10 to 0.12%
KCl	0.06 to 0.066%
$NaHCO_3$	0.01 to 0.020%
KBr	0.0080 to 0.0095%

TABLE 4

Alloy No.	artificial sweat	artificial sea water	10% NaCl	10% HCl	5% H_2SO_4	10% NH_4Cl	10% NH_4OH	5% Na_2S	10% lactic acid	20% Na_2CO_3
1	θ	0	Δ	0	Δ	0	θ	θ	θ	θ
2	θ	θ	Δ	Δ	Δ	θ	θ	θ	θ	θ
3	θ	θ	Δ	Δ	Δ	θ	θ	θ	θ	θ
4	θ	θ	0	0	Δ	θ	θ	θ	θ	θ
5	θ	θ	0	0	0	θ	θ	θ	θ	θ
6	θ	θ	0	0	0	θ	θ	θ	θ	θ
7	0	0	Δ	Δ	Δ	0	0	0	θ	θ
8	0	0	Δ	Δ	Δ	0	θ	θ	θ	θ
9	θ	0	Δ	Δ	Δ	0	0	θ	θ	θ
10	θ	θ	0	Δ	Δ	θ	θ	θ	θ	θ
11	0	0	Δ	Δ	Δ	0	0	θ	θ	θ
12	θ	0	Δ	0	Δ	0	θ	θ	θ	θ
13	θ	θ	θ	0	0	θ	θ	θ	θ	θ
14	θ	θ	θ	0	0	θ	θ	θ	θ	θ
15	θ	θ	θ	0	0	θ	θ	θ	θ	θ
16	θ	0	Δ	0	Δ	0	θ	θ	θ	θ
17	θ	θ	0	0	0	θ	θ	θ	θ	θ
18	θ	θ	θ	0	0	θ	θ	θ	θ	θ
19	θ	θ	0	0	0	θ	θ	θ	θ	θ
20	θ	0	Δ	0	Δ	0	θ	θ	θ	θ
21	θ	θ	0	0	0	θ	θ	θ	θ	θ
22	θ	θ	θ	0	0	θ	θ	θ	θ	θ
23	θ	θ	0	0	0	θ	θ	θ	θ	θ
17—4 PH	Δ	Δ	x	x	x	0	0	0	Δ	0
17—7 PH	Δ	Δ	Δ	x	x	0	0	0	0	θ
18—8 50% rolled Material	θ	θ	Δ	Δ	Δ	θ	θ	θ	θ	θ

θ no discoloration or corrosion

0 slight discoloration

Δ discoloration and slight corrosion

x corrosion

From Table 4 it can be seen that the alloy according to the invention has higher corrosion resistance than 17—4 PH and 17—7 PH which are known as a hardenable stainless steel. It shows similar resistance to corrosion to that of 18—8 stainless steel which has high work hardenability.

As described above, the alloy according to the invention has excellent age hardenability and corrosion resistance and is suitable for watch cases.

It is easy to work a watch case employing a stainless steel according to our invention prior to age hardening. The watch case after being age hardened is not scratched by the usual materials. Further, the watch case resists the oxidizing action of the corrosive agents of the atmosphere.

Therefore the watch case keeps its original appearance during a period which is practically non-limited, even if it is used under many different conditions. Moreover, such watch cases can also be given new shapes comprising large polished visible surface portions.

The watch case may be formed entirely from the alloy as described in the specification or may be formed partly of said alloy and partly of other material.

In our British Patent No. 1,213,690 we have claimed an age hardenable alloy having the following percentage composition by weight:—

Cr	6—22%
Mo, or Mo and W together	4—13% such that $\frac{W}{Mo+W} \leqslant 0.6$
Co and/or Ni such that	
Ni only	0—5%
Co only	0—12%
Co and Ni together	0—12%
Ti and/or Be such that	
Ti only	0—4%
Be only	0—2%
Ti and Be together	0—4%
Si	less than 2%
Cu	0.35—3%
Nb	less than 0.3%
C	present, but less than 0.1%
Fe	balance

WHAT WE CLAIM IS:—

1. A watch case formed at least in part of an age hardenable stainless steel having the following percentage composition by weight:—

From Table 4 it can be seen that the alloy according to the invention has higher corrosion resistance than 17—4 PH and 17—7 PH which are known as a hardenable stainless steel. It shows similar resistance to corrosion to that of 18—8 stainless steel which has high work hardenability.

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Fe	balance

WHAT WE CLAIM IS:—

1. A watch case formed at least in part of an age hardenable stainless steel having the following percentage composition by weight:—

* C L M S *

Cr	6—22%
Mo (+W if present)	4—13% such that $0 \leqslant \frac{W}{Mo + W} \leqslant 0.6$
C	0—0.1%
Si	0—2.5%
Cu	0.35—3%
Nb	0—0.3%
Ti and/or Be (If provided) such that	
Ti only	0.1—4%
Be only	0.05—2%
Ti and Be together	0—4%
Co and/or Ni (If provided) such that	
Ni only	0—5%
Co only	0.5—12%
Co and Ni together	0.5—12% (Ni not exceeding 4.5%)

the balance being iron and impurities.

2. A watch case as claimed in claim 1 in which the steel contains no tungsten, the molybdenum being present in the range 5—13% by weight.

3. A watch case as claimed in any preceding claim in which the chromium content of the steel is in the range 6 to 20% by weight.

4. A watch case as claimed in any preceding claim in which the titanium content of the steel, if no beryllium is present, is in the range 0.1—4% by weight; the beryllium content of the steel, if no titanium is present, is in the range 0.05—2% by weight, and the combined titanium plus beryllium content of the steel, if both elements are present, is in the range 0.05—3.5% by weight.

5. A watch case as claimed in any preceding claim in which the nickel content of the steel, if there is no cobalt present, is in the range 0.5%—5.0% by weight, the cobalt content of the steel, if there is no nickel present, is in the range 0.5—12% by weight; and the Co + Ni content of the steel, if both elements are present, is in the range 0.5—12% by weight, nickel being present in this case in an amount not exceeding 4.5% by weight.

6. A watch case as claimed in any preceding claim in which the silicon content of the alloy does not exceed 2.0% by weight.

7. A watch case as claimed in claim 1 and having the composition of any of Alloys Nos. 1 to 23 of Table 1.

J. MILLER & CO.,
Agents for the Applicants,
Chartered Patent Agents,
262 High Holborn,
London, W.C.1.

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