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(19) **United States**(12) **Patent Application Publication**
Barbosa et al.(10) **Pub. No.: US 2009/0081073 A1**(43) **Pub. Date: Mar. 26, 2009**(54) **ALLOYS WITH HIGH CORROSION
RESISTANCE FOR ENGINE VALVE
APPLICATIONS****Publication Classification**(51) **Int. Cl.**
C22C 30/02 (2006.01)(52) **U.S. Cl.** **420/582**(76) **Inventors:** **Celso Antonio Barbosa**, Campinas
(BR); **David Delagostini Jarreta**,
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Sokolowski, Sao Paulo (BR)(57) **ABSTRACT**

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Low cost alloys resistant to mechanical requirements related to high temperatures, resistant to corrosion, with high workability and which meet different requirements in the conditions for application in either exhaust or intake valves for internal combustion engines. The main features of the alloys is the precipitation of Ni_3Nb in its microstructure. In percentage, its mass consists of: 0.01 to 0.15% C, up to 3.0% Mn, up to 1.0% Si, 18.0 to 25.0% Cr, 25.0 to 49.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, up to 5.0% Cu, 1.0 to 3.0% Al, 0.5 to 2.5% Ti, 1.0 to 6.0% Nb, 0.001 to 0.02% B, 0.001 to 0.10% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass. As for the ration Al/Ti, it is lower than 2.0. The rest is made of iron and impurities inevitable to the Alloy manufacture procedure.

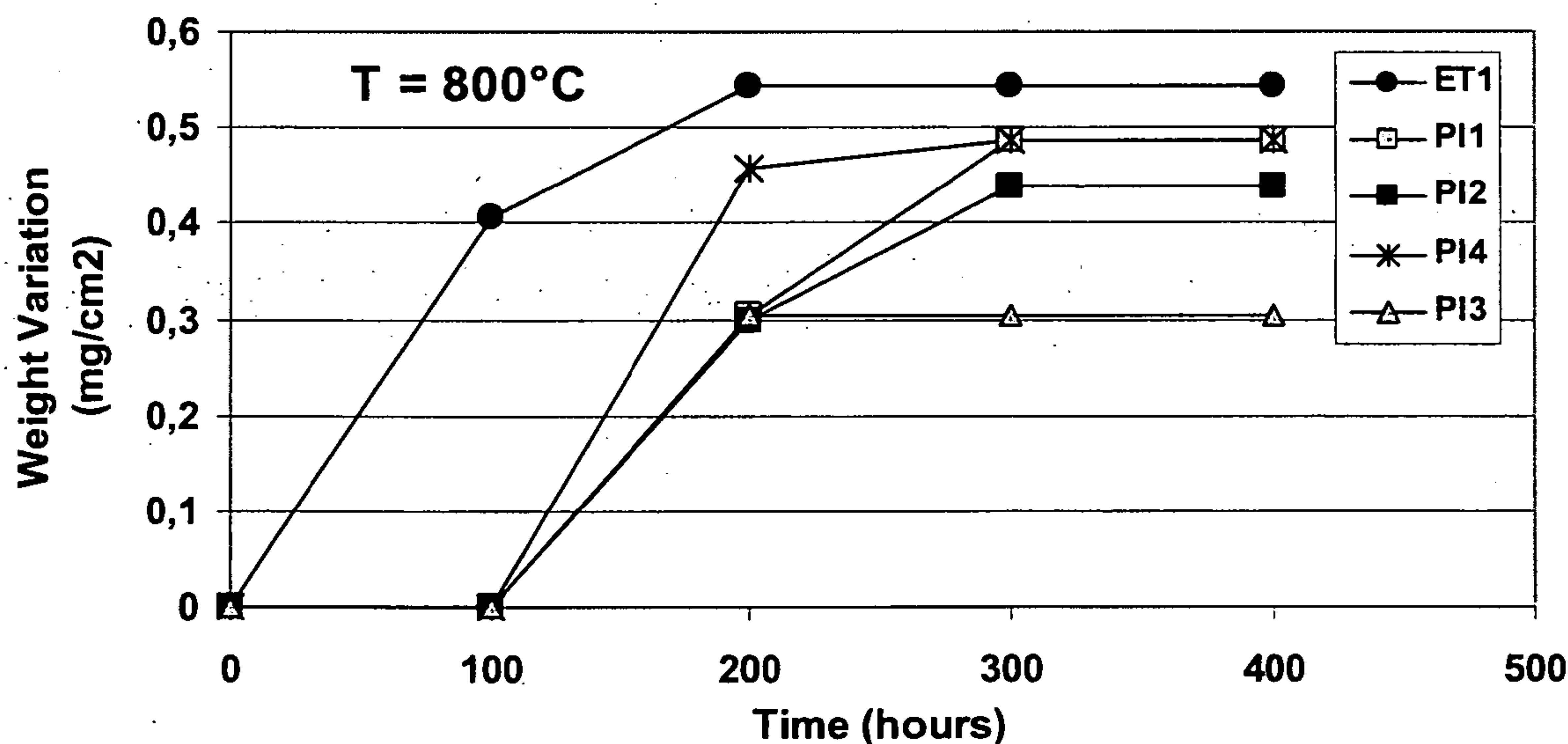
(21) **Appl. No.:** **12/155,702**(22) **Filed:** **Jun. 9, 2008****Related U.S. Application Data**(60) **Provisional application No. 60/924,974, filed on Jun. 7, 2007.**

Figure 1:

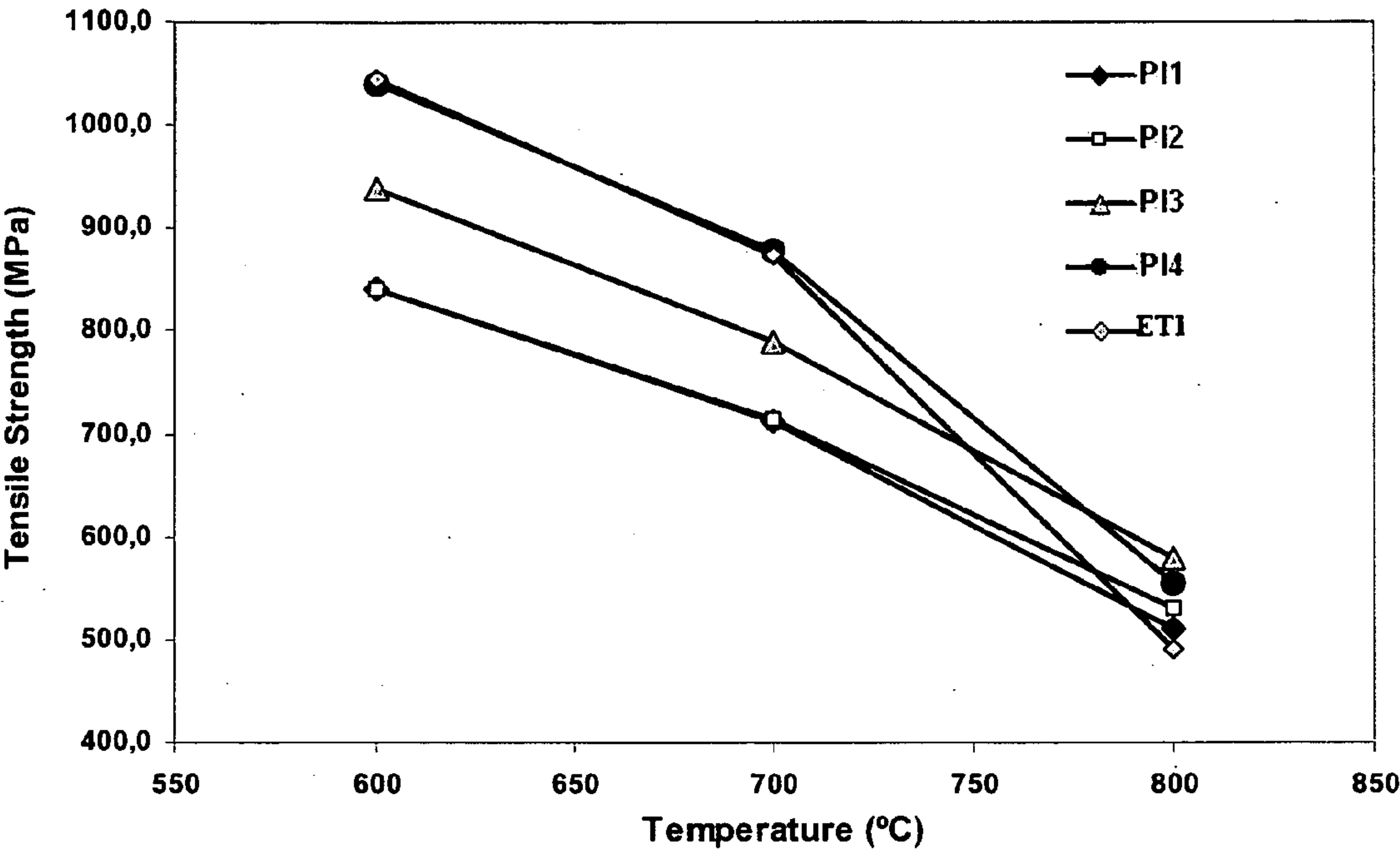


Figure 2:

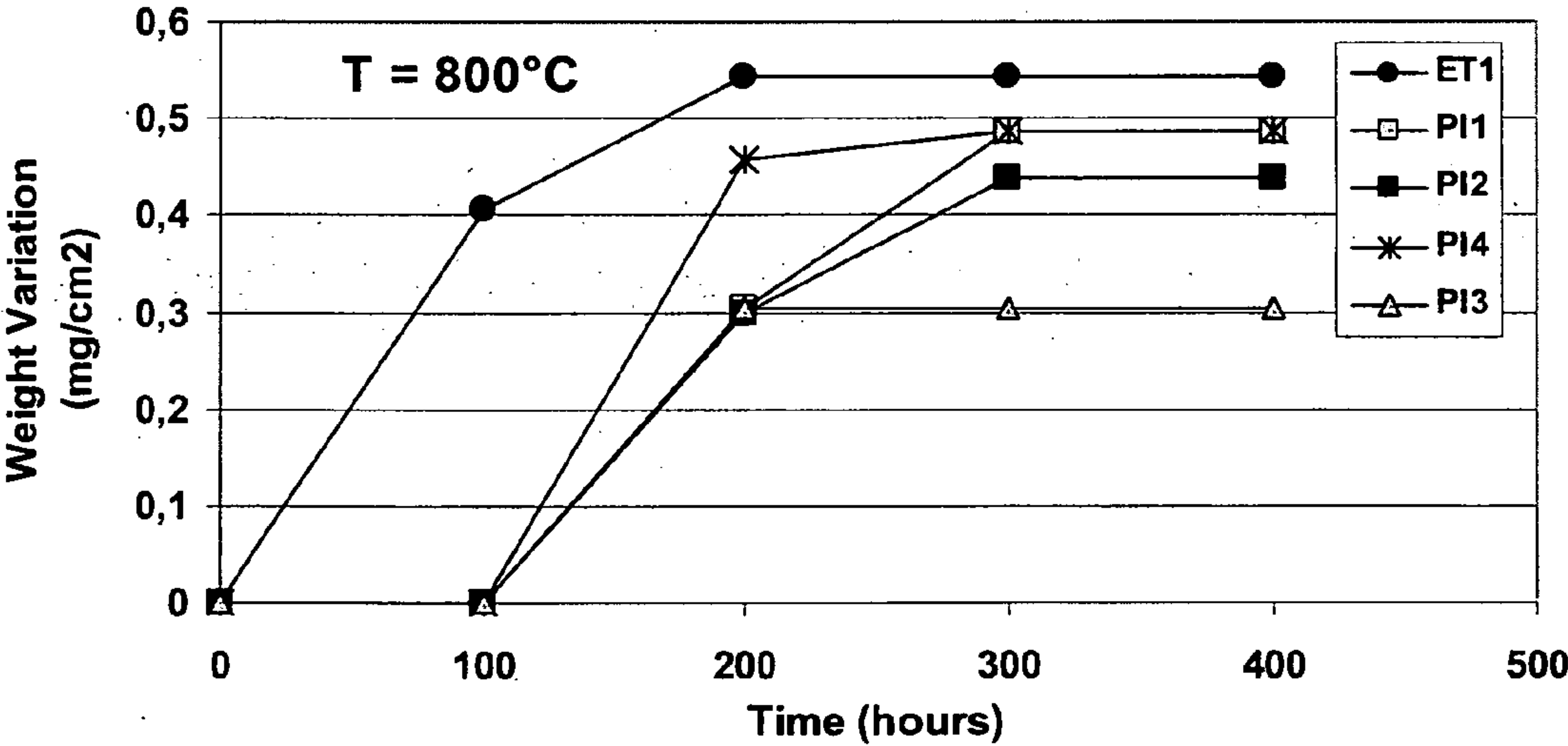
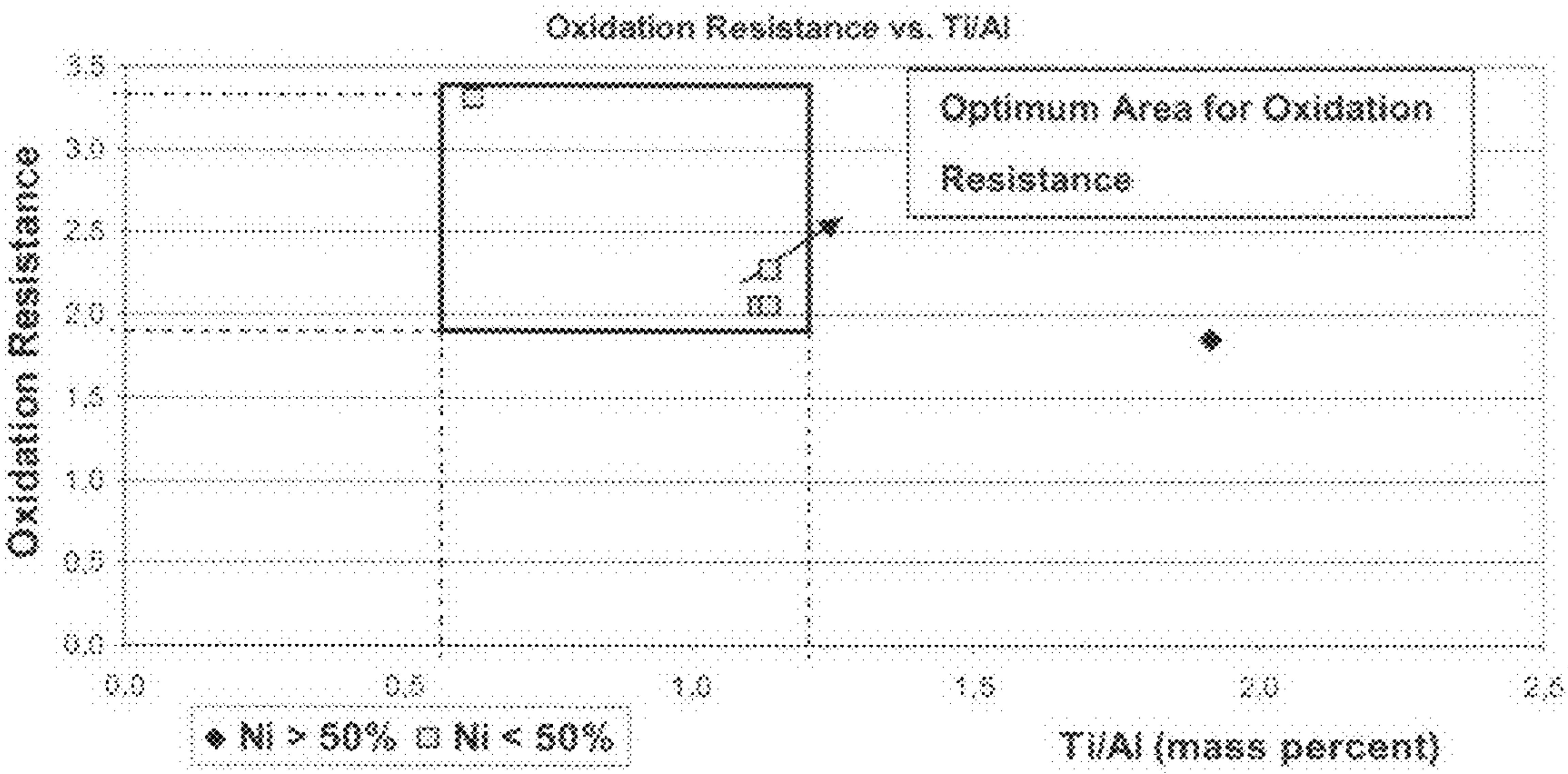


Figure 3:



ALLOYS WITH HIGH CORROSION RESISTANCE FOR ENGINE VALVE APPLICATIONS

[0001] This application claims benefit of provisional application 60/924,974, filed Jun. 7, 2007.

FIELD OF THE INVENTION

[0002] This invention deals with an Ni—Fe—Cr precipitation hardened superalloy for application in internal combustion engine valves, having as chief characteristics a high hot resistance through the precipitation of $\text{Ni}_3(\text{Al}, \text{Ti}, \text{Nb})$ and a higher oxidation resistance as compared to the state-of-the-art alloys. The alloy project, based on its microstructure aspects, also allows for the alloy hereof to be provided with properties equal to or higher than those of the high nickel alloys used in internal combustion engine valves, associated with the alloy's significant cost reduction because of the lower nickel content.

[0003] The alloy hereof is intended for valves' manufacture, where the alloy is required to have several properties, among them the following: high temperature oxidation resistance and heat resistance, because of the high temperatures used in the application.

BACKGROUND OF THE INVENTION

[0004] Conventionally, the materials used for exhaust valves in diesel and gasoline engines were JIS SUH 35 or JIS SUH 38 with Stellite coating (cobalt base alloy) on the valve's hardfacing. With the historic increased application temperatures of the new engines' valves, higher performance materials started to be used in some applications, as it occurs with nickel base superalloys.

[0005] Currently, the reduction in the production costs of high performance materials is a tendency of the industry, as it occurs with exhaust valves, which are parts that are exposed to the highest temperatures and highest mechanical stress in an internal combustion engine. Such extreme stresses in terms of mechanical resistance and corrosion resistance at high temperatures require the use of costly nickel-based superalloys.

[0006] One example of an excellent performance alloy in these applications is the NCF 751 alloy, which is very costly because of its high nickel content, above 70%. In this sense, alloys with lower nickel contents with high temperature resistance, corrosion resistance and long term microstructural stability at high temperature have been developed. Examples are the state-of-the-art alloys, NCF3015 (JIS3015D—U.S. Pat. No. 5,660,938) and the alloy of U.S. Pat. No. 5,951,789.

[0007] Through the use of the lead-free gasoline since the 70's, the requirement in terms of corrosion resistance of the exhaust valve material has been reduced, so that the lead oxide corrosion by the lead oxide is no longer a primary concern. The high temperature oxidation resistance is a property to be reviewed in terms of corrosion, having the good performance of the NCF 751 alloy.

[0008] Accordingly, the need is evident to develop new superalloy compositions resistant to high temperature mechanical stress in connection with high temperatures, corrosion resistant, with high hot workability, and meeting the different stresses under the conditions of using intake or exhaust valves, able to meet the need of a lower cost, which is

related to the lower content of costly alloy elements. Alloy NCF 751 is the most important material to be replaced.

[0009] The alloys hereof are intended to meet all such needs.

SUMMARY OF THE INVENTION

[0010] The properties of the Ni—Fe—Cr alloys used in exhaust valves are closely related to the presence of intermetallic phases in their microstructures. The intermetallic phases are very important for high temperature resistance. As regards the solid solution elements in the alloy, a composition providing the material with corrosion resistance required in the use environment is very important. The performance of the alloy elements to form these phases has been carefully reviewed and modified as regards the conventional concept. In this sense, this invention employs the niobium in relatively high quantities (higher than the state-of-the-art alloys) as an alloy element, mainly in the form of fine intermetallic precipitate.

[0011] Other elements used by this invention in higher quantities than the state-of-the-art alloys are aluminum and chromium, which have prevailing functions in the alloys' corrosion resistance. Chromium is responsible for the formation of a passivating film of chromium oxide on the material's surface, which prevents the corrosive process progression. Aluminum is also a builder of a coherent intermetallic containing niobium, $\text{Ni}_3(\text{Al}, \text{Nb})$, thus improving the material's heat resistance. Additionally, aluminum improves the alloy hot resistance oxidation.

[0012] As the carbon atoms are stabilized by the presence of titanium and niobium (strong carbide formers) in great quantities in the alloy, the chromium atoms are "free" to react with the outer oxygen on the alloy's surface and build a thin chromium oxide layer thereon. This is a protective layer as it is impermeable to oxygen and other gases and fluids of the outer environment, so as not to allow for a progressive corrosion process.

[0013] It is extremely important that a small distortion exists between the network parameters of the phases γ and γ' , which leads to a low interface energy (γ/γ'). The main coarsening driving force of these intermetallic precipitates is the minimization of the total interface energy, so that one coherent or semi-coherent low energy interface leads to a more stable microstructure. Metallurgical stability is a highly recommendable property for high temperature applications.

[0014] The morphology of these precipitates is determined by the surface energy of the γ/γ' interface, and the elastic energy generated by phases γ/γ' lattices mismatch, being primarily determined by the lattice distortion. If it is a small distortion, the morphology that will minimize the surface energy and the distortion energy per volume will be the spherical one. However, in case the lattice distortion is considerably big, the morphology of the precipitates will not be spherical, but rather cubic. Whenever the lattice mismatch is up to 0.02%, the γ' precipitates will be spherical; in case of mismatches between 0.5 and 1.0%, these precipitates will be cubic; above 1.25%, they are plate-shaped.

[0015] Niobium shows an ordered phase Ni_3Nb precipitation kinetics lower than when compared to elements such as titanium and aluminum in phases $\text{Ni}_3(\text{Ti}, \text{Al})$. In the Ni—Cr—Fe system superalloys, high niobium contents lead to the ordered phase γ'' (Ni_3Nb) precipitation, similar to phase γ' . Whenever added to lower content alloy, niobium only

increases the gamma prime precipitate volume and the solution temperature of this phase, leading its hardening effect to even higher temperatures.

[0016] With a view to meet the above referred conditions, the alloys hereof are provided with alloy element compositions, which, in bulk percentage, consist of:

[0017] 15.0 to 25.0 chromium, preferably 16.0 to 24.0 chromium, typically 18.6 chromium.

[0018] 3.0 to 10.0 for the (Nb+2 Ti) ratio, preferably (Nb+2Ti) between 3.0 and 7.0, typically (Nb+2Ti) equal to 4.2; in this equation, titanium and niobium can take any value within the limits; however, a minimum niobium content shall be maintained, equal to 1.20%, preferably higher than 1.8%.

[0019] 0.02 to 0.07 carbon, preferably 0.03 to 0.06 carbon, typically 0.05% carbon.

[0020] 0.1 to 3.0 aluminum, preferably 0.5 to 2.5 aluminum, typically 1.85% aluminum.

[0021] Maximum 1.0 copper, preferably maximum 0.5 copper, typically maximum 0.1 copper.

[0022] Iron balance and inevitable metallic and non-metallic impurities to the melting shop process, where said non-metallic impurities include, without limitation, the following elements, in bulk percentage:

[0023] Maximum 5.0 for the manganese, molybdenum and tungsten elements, preferably maximum 2.0, typically maximum 0.50.

[0024] Maximum 0.20 for phosphorus and sulfur, preferably maximum 0.05, typically maximum 0.005.

[0025] Find below the reasons for the specification of the new material composition, describing the effect of each alloy element. The indicated percentages relate to bulk percentages.

[0026] When defining this alloy, a crucial point was the chromium content variation. Chromium is used to provide the alloy with high temperature corrosion and oxidation resistance; accordingly, its content shall be higher than 10% in case of exhaust valve superalloys. Contents above 25% threaten the microstructure stability since they tend to form phases such as sigma and alpha prime phases (σ and α'), which deteriorate ductility. On the other hand, contents above 16% bulk show a positive answer as regards the improvement of high temperature oxidation resistance. Accordingly, one concludes that the alloy chromium content would be between such limits, preferably between 16.0% and 22.0%, typically 18.6%.

[0027] Titanium and niobium are carbide formers. Whenever they are added to the alloy, they firstly combine with carbon, because of the high chemical affinity between these elements. The resulting carbides contribute to the abrasive wear resistance. The titanium and niobium content that is non-combined with carbon will combine with nickel to form the γ' intermetallic phases. For these two effects, the titanium and niobium contents shall be added to the alloy hereof according to the Nb+2 Ti ratio, which accounts for the atomic mass difference of both elements. Thus, in order to obtain the desired effect in the hot resistance properties, the Nb+2Ti ratio must be higher than 3.0%, typically equal to 4.2%.

[0028] Another determining fact to define this alloy was the titanium and niobium content variation in order to define an optimum composition, within the ratio in question. It could be noticed that the niobium introduction in amounts above 1.2% causes beneficial effects as regards niobium residual content (non-combined in the form of carbides), and such content is

crucial to improve the alloy hot properties. What is desired when introducing Nb in higher quantities is to cause the γ'' intermetallic phase precipitation (Ni_3Nb) and the phase γ' modification through the introduction of a greater niobium content in its structure. A wide range for the Nb element is between 0.9 up to 4.0% (bulk), with an intermediate range of 1.2 up to 3.5% (bulk) of Nb and a narrow interval of 1.5 up to 3.0% (bulk) of Nb, or even narrower, of 1.8 up to 2.5%.

[0029] In addition to the improved heat resistance, Nb also improves the weldability of hardened superalloys by phase γ'' precipitation; additionally, it improves corrosion in sulfurous environments, such as diesel engines.

[0030] Nb can be partially replaced with tantalum (Ta) on equiatomic bases. Like Nb, Ta is also a builder of the intermetallic phase with nickel and strongly stabilizes primary carbides, being equally beneficial for hot hardness and abrasion resistance.

[0031] The increase in the niobium amount has shown effects in hot resistance properties. Although the mechanism is not completely defined, in the alloys hereof the niobium content that is not combined with carbon must build different intermetallics as compared to the titanium intermetallics, probably the two-line gamma type (γ'), which are very stable to coalescence and, accordingly, effective in improving the high temperature resistance properties.

[0032] For a same content of (Nb+2 Ti) ratio, niobium addition causes a reduction in the alloy's total titanium percentage. The studies hereof showed that such reduction is also beneficial to improve the high temperature oxidation resistance—an also essential property in high temperature working valves.

[0033] The reduced total titanium percentage in the alloy by the niobium addition in quantities higher than 1.2% improves its hot workability, since the alloy's hot ductility is threatened to values above 4.0% for the sum of titanium and aluminum contents; desired $(\text{Ti}+\text{Al}) < 4.0\%$.

[0034] For all such effects—hot resistance and oxidation resistance—the (Nb+2 Ti) ratio must show a minimum 1.2% niobium content, preferably niobium above 1.5%, with an optimum niobium content equal to or higher than 1.8%.

[0035] In spite of niobium and titanium beneficial aspects, the content of such elements cannot be excessively high, since it would cause the formation of coarse intermetallics, thus jeopardizing the mechanical properties of the alloy in terms of mechanical resistance and ductility, in addition to increasing the alloy cost. Accordingly, the value of the (Nb+2 Ti) ratio must be below 8.0%, preferably below 7.0%.

[0036] Carbon is added with the intent of combining titanium and niobium in order to form carbides, which precipitate in the grain contours and improve the alloy's creep resistance, since they hinder the deformation mechanism by “grain contour sliding”. For that function, the carbide content shall be at least 0.03%, preferably above 0.03% and below 0.06%, preferably 0.05%.

[0037] Aluminum is very important for the gamma line (γ') phase precipitation, and therefore for high temperature resistance. Another extremely important function of aluminum in the alloy is to increase high temperature oxidation resistance by increasing the formation of Al_2O_3 during the heating phase. Nevertheless, aluminum contents must be restricted, as very high quantities thereof can lead to deterioration of high temperature resistance and hot workability because of nitrite formation and such phases as η and δ for long heating

periods. Therefore, the aluminum content shall be between 0.5% and 4.0%, preferably between 1.0% and 3.0%, typically equal to 2.0%.

[0038] Copper must be controlled in low contents, as this element is harmful for some properties, mainly the high temperature oxidation, which is the great improvement obtained by the alloys hereof. Additionally, no nickel alloy or superalloy uses copper and, once such element is added, it cannot be removed by the melting shop processes. This causes the internal scrap, namely, the returns of the production process, not to be used in other alloys' process, thus considerably increasing the production cost or even rendering unfeasible the alloy production. Accordingly, in the alloys hereof the copper content must be below 1.0%, preferably below 0.5% and typically below 0.1%. As shown in Table 1 of the Example, U.S. Pat. No. 5,951,789 has a high copper content, and this is its main disadvantage as compared to the alloys hereof, because of such reasons of hot oxidation and scrap contamination.

[0039] Residual: Other elements such as manganese, tungsten, molybdenum, sulfur, phosphorus and those usually obtained as regular residual elements in the preparation process of steel or liquid nickel alloys, shall be understood as impurities in connection with the melting shop deoxidization processes or inherent to the manufacturing processes. Therefore, the manganese, tungsten and molybdenum content is reduced to 5%, preferably below 2.0%, because of the ratio destabilization between the austenite and ferrite phases, and because of any effects in the intermetallic phases present in the alloy. Phosphorus and sulphur segregate in grain boundaries and other interfaces, and therefore they shall be below 0.20%, preferably below 0.05%, preferably maximum 0.005%.

[0040] The described alloy can be made by conventional or special processes such as melting in electric or vacuum furnaces, followed by re-melting processes or not. Casting can be made in ingots by means of conventional or continuous casting, or even by other manufacturing processes involving disaggregation of the liquid metal and further aggregation, such as power metallurgy and the spray forming or continuous casting process. The end products can be obtained after hot or cold forming, and end products are produced in the

form of wire rods, blocks, bars, wires, sheets, strips, or can be even products in the as cast state.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] FIG. 1 compares the heat resistance of the alloys hereof (PI) to the state-of-the-art alloys ET1 and ET2 as of the resistance limit thereof for several temperatures;

[0042] FIG. 2 shows the test oxidation resistance results; and

[0043] FIG. 3 shows the oxidation resistance results as related to the Ti/Al ratio.

DETAILED DESCRIPTION OF THE INVENTION

[0044] FIG. 1 depicts the heat resistance of the alloys compared to other known alloys. FIG. 2 shows the test oxidation resistance results. In such test, cylindrical test specimens (diameter=12 mm, height=14 mm), as solubilized and aged, were duly weighed and kept at an 800° C. temperature for 100 hours. After being removed from the furnace, the test specimen is air cooled and weighed again, and the mass variation is measured. The bigger the mass gain, the lower the oxidation resistance. Such process is repeated until the total test time is completed. Ceramic alumina crucibles were used as sample holders during the test. The oxidation process at 800° C. was reviewed for 400 hours, when it was possible to notice a stabilization of the corrosion process. The test was carried out so that all samples of all alloys involved had identical sizes, for them also to have an identical contact surface. FIG. 3 shows the oxidation resistance results as related to the Ti/Al ratio. The oxidation resistance calculation is made by inverting the mass variation after 200 hours at 800° C. (g^{-1}).

[0045] In order to define the compositions of the alloys hereof, several alloys were made and compared to the state-of-the-art alloys. The chemical compositions are shown in Table 1. The alloys hereof are hereinafter called PI, and the state-of-the-art alloys are hereinafter called ET. ET1 alloy corresponds to NCF 751, and ET2 alloy corresponds to NCF 3015 alloy (of U.S. Pat. No. 5,660,938). The following ratios are also quantified: (Nb+2 Ti) and (Ti/Al) in Table 1.

[0046] In Table 1 one can notice a significant reduction in the nickel content of the alloy in the compositions hereof as regards ET1 alloy, thus resulting in considerably lower cost. Table 1 also shows the addition of different niobium contents to the alloys hereof, and aluminum and titanium contents.

TABLE 1

Chemical compositions of two alloys of the state of the art (ET1 and ET2) and the alloys of the present invention (PI1 to PI4). Percentage in mass and balance in iron.											
	C	Si	Mn	Cr	Ni	Al	Ti	Nb	Cu	Nb + 2 Ti	Ti/Al
ET1 (NCF 751)	0.05	0.03	0.05	15.5	70	1.2	2.45	0.9	0.01	5.5	1.92
ET2 (NCF 3015)	0.04	0.03	0.05	16.0	32	1.4	2.50	0.65	0.01	5.65	1.79
ET3 (U.S. Pat. No. 5,951,789)	0.03	0.21	0.21	16.0	32.3	1.43	2.53	0.82	2.05	3.35	1.77
PI1	0.05	0.1	0.16	18.2	35.2	1.87	2.1	0.89	0.01	5.09	1.12
PI2	0.05	0.1	0.15	21.5	35.9	1.85	2.1	0.90	0.01	5.1	1.14
PI3	0.05	0.1	0.15	18.6	35.6	1.83	1.14	1.92	0.01	4.2	0.62
PI4	0.06	0.1	0.15	19.1	36.8	1.82	2.08	1.93	0.01	6.09	1.14

[0047] This new alloy project showed to be of great benefit to the end properties, as discussed below, when comparing the alloys of the present invention with alloys ET1 and ET2. As for alloy ET3, the alloys of the present invention have an important advantage—they reaching higher mechanical and corrosion properties, without the need of high contents of copper. As discussed above, copper is an important contaminant of nickel alloy scrap, because copper cannot be removed through the process of scrap remelting and, thus, returns of materials with a high content of copper cannot be used to prepare conventional alloys, which have limits to the maximum content of copper. Besides, copper tends to be damaging to corrosion properties at high temperature.

[0048] The differences between the titanium and aluminum contents in the different alloys can be evaluated through the ratio (Ti/Al), which is very important as for the alloy properties of resistance to hot oxidation and workability. Such ratio (Ti/Al) is displayed in Table 1 as well.

[0049] The ingots were cast by means of a close procedure for such six alloys (ET1, ET2, PI1, PI2, PI3 and PI4), in a vacuum induction furnace. The casting was made into cast iron moulds, producing an ingot of about 55 kg. After the solidification, the ingots were forged and rolled for round gauges with diameter of 18 mm. In addition to these alloys, the typical composition of U.S. Pat. No. 5,951,789 is also displayed for comparison purposes (called ET3).

[0050] Table 2 displays the hardness of alloys ET1, ET2, PI1, PI2, PI3, and PI4 after solution at 1050° C. and aging at 750° C. for 1 hour and, also after solution at 1050° C. and aging for 4 hours. These data show equivalent values as for the hardness of aged alloys, except for alloy ET3, which has lower hardness. The alloys with niobium have lower hardness in the solution state, what is interesting to machine the material in this condition.

TABLE 2

Response to the heat treatment of the alloys of the state of the art (ET1, and ET2), and the alloys of the present invention (PI1, PI2, PI3, and PI4). Results of hardness in HB after solution at 1050° C. and aging at 750° C. for 1 hour and 4 hours.			
	Solution	Aging (750° C. - 1 h)	Aging (750° C. - 4 h)
ET1	254	330	330
ET2	250	335	335
PI1	307	333	357
PI2	323	343	359
PI3	276	327	346
PI4	319	352	374

[0051] Another important parameter for these alloys are the mechanical properties at high temperature, as displayed in FIG. 1. The alloys of the present invention, despite having nickel content substantially lower than alloy ET1, are more resistant at high temperature than alloy ET1. The values of the limit of traction resistance (FIG. 1), for instance, show that all the alloys of the present invention, PI1, PI2, PI3, and PI4, are more resistant than alloy ET1 for 800° C. temperature. Alloy PI4 is highlighted, seen as equivalent to or even more resistant than alloy NCF 751 (ET1) in all temperatures tested.

[0052] In terms of oxidation resistance, the alloys of the present invention are also superior to alloy ET1, as shown in Table 3 and in FIG. 2; we see that the higher the content of chromium and aluminum, the lower the content of titanium, and the higher the resistance to the oxidation. This is the best

resistance seen for alloy PI3. This occurs for two reasons. Firstly, because a higher content of chromium and aluminum provides a larger and quicker formation of the passive film made of chromium oxide or aluminum oxide on the surface of the material. Secondly, the effect caused by titanium, i.e., the destabilization of the oxide layer formed on the surface of the alloys in the iron-nickel-chromium system and, thus, the decrease in the oxidation resistance of alloys with a higher content of such element. For instance, it is interesting to notice that, among the alloys with high content of chromium (PI1, PI2, PI3, and PI4), the one with the lowest titanium content (PI3) has the highest hot oxidation resistance in the tested conditions.

TABLE 3

Gain in mass (in mg/cm ²) after 100, 300 and 400 hours in atmosphere air (800° C.). The lower the gain in mass, the higher the resistance to the oxidation of the material.			
	100 hours	300 hours	400 hours
ET1 (Ti = 2.5%; Cr = 15.5%)	0.40	0.54	0.54
PI1 (Ti = 3.0%; Cr = 18.2%)	0.00	0.49	0.49
PI2 (Ti = 2.0%; Cr = 21.5%)	0.00	0.44	0.44
PI3 (Ti = 1.1%; Cr = 18.6%)	0.00	0.30	0.30
PI4 (Ti = 2.1%; Cr = 19.1%)	0.00	0.49	0.49

[0053] The property of resistance to hot oxidation can be examined in accordance with ratio (Ti/Al) as well. FIG. 3 shows this analysis concerning the alloys of the present invention (PI1 to PI4) and of the state of the art (ET1). In these results, we can see clearly that the alloys of the present invention are in the optimum range of the ratio Ti/Al for the optimization of the property of hot oxidation resistance, represented by a reversal of the gain in mass (in mg/cm²) after 400 hours at 800° C. in atmosphere (air).

[0054] Therefore, the comparison between the alloys of the state of the art and the alloys of the present invention showed that the introduction of higher contents of niobium and aluminum, together with the contents of titanium, cause improvements in the hot resistance properties, creep resistance, and resistance to oxidation. A summary of such effects is displayed in Table 4. Alloys PI2, PI3, and PI4 are always superior to the alloys of the state of the art, in terms of all properties examined. Alloys PI3 and PI4 are highlighted, since they have the best results.

[0055] In summary, we can state that the results discussed herein show that the alloys of the present invention, in addition to the economic advantage of working with a lower content of nickel, have better properties as well. As for the alloys of the state of the art, the alloys of the present invention have higher levels of properties at high temperature. So, they are material improvements for industrial application in combustion engine valves or even other components used at high temperatures and corrosive sites. Besides, they can be produced with no scrap contamination problems, since they use a low content of copper.

TABLE 4

Comparison of Properties among all alloys studied, in absolute figures and relative figures (the reference is alloy ET1 = 100%).						
	ET1	ET2	PI1	PI2	PI3	PI4
Hardness After Aging Treatment (HB)	335	300	357	359	346	374

TABLE 4-continued

Comparison of Properties among all alloys studied, in absolute figures and relative figures (the reference is alloy ET1 = 100%).						
	ET1	ET2	PI1	PI2	PI3	PI4
Rupture Strength at 800° C. (MPa)	490	490	512	530	579	555
Oxidation Resistance (Inverse of weight variation) after 200 hours at 800° C. (g-1)	1.9	—	2.1	2.3	2.1	3.3
	In relation to ET1 (ET1 = 100)					
Hardness After Aging Treatment	100	90	106	107	103	112
Rupture Strength at 800° C.	100	100	104	108	118	113
Oxidation Resistance (Inverse of Weight Variation) after 200 hours at 800° C.	100	—	111	121	111	174

[0056] While the invention has been described with reference to preferred embodiments, variations and modifications would be apparent to one of ordinary skill in the art. The invention encompasses such variations and modifications.

We claim:

1. A Fe—Ni—Cr alloy for internal combustion engine valves, presenting a chemical composition of elements comprising,

C, Mn, Si, Cr, Ni, Mo, W, V, Al, Ti, Nb, B, Zr, Cu, Co,

2. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass,

up to 0.15% C,
up to 3.0% Mn,
up to 1.0% Si,
18.0 to 25.0% Cr,
25.0 to 49.0% Ni,
up to 1.0% Mo,
up to 1.0% W,
up to 1.0% V,
1.0 to 3.0% Al,
0.5 to 2.5% Ti,
1.0 to 6.0% Nb,
0.001 to 0.02% B,
0.001 to 0.1% Zr,

up to 1.0% Cu,
up to 2.0% Co,
where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 2:1.

3. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass,

up to 0.15% C,
up to 3.0% Mn,
up to 1.0% Si,
18.5 to 25.0% Cr,
27.0 to 49.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
1.0 to 3.0% Al,
1.0 to 2.0% Ti,
1.0 to 6.0% Nb,

0.001 to 0.02% B,
0.001 to 0.1% Zr,
up to 0.5% Cu,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 2:1.

4. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass, up to 0.10% C,

0.05 to 1.0% Mn,
0.05 to 1.0% Si,
18.6 to 25.0% Cr,
27.0 to 49.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
1.0 to 3.0% Al,
0.5 to 1.5% Ti,
1.0 to 4.0% Nb,

0.001 to 0.02% B,
0.001 to 0.1% Zr,
up to 0.5% Cu,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 2:1.

5. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass,

0.01 to 0.10% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
18.6 to 23.0% Cr,
30.0 to 40.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
1.0 to 3.0% Al,
0.5 to 1.5% Ti,
1.0 to 4.0% Nb,
0.001 to 0.02% B,
0.001 to 0.1% Zr,
up to 0.5% Cu,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 1.5:1.

6. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass,

0.01 to 0.10% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
18.6 to 23.0% Cr,
30.0 to 40.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
1.5 to 3.0% Al,
0.5 to 1.5% Ti,
1.0 to 3.0% Nb,
0.001 to 0.02% B,
0.001 to 0.1% Zr,

up to 0.2% Cu,
 up to 2.0% Co,
 where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass and the ratio of percentages in mass Ti:Al is lower than 1.5:1.

7. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass, 0.01 to 0.10% C,

0.05 to 1.0% Mn,
 0.05 to 1.0% Si,
 18.6 to 23.0% Cr,
 35.0 to 40.0% Ni,
 up to 0.50% Mo,
 up to 0.50% W,
 up to 0.50% V,
 1.0 to 3.0% Al,
 0.5 to 1.5% Ti,
 1.0 to 4.0% Nb,
 0.001 to 0.02% B,
 0.001 to 0.1% Zr,
 up to 0.2% Cu,
 up to 2.0% Co,
 where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 1.5:1.

8. The Fe—Ni—Cr alloy according to claim 1, presenting a chemical composition of elements comprising, in percentage in mass,

0.01 to 0.10% C,
 0.05 to 1.0% Mn,
 0.05 to 1.0% Si,
 18.6 to 23.0% Cr,
 30.0 to 40.0% Ni,
 up to 0.50% Mo,
 up to 0.50% W,
 up to 0.50% V,
 1.5 to 3.0% Al,
 0.5 to 1.5% Ti,
 1.0 to 3.0% Nb,

0.001 to 0.02% B,
 0.001 to 0.1% Zr,

up to 0.1% Cu,
 up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, and the ratio of percentages in mass Ti:Al is lower than 1.2:1.

9. The Fe—Ni—Cr alloy according to claim 1, where the value of M, calculated by the equation below, follows the ratio $2.0 \leq M \leq 15.0$;

$$M = (\text{Nb}) + 2(\text{Ti}) * (\text{percentage in mass})$$

10. The Fe—Ni—Cr alloy according to claim 1, where the value of M, calculated by the equation below, follows the ratio $5.0 \leq M \leq 11.0$;

$$M = (\text{Nb}) + 2(\text{Ti}) * (\text{percentage in mass})$$

11. The Fe—Ni—Cr alloy according to claim 1, where residual impurities from the manufacture process, such as Ca and Mg, are not in excess of 0.03% in mass;

12. The Fe—Ni—Cr alloy according to claim 1, where impurities are controlled, in order to achieve the maximum of 0.02% in mass of P and the maximum of 0.0050 of S;

13. The Fe—Ni—Cr alloy according to claim 1, produced via air induction furnace, vacuum induction furnace or arc electric furnace, by processes of conventional casting, continuous casting or processes which involve alloy fragmentation and aggregation, among them, powder metallurgy, powder injection, and spray formation, resulting in end product obtained through hot formation, cold formation, or products used directly under the “as cast” condition;

14. The Fe—Ni—Cr alloy according to claim 1, applied as exhaust valves or intake valves of internal combustion engines;

15. The Fe—Ni—Cr alloy according to claim 1, applied as components, tools or structural, static or dynamic parts, in applications which demand resistance at high temperatures, resistance to creep, and resistance to abrasion;

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