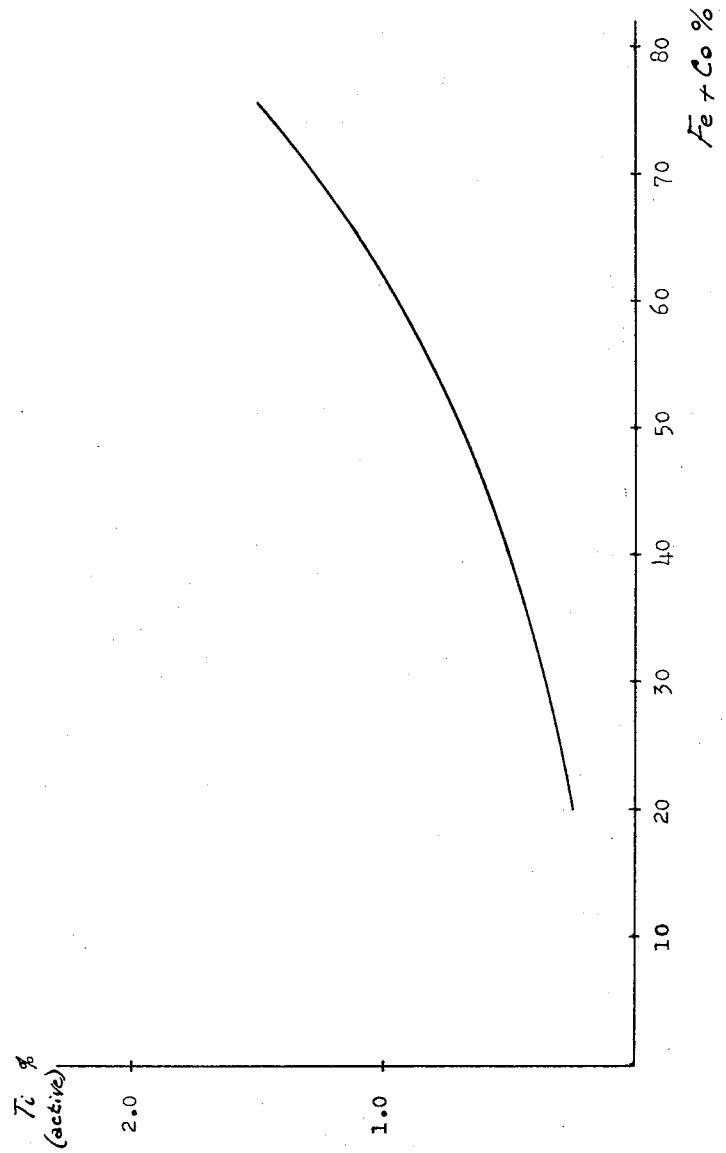
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RESTORABLE ALLOYS

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Fig. 1.



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Fig. 2.

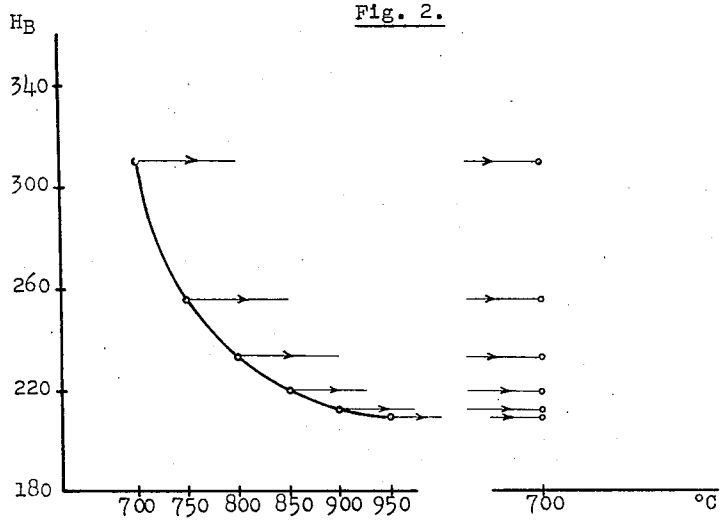
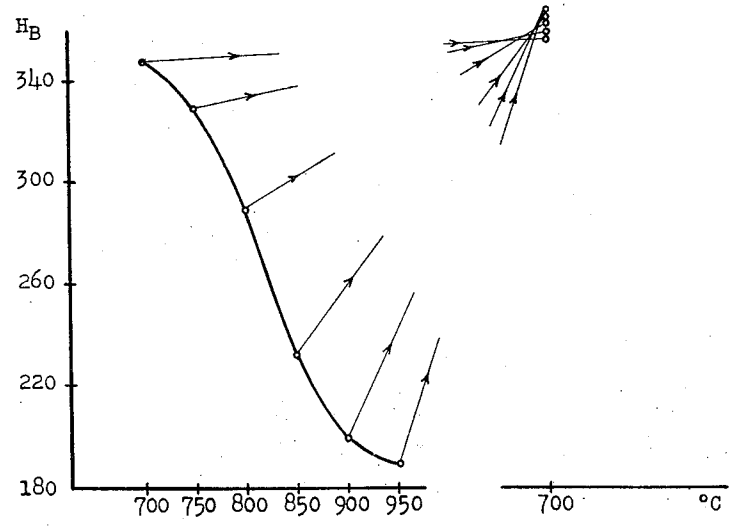


Fig. 3.



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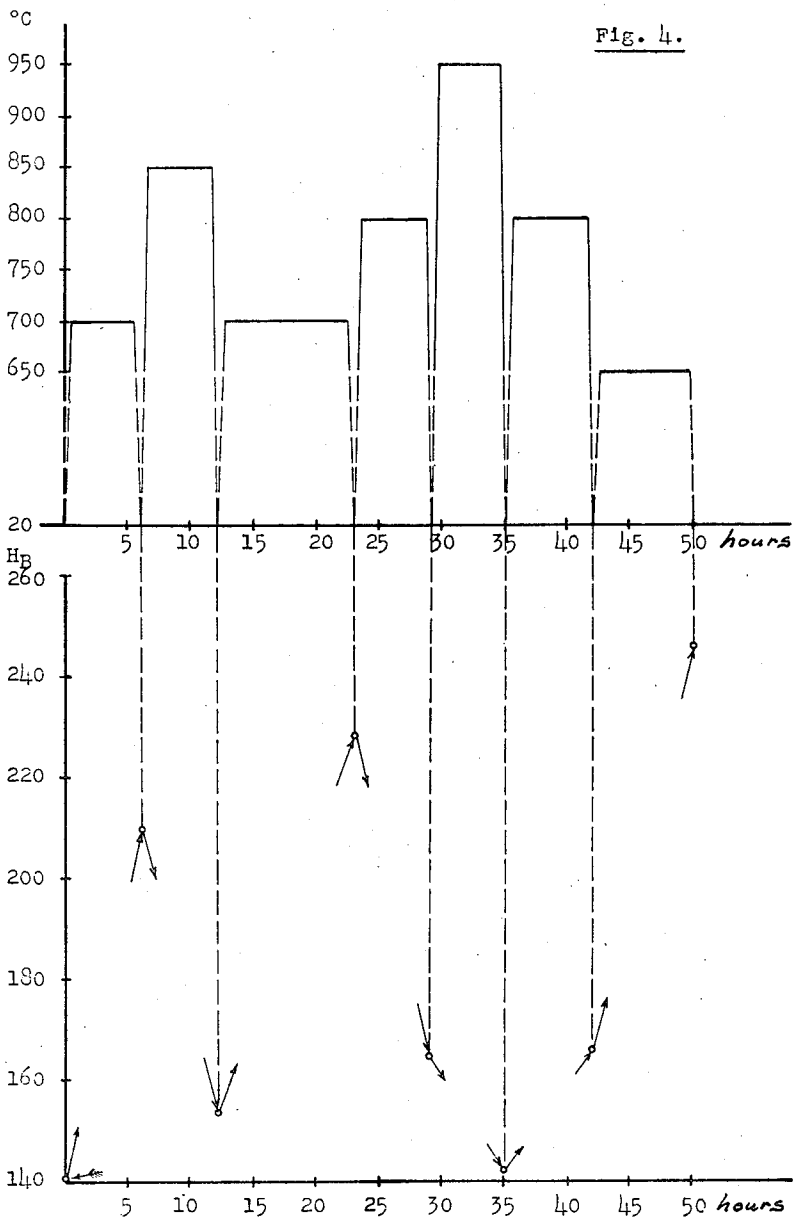
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RESTORABLE ALLOYS

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Fig. 4.



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United States Patent Office

2,763,543

Patented Sept. 18, 1956

2,763,543

RESTORABLE ALLOYS

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Application May 25, 1953, Serial No. 357,250

11 Claims. (Cl. 75—122)

In modern technic there is a continuously increasing demand for heat resistant materials, and particularly for heat resistant steels. The demand for high heat resistant properties of heat resistant steels, and particularly for low sensitivity to overheating, has also increased due to the rapid development of gas turbines. A number of alloy compositions have been suggested for the purpose of attaining better properties at higher temperatures. At a relatively early date it was found and confirmed that austenitic steel alloys with sufficiently high contents of chromium and nickel and certain other elements such as tungsten and cobalt have excellent heat resistant properties at temperatures around and somewhat above 500° C. For the purpose of counteracting precipitation of carbides at the grain boundaries it has also been suggested to add such carbide forming elements as columbium, titanium, tantalum and vanadium.

However, it very soon turned out particularly due to the rapid development of the aviation technic during the Second World War that the austenitic heat resistant Cr Ni-steels of the older types were not up to requirements when subjected to high temperature for longer periods. Then the search for new materials was started, and thereby inter alia by researches in the Mond Nickel Company the modern high alloyed materials were invented on the basis of nickel and chromium with a basic composition of about 80% Ni and 20% Cr. These alloys further shall contain 0.05–0.5% C and one or more carbide forming elements among which titanium has been given preference.

Important progress has been made with heat resistant chromium-nickel steels as well as with special alloys on chromium-nickel basis in that said alloys have been given such a composition that they can be subjected to a heat treatment causing precipitation hardening.

In alloys hardenable by precipitation which hereinafter will be referred to as "ordinary aging" as is known there is obtained after a common quenching from a high dissolving temperature a supersaturated solid solution of certain alloying elements in the basic mass of the alloy. On reheating to a temperature considerably below the above mentioned dissolving temperature the substances which were present in solid solution will be precipitated in a phase of very fine distribution giving the alloy certain improved properties such as hardness and increased heat strength. However, if for an ordinary aging material a certain temperature which is characteristic for each composition is surpassed the precipitated particles become coarser and the properties become considerably deteriorated (so called over aging). This disadvantage is maintained even when the temperature is restored to a degree below the said characteristic temperature. In order to arrive again at the most advantageous properties such a precipitation hardening alloy must be subjected to a complete new heat treatment for dissolving and renewed precipitation of the precipitable constituents. Alloys having the ability of restoration have a much higher resistancy against exhaustion and vibration

stresses than precipitation hardening alloys due to the absence of precipitated stable phases.

From aluminium alloys and especially Duralumin it is known that the aging at room temperature which is characteristic for these alloys is due to the precipitation of a meta stable phase and that this phase can be dissolved by heating to a moderate temperature considerably below the dissolving temperature of stable equilibrium and that upon a succeeding cooling to room temperature the said aging process after some time occurs again. This phenomonon which can be repeated any number of times is generally called "restoration" and alloys having such properties will hereinafter be referred to as restorable alloys in contradistinction to the ordinary aging alloys which cannot be restored.

During his research on heat-resistant and fireproof steel alloys the inventor made some discoveries which seemed to hint at the possibility that restoration can be achieved in steel alloys of a suitable composition and at considerably higher temperature than in the case of Duralumin. Through a systematic investigation of heat resistant steels with varying compositions and mainly austenitic structure it has now been verified that the observations were correct and that some of these alloys have the property of being restorable. One condition for this effect is that the alloy contains titanium. A further condition is that the titanium content is in a certain relation to the sum of the contents of iron and cobalt on one hand and to the contents of carbon and nitrogen on the other hand. This relation is best seen from the accompanying Fig. 1 diagrammatically showing the lowest required content of "active" titanium as a function of the sum of the iron and cobalt contents. "Active" titanium means that titanium content which is not combined with carbon and nitrogen. The titanium content combined can be calculated with sufficient accuracy by multiplying the sum of the nitrogen and carbon contents by four.

Based upon the above related discoveries the present invention involves objects which are intended during their use to be subjected to temperatures of at least 650° C. and which are insensible to accidental superheatings above the temperature at which said objects are intended to work in that their resistancy and hardness are restored when returning from superheating to the normal working temperature. These objects are characterized in that they are obtained from a non-precipitation-hardenable steel alloy having at least predominating austenitic structure and containing at least one gamma forming element, taken from the group consisting of nickel and manganese, at least 20% of iron +cobalt, at least 13.7% Cr, maximum 0.6% C, and nitrogen in contents usual in steel alloys, said alloy further containing titanium in such contents that the active titanium content depending upon the sum content of iron and cobalt is at least as high as the content defined by a curve in a coordinate system passing through the points 20% Fe+Co and 0.25% Ti; 30% Fe+Co and 0.35% Ti; 40% Fe+Co and 0.5% Ti; 50% Fe+Co and 0.7% Ti; 60% Fe+Co and 0.9% Ti; 70% Fe+Co and 1.25% Ti; 75% Fe+Co and 1.5% Ti.

In the following the invention is to be described more in detail with reference to the accompanying diagrammatical drawings.

Fig. 1 illustrates the lower limit for the active titanium content as a function of the sum of the iron and cobalt contents.

Fig. 2 illustrates the lack of restoration in steels of the type hitherto used in that the hardness is decreased by superheating and is maintained at the lower value when cooling again to working temperature (in this case 700° C.).

Fig. 3 illustrates the effect of restoration in alloys ac-

cording to the invention in that the hardness decreases due to superheating above the working temperature (700° C.) is restored when returning to said working temperature.

Fig. 4 finally illustrates the behavior of restoration at repeated superheatings.

All points of the diagrams have been established by practical trials.

The curve in Fig. 1 gives the total titanium content for alloys which are practically free from carbon and nitrogen. When carbon and nitrogen are present the value of the titanium content taken from the curve must be increased, advantageously by about 4 times the sum of the carbon and the nitrogen contents. Said increase of the titanium content is due to the fact that titanium is bonded as titanium carbide and titanium nitride wherefore the active titanium content at disposal for creating the effect of restoration becomes lower than the total content. If other carbide forming elements such as banadium, tantalum and columbium are present these also will be bonded to carbon whereby the active titanium content becomes correspondingly higher. The active titanium content therefore could be defined as that part of the total titanium content which is in solid solution in the alloy.

Sometimes alloys containing the minimum contents of titanium defined by the curve of Fig. 1 have the ability of restoration only partially developed. In order to have said ability with certainty and fully developed the titanium content should be somewhat higher than the values defined by the curve. With regard to the desirability that the alloys shall be easily workable at high temperatures the titanium content on the other hand should, as a rule, not be kept too high. The most advantageous active titanium contents therefore are between the curve of Fig. 1 and about 2 per cent.

In the following four examples are given of different basic alloys which possess the properties aimed at by the invention.

1. Cr 18–28%, Ni 8–25%, active Ti 0.65–1.35%. Co can advantageously be added in contents of between 10–25%.

2. Cr 13.7–18%, Ni 14–28%, active Ti 0.8–1.40%. Co can advantageously be added in content of between 10–25%.

3. Cr 15–30%, Ni 32–45%, active Ti 0.4–0.75%. Co can advantageously be added in contents of between 10–25%.

4. Cr 13.7–30% and preferably 18–30%, Ni 10–45%, preferably 25–28%, at least one of the elements Mo, W and V each in a content of up to 1%, active Ti 0.35–1.68%. Co can advantageously be added in contents of between 10–25%.

Also in alloys of Examples 1–3 above at least one of the elements Mo, W and V can be added in contents of below 1% each.

In all alloys according to the above examples the rest is iron with its common accessory elements such as C, Si, Mn, N, S and P. When the titanium content is near the lower limit it is, as a rule, suitable to have a silicon content of about 0.5–1.0%. The alloys further may contain such additional elements which favorably influence such properties as strength and malleability at high temperatures as well as at room temperature. Such additions may be one or more of the alloying elements Si, Al, W, Mo, V, Nb, Ta, Cu, Th, Mg, Zr and low contents of rare earth metals, alkaline earth metals, beryllium, boron and uranium as well as phosphorus, arsenic, antimony, nitrogen and sulfur.

On trials it has been determined that the above enumerated elements in such amounts as are usually required do not deteriorate the restoration effect. A certain low aluminium content is practically always obtained from the available titanium alloys used as alloying element in the production of the alloys.

The invention also involves a method of producing restorable objects. This method comprises forming the objects at a temperature above 900° C. and suitably above 1000° C., then bringing them to a temperature at which they are intended to be used or the temperature giving the highest heat strength. This alteration of the temperature of the objects can be performed either by cooling from the temperature at which the objects have been formed, possibly with a stall in the temperature range between 850 and 980° C. or by cooling from the temperature at which the objects are formed down to room temperature and reheating to the temperature at which the objects are intended to be used or to that temperature which gives the highest heat strength. Also in this last mentioned case it can be advantageous for a short period of time to keep the temperature between 850–980° C., since thereby the time of heating can be considerably decreased. The cooling can be performed in a furnace, in air, in oil or water, and shall, as a rule, be made slowly, although quenching in a liquid is sometimes possible. Generally it is most advantageous to perform the cooling stepwise in a furnace.

Heating in the temperature range 850–980° C.—the exact temperature being chosen according to the composition of the alloy—is not absolutely necessary but it has been found that thereby the necessary time for which the alloy must be kept at its temperature of working or at that temperature which after cooling gives the highest heat strength can be considerably decreased.

The heating at the working temperature which is required in order to develop the desired properties completely can be performed during the utilization of the alloy.

In the following there is made a comparison between a normally aging alloy and a restorable alloy and, further, it is shown how the hardness is influenced by variations in the temperature. Then in Table IV there are given a number of alloys which have been treated according to this invention.

Table I and Fig. 2 illustrate how the hardness is varied when heat treating cylindrical samples of 22 mm. diameter and 10 mm. height of a normally aging alloy with the composition: C=0.22%, Cr=14.7%, Ni=24.6% and Al=3.5%, which samples first were heated at 1050–1100° C. for 1 hour and then cooled in air. Each of the samples were then heated at a fixed temperature within the range 700–950° C. for a period of 15 hours. After the first heating and cooling to room temperature the hardness was measured. Then the samples were subjected to the second heating, cooled again to room temperature and the hardness again measured. From the table and the curve of Fig. 2 it is seen how the hardness decreases at higher temperatures. The left hand part of the figure shows the hardness values after the first heating and the right hand part the values after the second heating. The arrows illustrate the directions in which the resistance values are altered from which it is seen (just as from Table I below) that the hardness values obtained after the superheating are maintained even after reheating at 700° C. for 15 hours.

Table I

First heating		Second heating	
Temp., °C.	H_B	Temp., °C.	H_B
700	310	700	300
750	260	700	255
800	235	700	230
850	220	700	215
900	212	700	212
950	210	700	210

Table II and Fig. 3 illustrate in a corresponding manner the course when using a restorable alloy according to the present invention with the composition C=0.18%,

Cr=14.7%, Ni=27.7%, Ti=2.7% (active Ti content 2.0%). For this alloy the hardness was increased when reheating at 700° C. as is seen from Table II and the points and arrows inserted in Fig. 3.

Table II

First heating		Second heating	
Temp., °C.	H_B	Temp., °C.	H_B
700	350	700	350
750	330	700	352
800	290	700	355
850	235	700	358
900	200	700	360
950	190	700	360

In Table III and corresponding Fig. 4 there is illustrated how the hardness is varied for one and the same alloy according to this invention with the composition C=0.15%, Cr=15%, Ni=26% and Ti=1.7% (active Ti=1.1%), when one and the same sample is subjected to successively alternating temperatures within the range 650–950° C. After each treatment at the temperature stated in Table III and under the stated times the measuring of the hardness has been performed at room temperature. From this it is clear how the hardness depends upon the temperature.

Table III

Temp., °C.	Time in hours	H_B
700	5	210
850	5	155
700	10	220
800	5	162
950	5	142
800	6	161
650	7	240

In the examples there are given the values of hardness measured at room temperature. Normally it is not possible from the hardness at room temperature to draw definite conclusions regardness hardness and resistancy at high temperatures. However, with the austenitic alloys here in question a variation in hardness at room temperature can be utilized as a criterion of the variation of the heat strength in the same direction. Practical trials have proved that this theory is correct. Thus, if a material has been superheated so that its hardness at room temperature is decreased, its heat strength was simultaneously decreased, and when such material then

due to restoration recovers its earlier hardness (at room temperature) this shows that it has also recovered its earlier heat strength.

In Table IV there are given examples of a number of steel alloys within the scope of this invention and also a number of alloys outside of but near the limits of the invention. In the last mentioned group there are given some of the commonly utilized heat resistant steel alloys.

Sometimes, and particularly in the cases of more complex alloys, it is advantageous after hot working the objects to reheat them to at least 1000° C. and suitably to about 1100° C. as stated for the samples according to Table I and Fig. 2 in order thereby to complete the diffusion or dissolving of the alloying elements and thereby to equalize the structure. Such reheating is particularly advantageous in combination with a stall in the temperature range 850–980° C. during the cooling.

Table IV

Alloy	C	Cr	Ni	Ti		Mo	W	V	Co	Nb/Ta	Be	Restorable
				total	active							
1	0.038	15.4	45.7	0.68	0.53							no.
2	0.038	15.4	46.4	0.94	0.79							yes.
3	0.14	19.6	20.6			2.9	2.7		20	1.1		no.
4	0.09	20.1	18.8	1.0	0.64	3.04	3.17		20.3			no.
5	0.08	19.2	18.8	2.1	1.8	3.0	2.97		19.8			yes.
6	0.14	14.9	25.7	1.06	0.50		0.44			0.82		no.
7	0.06	14.7	24.1	0.85	0.61							no.
8	0.15	15.2	26.0	1.7	1.1		0.52			0.71	0.003	yes.
9	0.21	14.0	24.4	2.1	1.26							yes.
10	0.047	15.0	24.9	2.1	1.91							yes.
11	0.08	14.4	23.6	2.2	2.0							yes.
12	0.19	18.7	20.1	1.1	0.44							no.
13	0.18	18.4	18.5	2.6	1.88	0.5	0.78	0.33		1.07		yes.
14	0.20	17.7	19.1	2.7	1.9							yes.
15	0.032	15.7	20.1	0.8	0.67							no.
16	0.036	15.9	15.2	0.94	0.8							no.
17	0.066	15.9	15.2	1.8	1.51							yes.
18	0.12	25.4	23.4	0.30		1.08				1.9		no.
19	0.16	24.7	19.9	0.62								no.
20	0.15	25.0	12.8	0.49								no.
21	0.09	17.7	11.6	0.27								no.
22	0.13	19.9	9.5	0.33		0.28	1.21			0.48		no.
23	0.05	18.0	8.7	0.48								no.

Remarks: The alloys contain silicon and manganese in contents up to 2% and aluminum up to 0.5% and further the usual accessory elements in steel alloys.

I claim:

1. Objects which during their use are to be subjected to temperatures of at least 650° C. and which are nonsensible to superheating above their temperature of utilization by recovering their strength and hardness when the temperature is returned to said temperature of utilization, characterized in that they are produced from a non-precipitation hardening alloy of at least predominatingly austenitic structure and containing at least one of the gamma forming elements Ni and Mn within the range from 10% to 45%, from a trace up to 1% of at least one of the elements V, Mo and W, at least 20% Fe+Co, not more than 0.6% C, Cr within the range from 13.7 to 30%, the common accessory elements Si, N, P and S and further Ti in such content that the active Ti-content is at least the one defined by a curve in a coordinate system set forth in Fig. 1 of the drawings, said curve passing through the points 20% Fe+Co and 0.25% Ti; 30% Fe+Co and 0.35% Ti; 40% Fe+Co and 0.5% Ti; 50% Fe+Co and 0.7% Ti; 60% Fe+Co and 0.9% Ti; 70% Fe+Co and 1.25% Ti; 75% Fe+Co and 1.5% Ti but not exceeding 2%.

2. Objects according to claim 1, in which at Ti contents close to the values defined by the curve the Si content is between 0.5 and 1.0%

3. Objects according to claim 1 containing up to 5% of at least one of the elments Ta, Nb, Al, Cu, Mg, Zr, and low percentages of at least one of the elements Th, Ce, Be, B, U, P, As, Sb, S, and alkaline earth metals.

4. A method of heat treating heat resistant objects of an at least predominantly austenitic alloy containing at least one of the gamma forming elements Ni and Mn within the range from 10 to 45%, at least 20% Fe+Co,

from a trace up to 1% of at least one of the elements V, Mo and W, not more than 0.6% C, Cr within the range from 13.7 to 30%, the common accessory elements Si, N, P and S and further Ti in such content that the active Ti-content is at least the one defined by a curve in a coordinate system set forth in Fig. 1 of the drawings, said curve passing through the points 20% Fe+Co and 0.25% Ti; 30% Fe+Co and 0.35% Ti; 40% Fe+Co and 0.5% Ti; 50% Fe+Co and 0.7% Ti; 60% Fe+Co and 0.9% Ti; 70% Fe+Co and 1.25% Ti; 75% Fe+Co and 1.5% Ti but not exceeding 2%, which heat treatment comprises hot working at 90° C. at least and preferably at a temperature above 1000° C. with subsequent restoring the temperature at a value at which the objects are to be utilized or at which the best heat resistant properties are obtained.

5. A method as claimed in claim 4 in which the temperature is restored by cooling directly to said temperature of utilization.

6. A method as claimed in claim 4 in which the temperature is restored by cooling with a stall in the temperature range between 850 and 980° C.

7. A method as claimed in claim 4 in which after hot working the object is cooled down to room temperature and then reheated to the temperature at which the object is intended to be utilized or to the temperature giving the highest heat resistancy.

8. A method as claimed in claim 4 in which the object after hot working is cooled down to room temperature then reheated within the temperature range 850–980° C. and finally cooled to the temperature at which the object is intended to be utilized or to the temperature giving the best heat resistant properties.

9. A method as claimed in claim 7 characterized in that the heating to the temperature at which the object is intended to be used is first performed during the utilization of the object.

10. A method as claimed in claim 8 characterized in that the heating to the temperature at which the object is intended to be used is first performed during the utilization of the object.

11. A method as claimed in claim 4 in which the hot worked objects are reheated to a temperature of at least 1000° C. and suitably about 1100° C.

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