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(54) **WEAR RESISTANT ALLOY FOR HIGH TEMPRATURE APPLICATIONS**

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(57) **ABSTRACT**

Low cost alloys resistant to mechanical requirements related to high temperatures, resistant to corrosion, resistant to abrasion, 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 Ni₃Nb and niobium carbides in its microstructure. In percentage, its mass consists of: 0.15 to 0.50% C, up to 3.0% Mn, up to 1.0% Si, 12.0 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, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.0 to 4.5% Ti, 3.1 to 8.0% 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. The rest is made of iron and impurities inevitable to the Alloy manufacture procedure.

Figure 1:

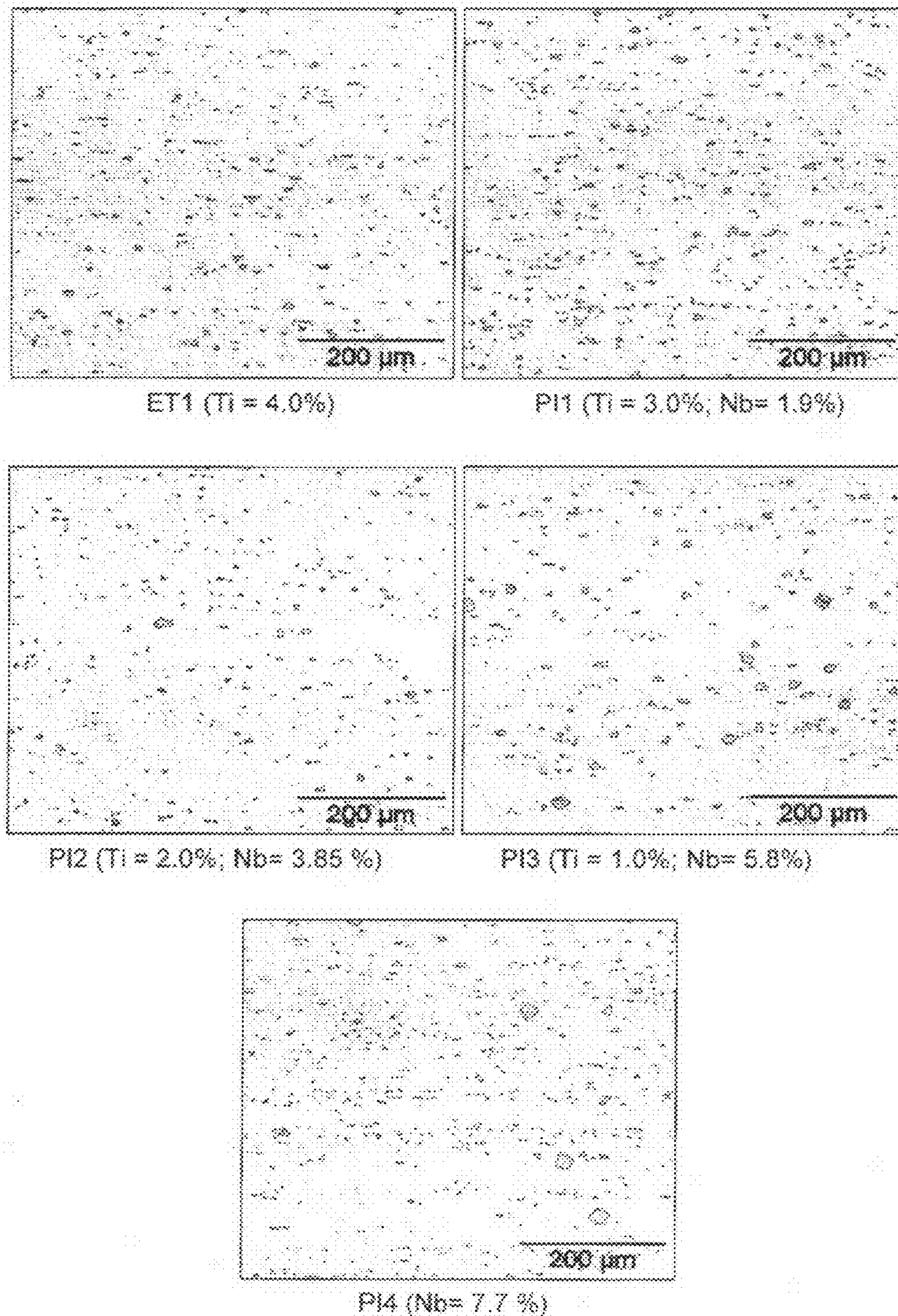


Figure 2:

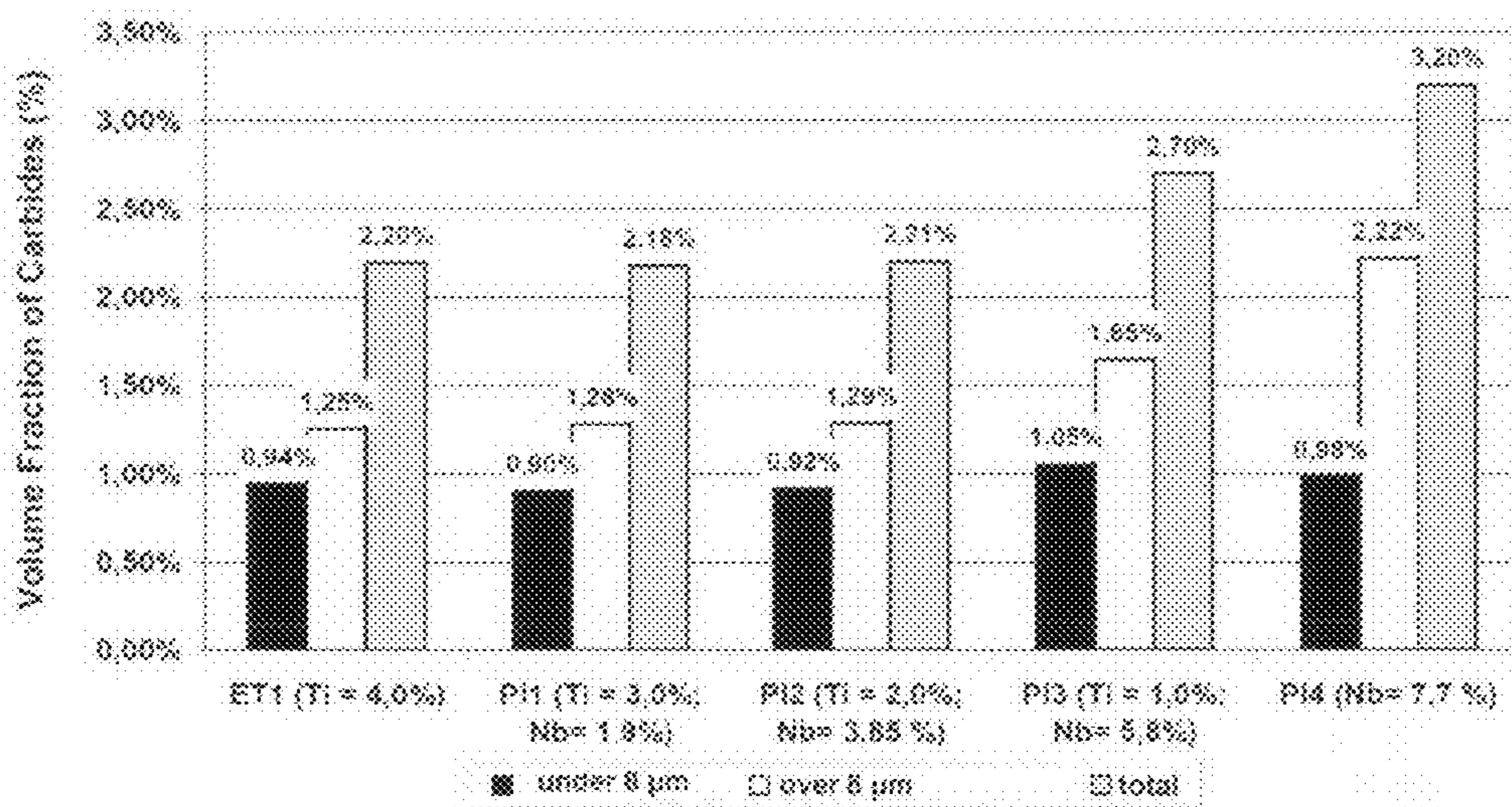


Figure 3:

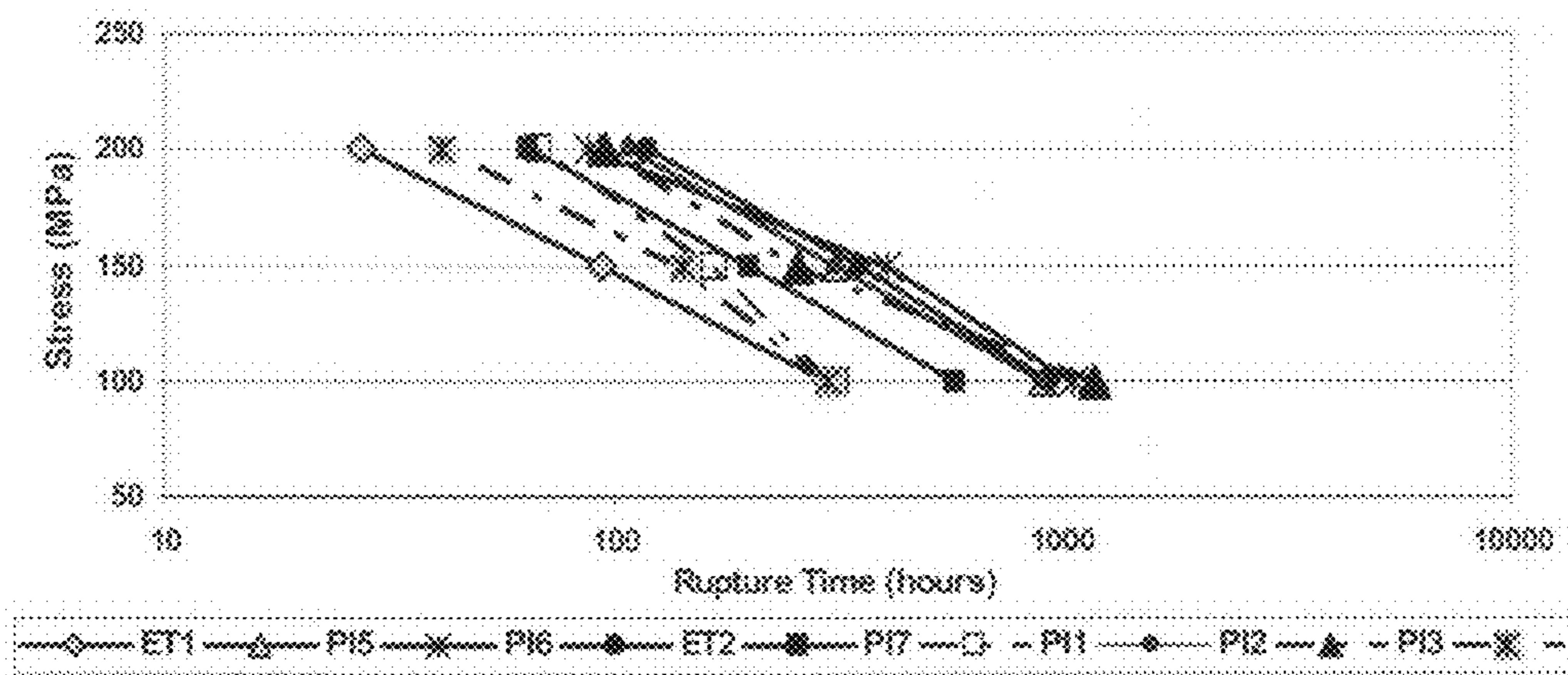


Figure 4:

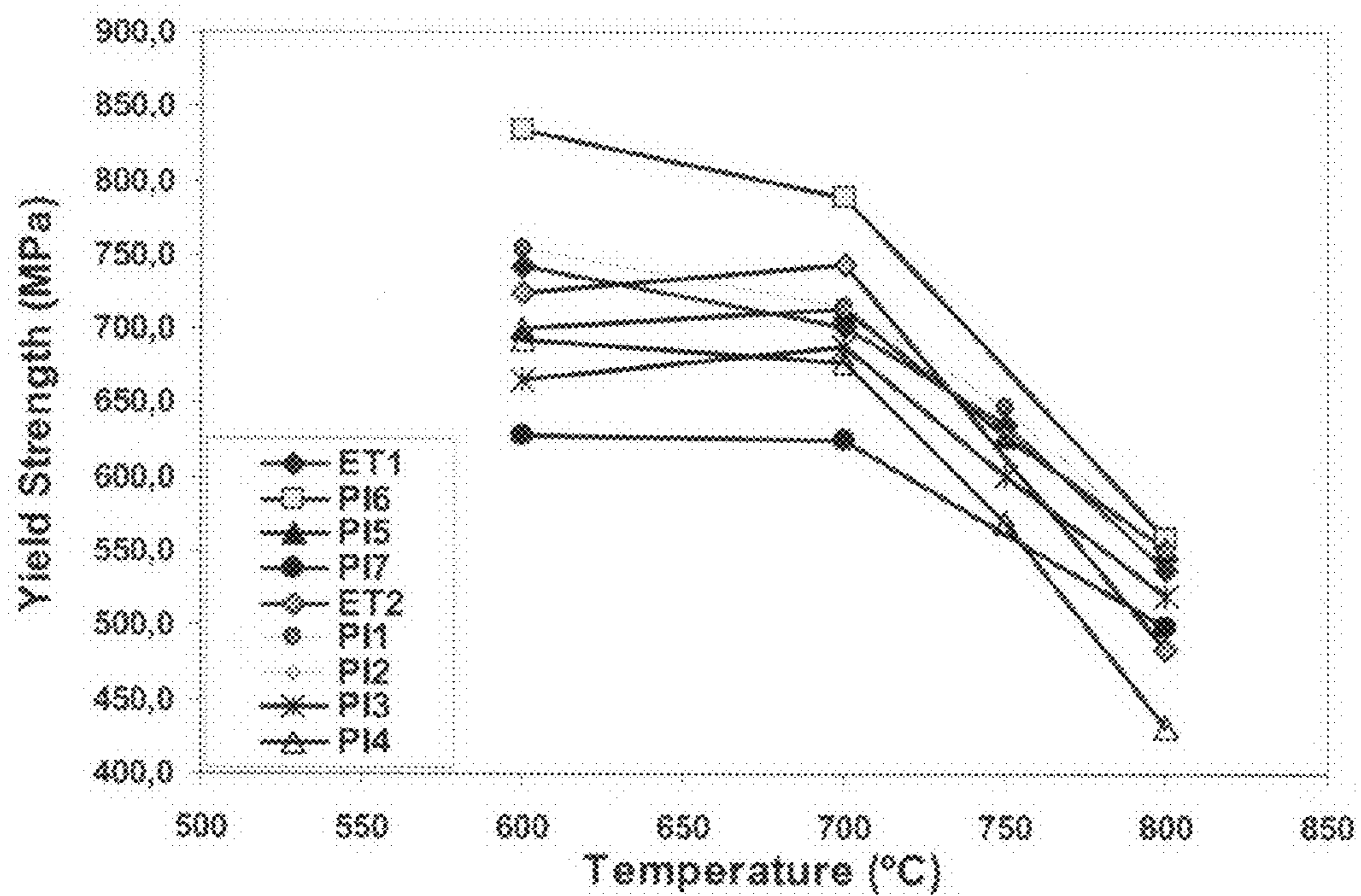


Figure 5:

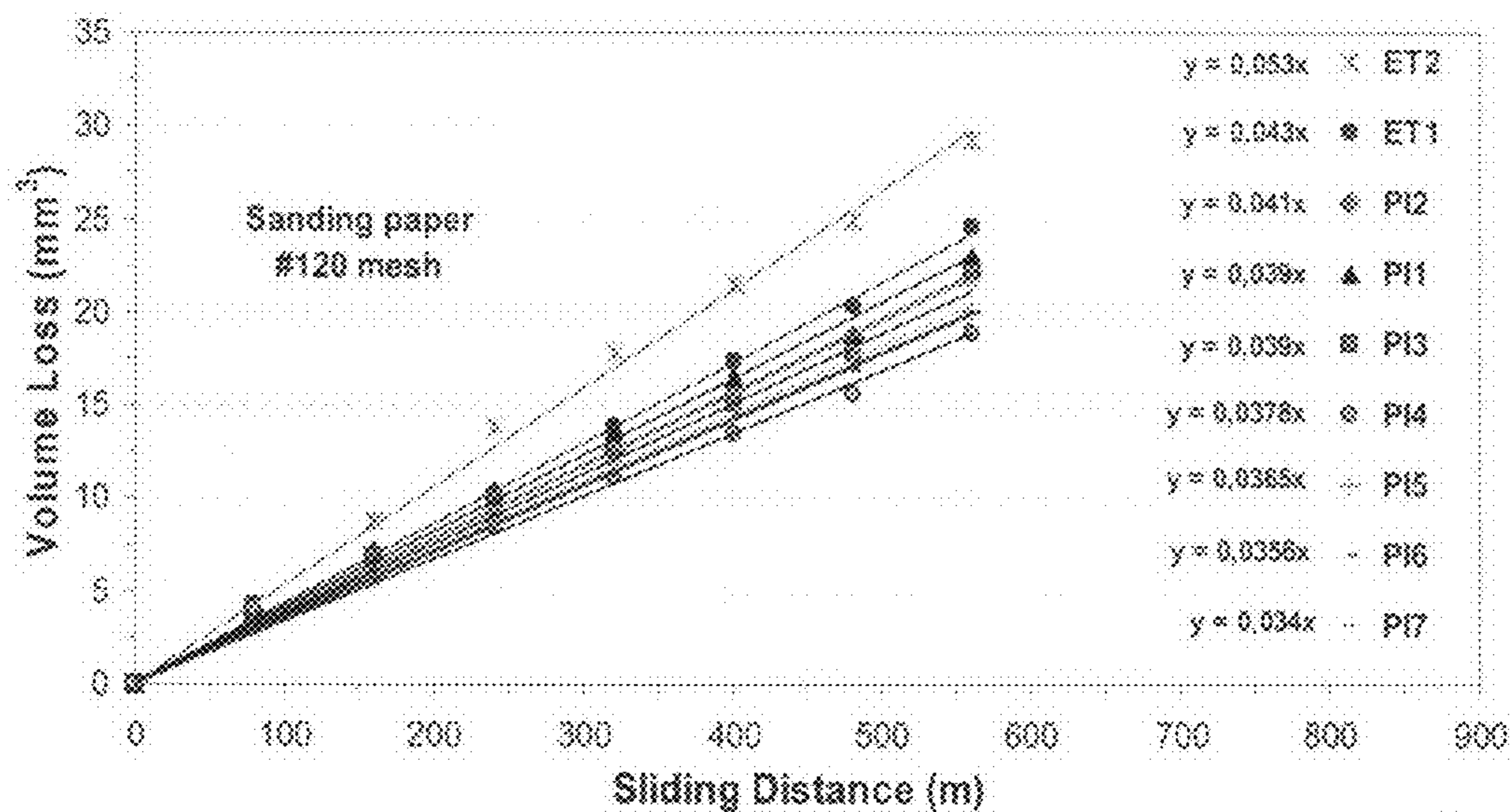


Figure 6:

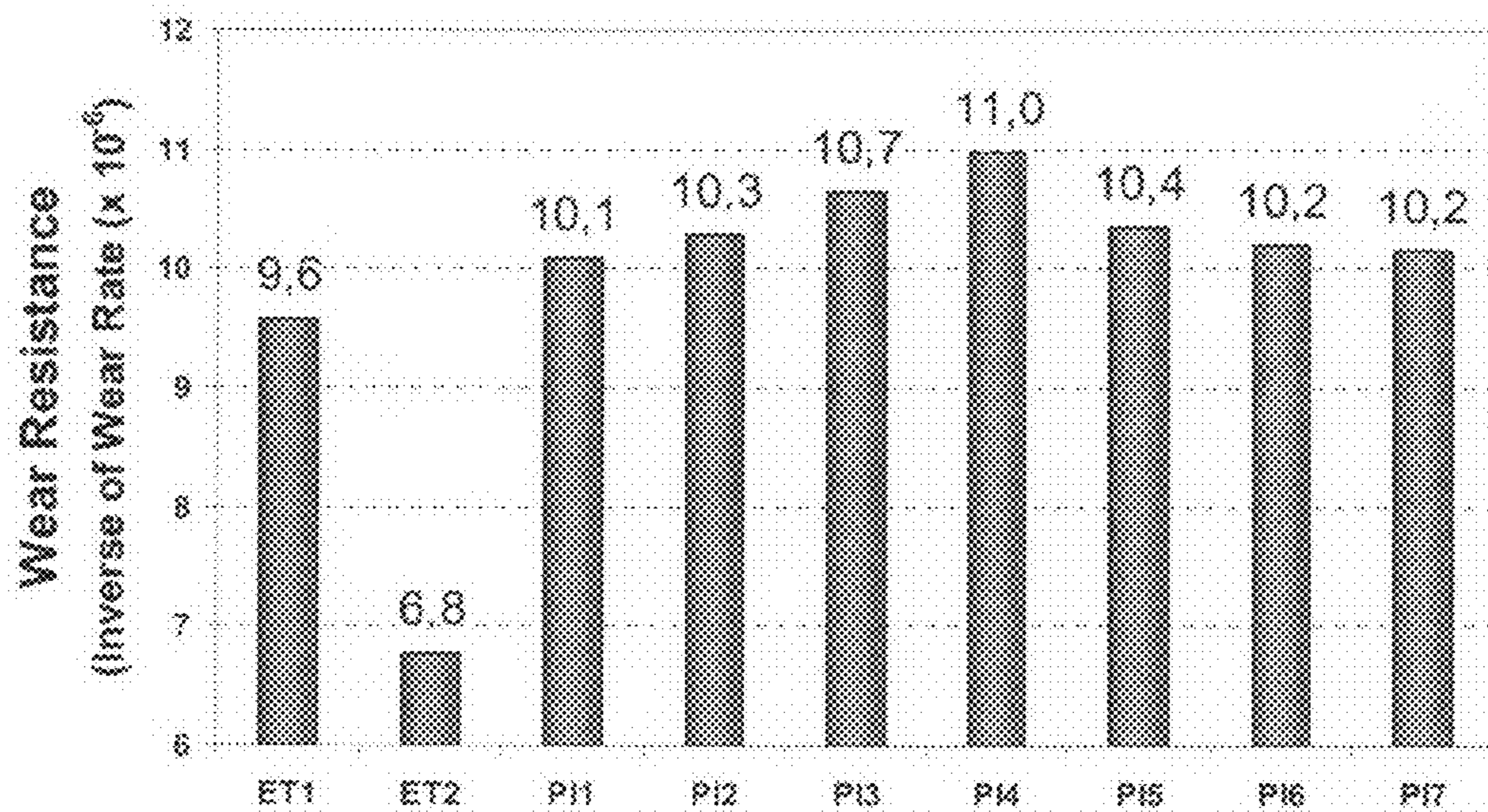


Figure 7:

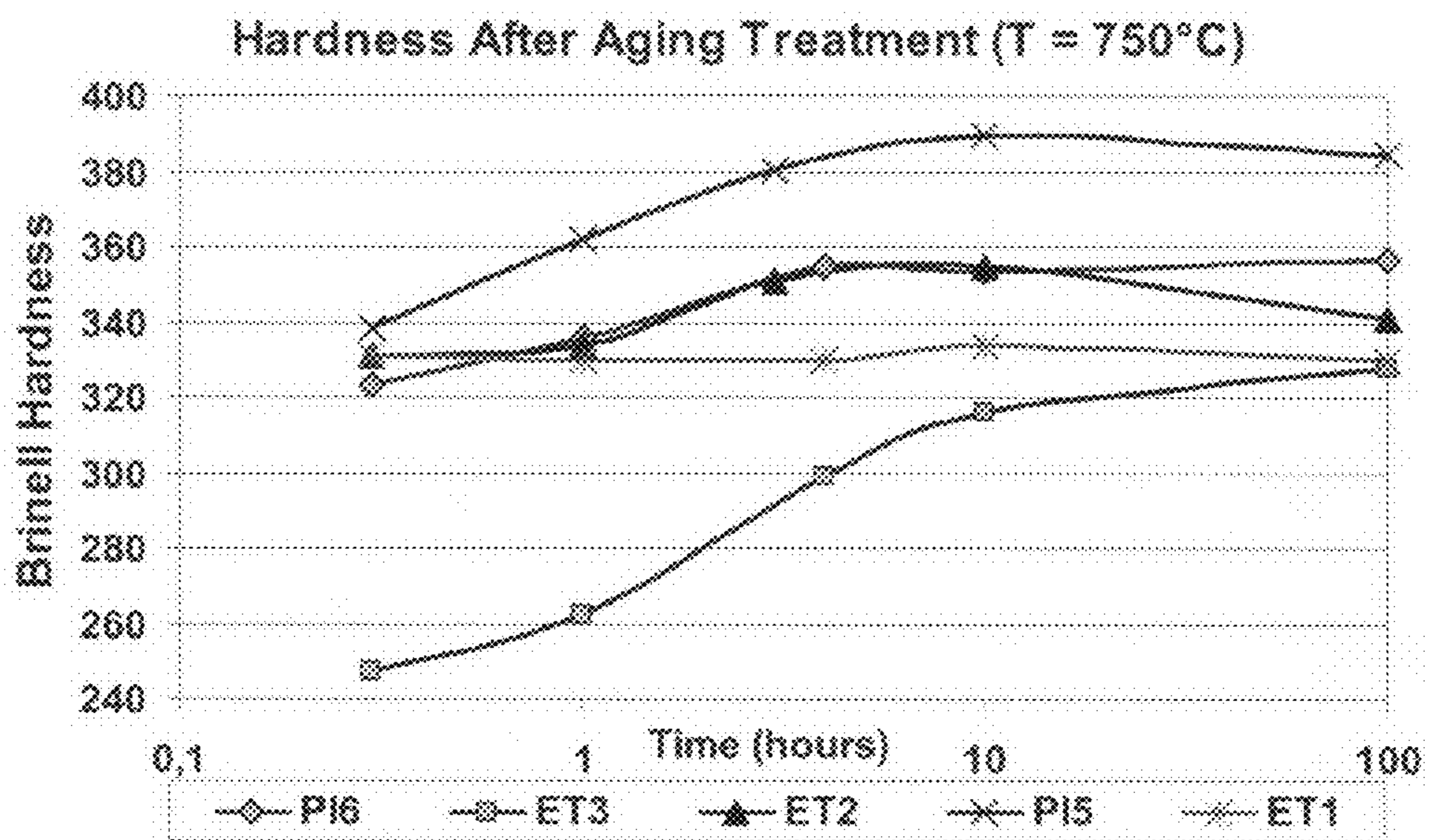


Figure 8:

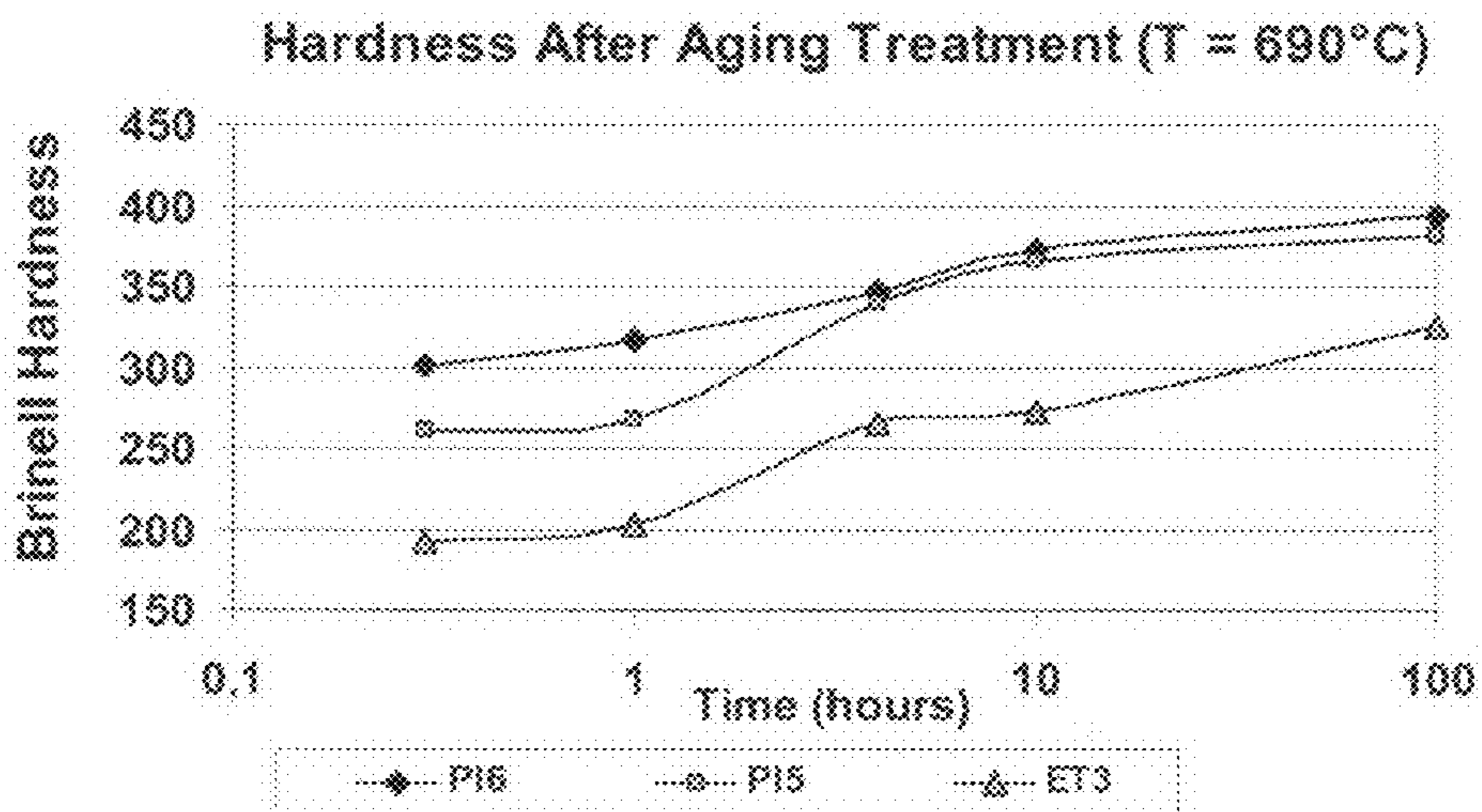


Figure 9:

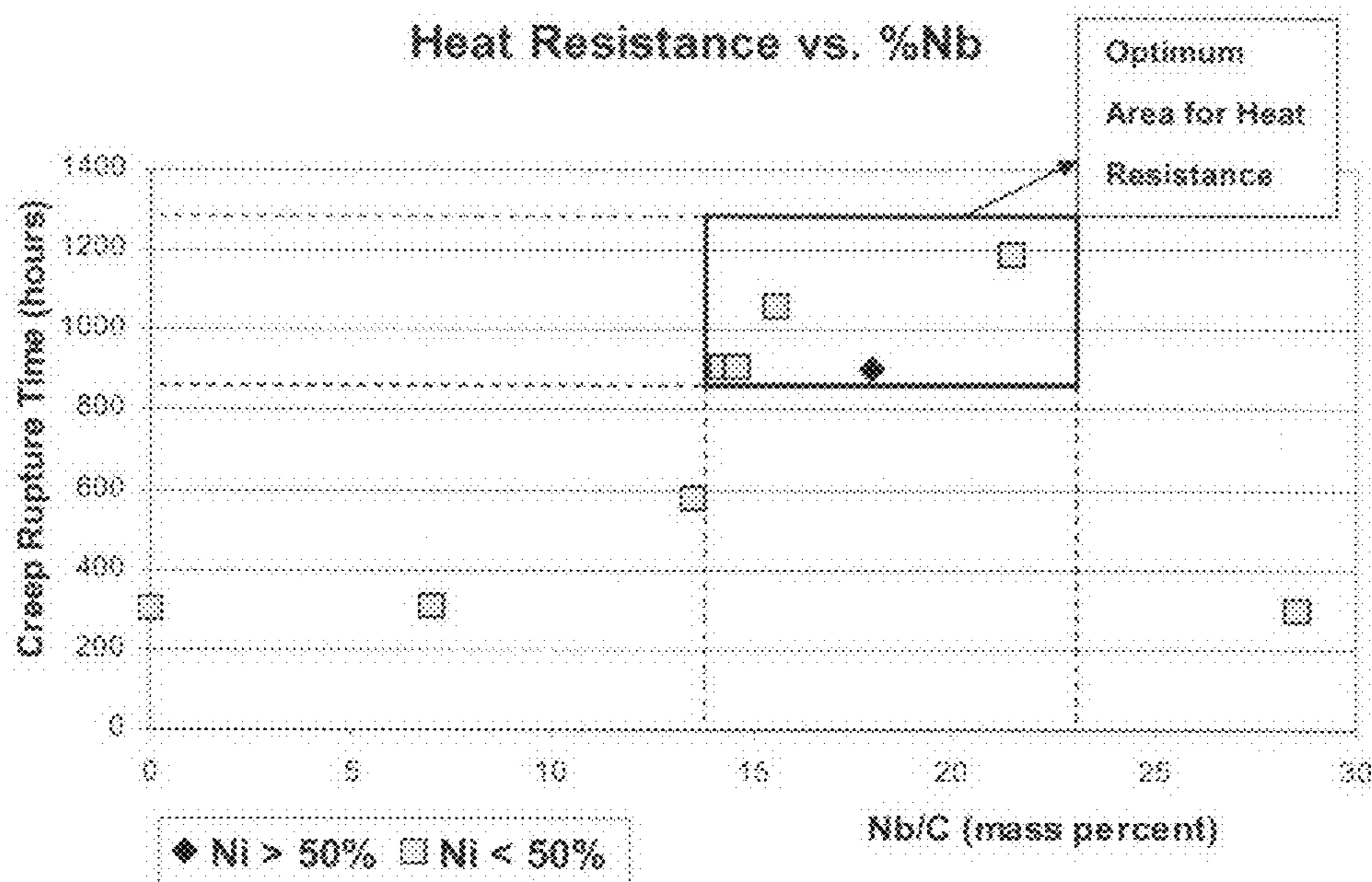
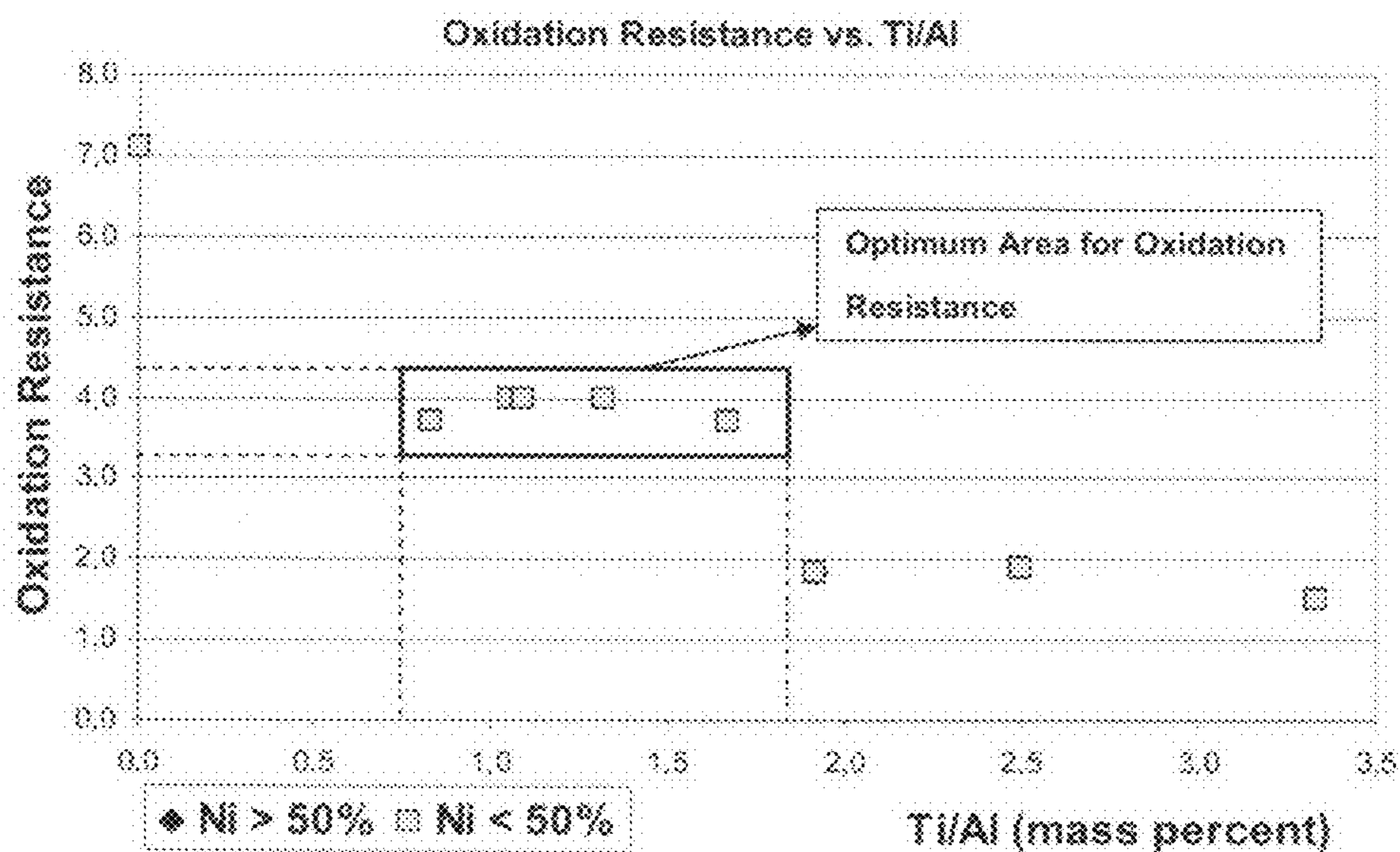


Figure 10:



WEAR RESISTANT ALLOY FOR HIGH TEMPERATURE APPLICATIONS

[0001] This application claims benefit of provisional application 60/924,973, filed Jun. 7, 2007.

FIELD OF INVENTION

[0002] This invention deals with an Ni—Fe—Cr precipitation hardened superalloy for application in internal combustion engine valves, having as chief characteristics the precipitation of $\text{Ni}_3(\text{Al}, \text{Ti}, \text{Nb})$ and niobium and titanium carbides in its microstructure. The alloy project, based on its microstructure aspects, allows for the alloy hereof to be provided with properties equal to or higher than those of the 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: oxidation resistance, wear 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. Another point to be reviewed is the abrasion resistance. Many alloys are coated with Stellite (cobalt base alloy) on the valve's hardfacing, which also increases the final cost of the valve. Accordingly, high performance materials have been increasingly sought in terms of abrasion, so as to eliminate the need to coat the valve's face.

[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, long term microstructural stability at high temperature and abrasion resistance have been developed. Examples are the state-of-the-art alloys, NCF3015 (JIS3015D—U.S. Pat. 5,660,938) and HI 461 alloy.

[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, cor-

rosion resistant, abrasion 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, alloy elements and carbides 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. Additionally, the presence of carbides is important for wear resistance as a result of abrasion to the material. 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, not only as a carbide builder, but mainly in the form of fine intermetallic precipitate.

[0011] Another element used by this invention in higher quantities than the state-of-the-art alloys is aluminum, which has a prevailing function of coherent intermetallic containing niobium, $\text{Ni}_3(\text{Al}, \text{Nb})$, thus improving the material's heat resistance. Additionally, aluminum improves the alloy hot oxidation resistance.

[0012] 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.

[0013] The morphology of these precipitates is determined by the surface energy of the γ/γ' interface, and the elastic energy generated by phases γ e 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.

[0014] 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.

[0015] With a view to meet the above referred conditions, the alloys hereof are provided with alloy element compositions, which, in bulk percentage, consist of:

[0016] 12.0 to 25.0 chromium, preferably 14.0 to 24.0 chromium, typically 18.0 chromium.

[0017] 4.0 to 15.0 for the (Nb+2 Ti) ratio, preferably (Nb+2Ti) between 5.0 and 11.0, typically (Nb+2Ti) equal to 8.0; in this equation, titanium and niobium can take any value within the limits; however, a minimum niobium content shall be maintained, equal to 3.1%, preferably higher than 3.7%.

[0018] 0.05 to 1.0 carbon, preferably 0.20 to 0.40 carbon, typically 0.27% carbon.

[0019] 0.1 to 4.0 aluminum, preferably 1.0 to 3.0 aluminum, typically 2.0% aluminum.

[0020] Iron balance and inevitable metallic and non-metallic impurities to the steel mill process, where said non-metallic impurities include, without limitation, the following elements, in bulk percentage:

[0021] Maximum 5.0 for the manganese, copper, molybdenum and tungsten elements, preferably maximum 2.0, typically maximum 0.50.

[0022] Maximum 0.20 for phosphorus and sulfur, preferably maximum 0.05, typically maximum 0.005.

[0023] 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.

[0024] 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. Accordingly, one concludes that the alloy chromium content would be between such limits, preferably between 14.0% and 22.0%, typically 18.0%.

[0025] 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' e 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 both wear and hot resistance properties, the Nb+2Ti ratio must be higher than 4.0%, preferably higher than 5.0%, typically equal to 8.0%.

[0026] When defining this alloy, a crucial point 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 3.0% causes beneficial effects, both as regards the carbides that were formed and the residual niobium 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. Additionally, a high niobium amount causes the precipitation of primary NbC-type carbides. These MC-type niobium carbides are more effective as regards abrasion resis-

tance that titanium carbides, because of their greater hot hardness. The niobium content shall be carefully balanced to the carbide content. Since niobium has a greater chemical affinity to carbon, the available niobium to form the intermetallic phase with nickel will be the quantity of this element as dissolved in the alloy matrix after reaction with carbon to form the primary carbides. Accordingly, the Nb:C ratio shall be higher than 7.4:1 (bulk), so that dissolved Nb in the austenitic matrix still exists, which will precipitate as Ni_3Nb . A wide range for the Nb element is between 2.0 up to 8.0% (bulk), with an intermediate range of 3.0 up to 8.0% (bulk) of Nb and a narrow interval of 3.1 up to 8.0% (bulk) of Nb, or even narrower, of 3.5 up to 8.0%.

[0027] In addition to the improved heat and abrasion resistance, Nb also improves the weldability of hardened superalloys by phase γ'' precipitation; additionally, it improves corrosion in sulfurous environments, such as diesel engines.

[0028] 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.

[0029] 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. As regards carbides, a greater volumetric fraction of large-sized carbides was noticed, with increased niobium content and reduction of the titanium content, thus resulting in greater wear resistance.

[0030] 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.

[0031] The reduced total titanium percentage in the alloy by the niobium addition in quantities higher than 3.5% 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 (Ti+Al).

[0032] For all such effects—hot resistance, oxidation resistance and wear resistance—the (Nb+2 Ti) ratio must show a minimum 2.0% niobium content, preferably niobium above 3.5%, with an optimum niobium content equal to or higher than 3.7%.

[0033] 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 15.0%, preferably below 13.0%.

[0034] Carbon is added with the intent of combining titanium and niobium in order to form hard carbide particles and provide abrasion resistance. For that function, the carbide content shall be at least 0.05%, preferably above 0.1%. However, the percentage of hard particles shall be below 5% in volume, so as not to deteriorate the toughness and hot workability properties, the latter being essential for hot forged valves. Such particles' volume is determined by carbon, since, when forming NbC or TiC, the alloy is provided with excessive Ti and Nb. Accordingly, the carbon content is used as controlling element of the volume of particles that was formed, being below 1.0%, preferably below 0.40%.

[0035] 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 formation of Al_2O_3 upon heating. Nevertheless, aluminum contents must be restricted, as very high quantities thereof can lead to deterioration of high temperature resistance and hot workability because of the formation of nitrides 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%.

[0036] Residuals: Other elements such as manganese, tungsten, molybdenum, copper, sulphur, 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, copper, 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 contours and other interfaces, and therefore they shall be below 0.20%, preferably below 0.05%, preferably maximum 0.005%.

[0037] The described alloy can be made by conventional or special processes such as melting in electric arc 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

[0038] FIG. 1 shows the microstructure observed in an optical microscope of alloys ET1 and PI1 through PI9;

[0039] FIG. 2 shows the result of the image computer analysis to quantify the carbides observed in the alloys studied with different Ti, Nb and Al contents;

[0040] FIG. 3 shows the results of the creep testing of the alloys hereof as compared to ET1 and ET2 alloys;

[0041] FIG. 4 compares hot resistance of the alloys hereof to ET1 e ET2 alloys, as of the flow stress for several temperatures.

[0042] FIGS. 5 and 6 show the result of the abrasive wear test carried out with ET1, ET2 alloys and PI1 through PI7 alloys;

[0043] FIGS. 7 and 8 show the aging response after heat treatment at 750° C. and 690° C. respectively; and

[0044] FIGS. 9 and 10 show the properties of resistance to temperature and resistance to hot oxidation can be examined in accordance with ratios (Nb/C) and (Ti/Al), respectively.

DETAILED DESCRIPTION OF THE INVENTION

[0045] FIG. 1 shows the microstructure observed in an optical microscope of alloys ET1 and PI1 through PI9, after polishing and attack with Gliceregia reagent for 15 seconds and 120 times magnification.

[0046] FIG. 2 shows the result of the image computer analysis to quantify the carbides observed in the alloys studied with different Ti, Nb and Al contents. Such analysis was performed in a total surface area of 65,990,417 μm^2 of the sample, in 50 random fields with 500 times magnification.

[0047] FIG. 3 shows the results of the creep testing of the alloys hereof as compared to ET1 and ET2 alloys, by assessing the creep rupture time for an 800° C. temperature and 3 tensile stress levels. FIG. 4 compares hot resistance of the alloys hereof to ET1 e ET2 alloys, as of the flow stress for several temperatures.

[0048] FIGS. 5 and 6 show the result of the abrasive wear test carried out with ET1, ET2 alloys and PI1 through PI7 alloys. The test was made by pin against sandpaper; the test specimens pins were provided after aging heat treatment and using alumina abrasive paper grit # 120. The average contact speed between the abrasive paper and the pins was 100 m/min.

[0049] FIGS. 7 and 8 show the aging response after heat treatment at 750° C. and 690° C. respectively. The hardness is always higher for the alloys of the present invention (PI5, PI6) when compared with the alloys of the state of the art for the same time of treatment. In FIG. 8, Alloys PI5 and PI6 also have a better response to the aging heat treatment at 690° C. than the alloy of the state of the art ET3, by reaching hardness higher than the minimum value required for application after one hour of treatment.

[0050] FIGS. 9 and 10 show the properties of resistance to temperature and resistance to hot oxidation can be examined in accordance with ratios (Nb/C) and (Ti/Al), respectively. In FIG. 9, shows the optimum range of the ratio Nb/C for the optimization of the heat resistance property, represented by the time of creep disruption at 800° C. under 100 MPa stress. FIG. 10 shows that the alloys of the present invention are at the optimum range of the ratio Ti/Al to optimize the property of hot oxidation resistance, represented by a reversal of the gain in mass (in mg/cm^2) after 400 hours at 800° C. in atmosphere (air).

[0051] 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 HI 461 alloy, ET2 alloy corresponds to NCF 751 alloy, and ET3 alloy corresponds to NCF 3015 alloy (of U.S. Pat. No. 5,660,938). The following ratios are also quantified: (Nb+2 Ti); (Nb/C) and (Ti/Al) in Table 1.

[0052] In Table 1 one can notice a significant reduction in the nickel content of the alloy in the compositions hereof as regards ET2 alloy, thus resulting in considerably lower cost. ET2 and ET3 alloys are not either provided with significant carbon contents, causing no formation of carbides or the high wear resistance shown by the other alloys.

[0053] Table 1 also shows the addition of different niobium contents to the alloys hereof, unlike the state-of-the-art alloy (ET1), which shows titanium only. The review of the (Nb+2 Ti) ratio is also interesting, since it normalizes the atomic mass difference and is then related to the atomic content.

[0054] This is approximately consistent between the ones in the present invention (PI1 to PI6) and in alloy ET1. Thus, the atoms of Ti in the alloys of the present invention are gradually replaced with niobium, until titanium is fully replaced with niobium in alloy PI4. Despite having similar chemical nature, titanium and niobium have different effects in the alloys studied, so that such replacement made was of great benefit to end properties, as described below. In this sense, the quantification and the differentiation of the alloys under study through the content of niobium not combined in form of carbides becomes very interesting. This quantification can be evaluated through the ratio (Nb/C).

[0055] The differences between the titanium and aluminum contents in the different alloys can be evaluated through the ratio (Ti/Al), which is very important for the hot oxidation resistance and the hot workability properties. Such ratio (Ti/Al) is displayed in Table 1 as well.

[0056] The ingots were cast by means of a close procedure for such ten alloys (ET1, ET2, ET3, PI1, PI2, PI3, PI4, PI5, PI6, PI7), 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. The bars were examined in an optical microscope after the solution treatment, and the result is shown in FIG. 1. Such images display the increase in the size of the carbides due to the replacement of titanium with niobium. Such fact is confirmed through the quantitative analyses of the images displayed in FIG. 2.

displayed in FIGS. 3 and 4. The alloys of the present invention are significantly more resistant concerning creep than alloy ET1. Alloys PI2, PI3, PI5, and PI6 are either equivalent to or better than alloy ET2 (NCF 751), despite having nickel content substantially lower than this alloy. As for resistance at high temperature, measured by the yield stress (FIG. 4), the same behavior is seen. Alloys PI2, PI3, PI5, and especially PI6, are more resistant than alloys ET1 and ET2. Due to a higher concentration of coarse phases, alloy PI4 has reduction in the hot resistance in terms of creep resistance.

[0059] In terms of oxidation resistance, the alloys of the present invention are also superior to alloys ET1 and ET2, as shown in Table 3; we see that the lower the content of titanium, the higher the resistance to the alloy oxidation. This is the best resistance seen for titanium-free alloy PI4. This occurs because titanium destabilizes the oxide layer formed

TABLE 1

Chemical compositions of three alloys of the state of the art (ET1, ET2, and ET3) and the alloys of the present invention (PI1 to PI7). Percentage in mass and balance in iron.											
	C	Si	Mn	Cr	Ni	Al	Ti	Nb	Nb + 2 Ti	Nb/C	Ti/Al
ET1 (HI 461)	0.27	0.10	0.15	18.0	46.0	1.20	4.00	—	8.00	—	3.3
ET2 (NCF 751)	0.05	0.03	0.05	15.5	70.0	1.20	2.45	0.90	5.50	18	1.9
ET3 (NCF 3015)	0.04	0.03	0.05	16.0	32.0	1.40	2.50	0.65	5.65	16.3	1.8
PI1	0.27	0.10	0.15	18.0	46.0	1.20	3.00	1.90	7.90	7	2.5
PI2	0.27	0.10	0.15	18.0	46.0	1.20	2.00	3.85	7.85	14.3	1.7
PI3	0.27	0.10	0.15	18.0	46.0	1.20	1.00	5.80	7.85	21.5	0.8
PI4	0.27	0.10	0.15	18.0	46.0	1.20	—	7.70	7.70	28.5	—
PI5	0.27	0.10	0.15	18.0	46.0	1.90	2.00	3.95	7.95	14.6	1.1
PI6	0.25	0.10	0.15	15.2	32.1	1.92	2.10	3.90	7.92	15.6	1.1
PI7	0.25	0.10	0.15	18.8	36.0	1.30	1.71	3.38	6.80	13.5	1.3

[0057] Table 2 displays the hardness of alloys ET1, ET2, ET3, PI1, PI2, PI3, PI4, PI5, PI6, and PI7 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, ET2, and ET3), and the alloys of the present invention (PI1, PI2, PI3, PI4, PI5, PI6, and PI7). 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
ET3	238	260	300
PI1	192	334	340
PI2	177	326	345
PI3	185	316	335
PI4	207	331	340
PI5	178	333	348
PI6	172	331	350
PI7	171	315	330

[0058] Another important parameter for these alloys are the mechanical properties at high temperature; such results are

on the surface of the alloys in the nickel-iron system and, thus, it reduces oxidation resistance. Another interesting effect to be seen is that, among the alloys with the lowest titanium content (PI2, PI3, PI4, PI5, PI6, and PI7), those with the highest aluminum content (PI5, PI6, and PI7) have higher resistance to hot oxidation under test conditions. The test was carried out so that all samples of all alloys involved had identical sizes, so that their contact surface was identical as well. Solution and aged cylindrical samples (diameter=12 mm and height=14 mm) were duly weighed and maintained at 800° C. for 100 hours. After being removed from the furnace, the sample is cooled by air and weighed again, by measuring mass variation. This process is repeated until the full test time is completed. Ceramic crucibles of alumina were used as sample holders during the test. The progress of the oxidation process at 800° C. was evaluated for 400 hours, when it was possible to see stabilization in the corrosion process.

TABLE 3

Mass variation (mg/cm ²) after 100, 200 and 400 hours at 800° C. in atmosphere (air). The lower the gain in mass, the higher the oxidation resistance to the oxidation of the material.			
	100 hours	200 hours	400 hours
ET1 (Ti = 4.0%; Al = 1.2%)	0.40	0.66	0.66
ET2 (Ti = 2.5%; Nb = 0.9%; Al = 1.2%)	0.41	0.54	0.54

TABLE 3-continued

Mass variation (mg/cm ²) after 100, 200 and 400 hours at 800° C. in atmosphere (air). The lower the gain in mass, the higher the oxidation resistance to the oxidation of the material.			
	100 hours	200 hours	400 hours
PI1 (Ti = 3.0%; Nb = 1.9%; Al = 1.2%)	0.40	0.54	0.54
PI2 (Ti = 2.0%; Nb = 3.85%; Al = 1.2%)	0.14	0.27	0.27
PI3 (Ti = 1.0%; Nb = 5.8%; Al = 1.2%)	0.14	0.27	0.27
PI4 (Nb = 7.7%; Al = 1.2%)	0.14	0.14	0.14
PI5 (Ti = 2.0%; Nb = 3.9%; Al = 1.9%)	0	0.25	0.25
PI6 (Ti = 2.0%; Nb = 3.9%; Al = 1.9%)	0	0.25	0.25
PI7 (Ti = 1.7%; Nb = 3.4%; Al = 1.3%)	0	0.25	0.25

[0060] The resistance to abrasive wear, compared in FIGS. 5 and 6, and quantified in Table 4, follows the same tendency of oxidation resistance, for different reasons, though. Alloys ET1 and PI1 to PI9 have wear resistance significantly higher than alloy ET2, due to the presence of hard particles in their microstructures (as shown in FIG. 1). However, we also see that the higher the content of niobium, the lower the rate of wear and, therefore, the higher the resistance to abrasive wear. This occurs because of the larger size of the carbides existing in the microstructure of alloys with the highest niobium content, as displayed in FIG. 1 and quantified in FIG. 2.

TABLE 4

Wear rate in the alloys studied, calculated from the division of the slopes in the curves of FIG. 5 by the area of the sample (Wear rate = (1/area) * $\partial \Delta V / \partial \Delta L$). The lower the wear rate, the higher the resistance to the wear of the material, since the loss of material for wear is lower. Thus, the material with the highest value toward the reverse of the wear rate is more resistant to wear. i.e.: 1/Rate = Wear Resistance.		
Alloy	Wear Resistance	
	Absolute Value	Concerning ET1
ET1 (Ti = 4.0%)	9.6	100%
ET2 (Ti = 2.5%; Nb = 0.9%)	6.8	71%
PI1 (Ti = 3.0%; Nb = 1.9%)	10.1	105%
PI2 (Ti = 2.0%; Nb = 3.85%)	10.3	107%
PI3 (Ti = 1.0%; Nb = 5.8%)	10.7	111%
PI4 (Nb = 7.7%)	11.0	115%
PI5 (Ti = 2.0%; Nb = 3.9%)	10.4	108%
PI6 (Ti = 2.0%; Nb = 3.9%)	10.2	106%
PI7 (Ti = 1.7%; Nb = 3.4%)	10.2	106%

[0061] The industrial application of these alloys includes a phase of aging heat treatment after the final formation of the

piece. The alloys of the present invention are easier to obtain the minimum hardness required for application purposes (about 330 HB—Brinell hardness scale), that is, the achievement of hardness over 330 HB is seen after only 20 minutes of treatment at 750° C. The hardness is always higher for the alloys of the present invention (PI5, PI6) when compared with the alloys of the state of the art for the same time of treatment, as seen in FIG. 7. Alloys PI5 and PI6 also have a better response to the aging heat treatment at 690° C. than the alloy of the state of the art ET3, by reaching hardness higher than the minimum value required for application after one hour of treatment. This can be seen in FIG. 8. Reducing the temperature and the time of the aging treatment is of the utmost importance to reduce costs and enhance yield when processing the material.

[0062] The properties of resistance to temperature and resistance to hot oxidation can be examined in accordance with ratios (Nb/C) and (Ti/Al), respectively. FIGS. 9 and 10 show this analysis concerning the alloys of the present invention (PI1 to PI7) and of the state of the art (ET1 and ET2). In FIG. 9, we can see clearly that the alloys of the present invention are in the optimum range of the ratio Nb/C for the optimization of the heat-resistance property, represented by the time of creep disruption at 800° C. under 100 Mpa stress. FIG. 10 shows that the alloys of the present invention are at the optimum range of the ratio Ti/Al to optimize 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).

[0063] 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 properties of resistance to hot, creep, resistance to oxidation and wear. A summary of such effects is displayed in Table 5. Alloys PI2, PI3, PI5, PI6 and PI7 are always superior to the alloys of the state of the art, in terms of all properties examined. However, alloy PI4 has better result in situations where resistance to wear and oxidation should prevail.

[0064] In summary, we can state that the results discussed herein shown 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 and resistance to wear. So, they are material improvements for industrial application in combustion engine valves or even other components used at high temperatures and corrosive sites.

TABLE 5

Comparison of Properties among all alloys studied, in absolute figures and relative figures (the reference is alloy ET1 = 100%).										
	ET1	ET2	ET3	PI1	PI2	PI3	PI4	PI5	PI6	PI7
	FIGURES									
Hardness After Aging Treatment (HB)	330	335	300	334	330	316	331	350	340	330
Yield Strength at 800° C. (MPa)	538	484	525	550	552	520	431	554	560	500
Rupture Time at 800° C. and 100 MPa (hours)	302	900	—	312	906	1188	301	906	1060	578

TABLE 5-continued

Comparison of Properties among all alloys studied, in absolute figures and relative figures (the reference is alloy ET1 = 100%).										
	ET1	ET2	ET3	PI1	PI2	PI3	PI4	PI5	PI6	PI7
Carbides Fraction over 8 microns (% Volume)	1.25	<0.1	<0.1	1.28	1.29	1.65	2.22	1.29	1.29	1.29
Wear Resistance (Inverse of Wear Rate)	9.6	6.8	—	10.1	10.3	10.7	11	10.4	10.2	10.2
Oxidation Resistance (Inverse of Weight Variation) after 200 hours at 800° C. (g ⁻¹)	1.5	1.9	—	1.9	3.7	3.7	7.1	4.0	4.0	4.0
PERCENTAGE ON THE ALLOY ET1 (%)										
Hardness After Aging Treatment	100	102	91	101	100	96	100	106	103	100
Yield Strength at 800° C.	100	90	98	102	103	97	80	103	104	93
Rupture Time at 800° C. and 100 MPa	100	298	—	103	300	393	100	300	351	191
Wear Resistance (Inverse of Wear Rate)	100	71	—	105	107	111	115	108	106	103
Oxidation Resistance (Inverse of Weight Variation) after 200 hours at 800° C.	100	122	—	122	244	244	471	264	264	106

[0065] 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.

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

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

2. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
up to 3.0% Mn,
up to 1.0% Si,
12.0 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,
0.50 to 5.0% Cu,
1.0 to 3.0% Al,
1.0 to 4.5% Ti,
2.0 to 8.0% 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, the proportion of percentages in mass Nb:C is in the interval from 4:1 to 54:1 and the ratio of percentages in mass (Ti/AL) is lower than 2.

3. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
up to 3.0% Mn,
up to 1.0% Si,
14.0 to 22.0% Cr,
27.0 to 49.0% Ni,
up to 0.50% Mo,

up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.5 to 3.0% Al,
1.0 to 3.5% Ti,
2.5 to 8.0% 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, the proportion of percentages in mass Nb:C is in the interval from 7:1 to 54:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

4. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
up to 3.0% Mn,
up to 1.0% Si,
14.0 to 22.0% Cr,
27.0 to 49.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.5 to 3.0% Al,
1.0 to 3.5% Ti,
2.5 to 8.0% 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, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 40:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

5. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
14.0 to 22.0% Cr,
27.0 to 49.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.8 to 3.0% Al,
1.0 to 3.5% Ti,
3.1 to 8.0% 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, the proportion of percentages in mass Nb:C is in the interval from 7:1 to 54:1, and the ratio of percentages in mass (Ti/Al) is lower than 2.

6. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
15.0 to 19.0% Cr,
30.0 to 48.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.8 to 3.0% Al,
1.85 to 2.15% Ti,
3.1 to 8.0% 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., the proportion of percentages in mass Nb:C is in the interval from 8:1 to 54:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

7. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
15.0 to 19.0% Cr,
30.0 to 48.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.8 to 3.0% Al,
1.85 to 2.15% Ti,
3.1 to 8.0% Nb,
0.001 to 0.005% B,
0.001 to 0.01% Zr,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 54:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

8. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.50% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
15.0 to 19.0% Cr,
30.0 to 48.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.85 to 3.0% Al,
1.85 to 2.15% Ti,
3.1 to 8.0% Nb,
0.001 to 0.005% B,
0.001 to 0.01% Zr,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 54:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

9. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.40% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
15.0 to 19.0% Cr,
30.0 to 48.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.85 to 3.0% Al,
1.85 to 2.15% Ti,
3.5 to 8.0% Nb,
0.001 to 0.005% B,
0.001 to 0.01% Zr,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 40:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

10. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass,

0.15 to 0.30% C,
0.05 to 1.0% Mn,
0.05 to 1.0% Si,
15.0 to 19.0% Cr,
30.0 to 48.0% Ni,
up to 0.50% Mo,
up to 0.50% W,
up to 0.50% V,
0.50 to 5.0% Cu,
1.85 to 3.0% Al,
1.85 to 2.15% Ti,
3.7 to 8.0% Nb,
0.001 to 0.005% B,
0.001 to 0.01% Zr,
up to 2.0% Co,

where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 30:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

11. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass, 0.15 to 0.50% C, up to 3.0% Mn, up to 1.0% Si, 14.0 to 25.0% Cr, 40.0 to 49.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.0 to 4.5% Ti, 2.0 to 8.0% Nb, 0.001 to 0.02% B, 0.001 to 0.1% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 7:1 to 40:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

12. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass, 0.15 to 0.50% C, up to 3.0% Mn, up to 1.0% Si, 14.0 to 18.0% Cr, 25.0 to 39.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.0 to 3.5% Ti, 2.5 to 8.0% Nb, 0.001 to 0.02% B, 0.001 to 0.1% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 7:1 to 40:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

13. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass, 0.15 to 0.50% C, 0.05 to 1.0% Mn, 0.05 to 1.0% Si, 15.0 to 25.0% Cr, 40.0 to 49.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.85 to 2.15% Ti, 3.1 to 8.0% Nb, 0.001 to 0.02% B, 0.001 to 0.1% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 30:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

14. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass, 0.15 to 0.50% C, 0.05 to 1.0% Mn, 0.05 to 1.0% Si, 14.0 to 20.0% Cr, 25.0 to 39.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.85 to 2.15% Ti, 3.5 to 8.0% Nb, 0.001 to 0.02% B, 0.001 to 0.1% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 12:1 to 40:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

15. The Ni—Fe—Cr alloys of claim 1, wherein the chemical composition of elements comprise, in percentage in mass, 0.15 to 0.50% C, 0.05 to 1.0% Mn, 0.05 to 1.0% Si, 14.0 to 20.0% Cr, 25.0 to 39.0% Ni, up to 0.50% Mo, up to 0.50% W, up to 0.50% V, 0.50 to 5.0% Cu, 1.85 to 3.0% Al, 1.85 to 2.15% Ti, 3.7 to 8.0% Nb, 0.001 to 0.02% B, 0.001 to 0.1% Zr, up to 2.0% Co, where (Ni+Co) is not higher than 50.0% in mass, nor lower than 25% in mass, the proportion of percentages in mass Nb:C is in the interval from 14:1 to 30:1 and the ratio of percentages in mass (Ti/Al) is lower than 2.

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

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

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

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

18. The Ni—Fe—Cr alloy for internal combustion engine valves 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;

19. The Ni—Fe—Cr alloy for internal combustion engine valves 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;

20. The Ni—Fe—Cr alloy for internal combustion engine valves 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 products obtained through hot formation, cold formation, or products used directly under the “as cast” condition;

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

22. The Ni—Fe—Cr alloy for internal combustion engine valves 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;

* * * * *