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(54) Fe-Ni-Cr-base super alloy, engine valve and knitted mesh supporter for exhaust gas catalyzer.

(57) An Fe-Ni-Cr-base superalloy essentially consists of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.6 to 3.0 % Al, one or more elements selected from Groups IVa and Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities. If necessary, Mo, W, Co, B, Mg, Ca, Y and REM can be added in predetermined ranges. The superalloy is suitable for engine valves, knitted mesh supporters for exhaust gas catalyzers and so forth, and is excellent in high-temperature strength and normal-temperature ductility after long-time heating and has a sufficient acid resistance property.

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BACKGROUND OF THE INVENTION

The present invention relates to an inexpensive Fe-Ni-Cr-base superalloy which is excellent in high-temperature strength, and an engine valve for a motor vehicle and a knitted mesh supporter for an exhaust gas catalyzer for a motor vehicle which are made of the alloy.

In recent years, there has been an even more demand for saving energy and treating exhaust gas to solve the global problems of environmental pollutions whereas reduction of resources for manufacturing component parts has been desired. In order to achieve such objects, there has been a strong demand for reducing resources of high-quality materials such as an engine valve material and an exhaust gas mesh material which are exposed to the highest temperature and the highest stress in an internal combustion engine of a motor vehicle or the like.

Conventionally, as a material for exhaust gas valves of a gasoline engine or a diesel engine, JIS SUH35 (Fe-8.5Mn-21Cr-4Ni-0.5C-0.4N) which is a high-Mn austenitic steel has been widely used. However, in accordance with an increase of the use temperature, JIS NCF751 (Ni-15.5Cr-1Nb-2.3Ti-1.2Al-7Fe) which is an Ni-base superalloy has started to be employed in some cases. However, JIS NCF751, which contains about 70 % Ni, is by far more expensive than JIS SUH35. Therefore, there have been developed alloys which contain less valuable alloying elements than JIS NCF751 and which have high-temperature strength and stability of alloy structure after long-time heating which are as close to those of JIS NCF751 as possible.

As a result, there have been made many suggestions such as JP-B2-1-12827, JP-A-62-214149, JP-A-58-189359, JP-A-63-213631, JP-A-61-238942, JP-B2-62-50542, JP-B2-4-11613, JP-A-60-211028 and so on.

As gasoline fuel for engines of motor vehicles, lead-free gasoline has recently been employed for answering the demand of treatment of exhaust gas, and engines for which lead-free gasoline is exclusively used have been mainly produced. For the engine parts which are used at a particularly high temperature, such as engine valves and knitted mesh supporters for exhaust gas catalyzers for a motor vehicle, use of lead-free gasoline leads to an improvement of wear environment. If the same level of acid resistance property as JIS NCF751 is provided, no consideration must be given to the wear resistance property with respect to lead oxide, which has conventionally been a problem to be considered.

On the other hand, in accordance of prolongation of the guarantee period of a motor vehicle, the performance in relation to durability must be improved, and an alloy whose strength deterioration and embrittlement after high-temperature long-time use are as small as possible has started to be demanded.

Of the resource-saving materials of JIS NCF751 which contains less valuable alloying elements, the alloys proposed in JP-A-63-213631, JP-B2-4-11613 and JP-A-60-211028 can provide high-temperature strength and long-time stability of alloy structure which are close to those of JIS NCF751. However, since the Ni content exceeds 50 %, reduction of resources and costs is not sufficiently accomplished as compared with JIS NCF751. The alloys proposed in JP-B2-1-12827, JP-A-62-214149 and JP-A-58-189359 have excellent acid resistance and wear resistance properties because Cr content is high. However, unfavorable phases which deteriorate normal-temperature ductility such as the a phase and the α' phase rich in Cr precipitate. The alloys proposed in JP-A-61-238942 and JP-B2-62-50542 have low-Ni low-Al compositions. Consequently, during long-time heating, coarsening of the γ' (gamma prime) phase which is a precipitation strengthening phase and transformation from the γ' phase into the η (eta) phase occur, thereby increasing a deterioration amount of high-temperature strength after long-time heating.

SUMMARY OF THE INVENTION

An objective of the present invention resides in providing a resource-saving Fe-Ni-Cr-base superalloy which is excellent in high-temperature strength and normal-temperature ductility after long-time heating, which could not be accomplished by the above-described conventional alloys, and which has a sufficient acid resistance property, and further to provide an engine valve and a knitted mesh supporter for an exhaust gas catalyzer which are made of this alloy.

In order to predict such material deterioration, samples were manufactured by heating at 800 °C for 400 hours, and their tensile strength at 800 °C and rotary bending fatigue strength were measured, to thereby measure high-temperature strength of the alloy after long-time heating. Meanwhile, normal-temperature (20 °C) U-notch Charpy impact tests of the samples were performed, and toughness of the material was evaluated from the impact values. In respect of the acid resistance property, weight changes after heating at 850 °C for 400 hours were measured.

On the basis of the foregoing evaluation results, novel alloys which contain not more than 50 % Ni for saving resources and which satisfy the objective have been invented by employing the following three methods.

(1) In the γ' phase consisting of $Ni_3(Al,IVa,Va)$, a ratio of $1.8Al/(Al+Ti+Zr+Hf+V+Nb+Ta)$ expressed by atomic percent is increased to stabilize the γ' phase (which results in increasing the Al content alone). On the basis of this idea, the Al content is limited to 1.6 to 3.0 % by weight percent, and also, a ratio of $Al/(Al+Ti+Zr+Hf+V+Nb+Ta)$ expressed by atomic percent is determined in a range of 0.45 to 0.75, so that it is possible to prevent deterioration of high-temperature strength owing to transformation from the γ' phase into the η phase or the δ phase during long-time heating which has been a problem of the conventional Fe-Ni-Cr-base alloy. Further, such an increase in the Al content serves to increase an amount of generation of Al_2O_3 during high-temperature heating, to thereby compensate for deterioration of the acid resistance property owing to a decrease in the Cr content described in the article (3). Among Fe-Ni-Cr-base superalloys containing less than 50 % Ni and up to 20 % Cr, there exists no conventional alloy having such a high Al rate and such a high rate of $1.8Al/(Al+Ti+Zr+Hf+V+Nb+Ta)$, and it is quite a novel invention.

(2) Deterioration of high-temperature strength owing to a decrease in the Ni content of the matrix is compensated by increasing an amount of the γ' phase. This can be attained by controlling additive amounts of elements of the Group IVa and the Group Va which partially overlap with the elements of the conventional alloy and also by adding a large amount of Al. More specifically, the amount of the γ' phase to obtain the intended strength correlates with an amount of $(Al+Ti+Zr+Hf+V+Nb+Ta)$ expressed by atomic percent, and this value is controlled to be within a range of 6.5 to 10.0 which is higher than that of the conventional forging alloy, so that short-time high-temperature strength can be improved (four times of this amount is a calculated γ' amount). Such a high calculated γ' amount has never been realized in actual forging alloys for engine valves, and it is likewise quite a novel invention in this respect. In the case of an Ni-base superalloy having not less than 50 % Ni, the γ' phase maintains stability up to a high temperature, and hot working of the alloy with this level of γ' amount is difficult. Also, in the case of an alloy having a low ratio of $Al/(Al+Ti+Zr+Hf+V+Nb+Ta)$ described in the article (1), hot working is difficult due to solid-solution strengthening of the IVa family and the Va family and an increase in the amount of lattice strain of the γ' phase. Therefore, the alloy having such a high calculated γ' amount can be worked only when the Ni content is below 50 % and when the ratio of $Al/(Al+Ti+Zr+Hf+V+Nb+Ta)$ described in the article (1) is high.

(3) In order to prevent precipitation of embrittlement phases rich in Cr, such as the σ phase and the α' phase, after long-time heating, the Cr content of the matrix is suppressed to the minimum not to deteriorate the acid resistance property. Further, additive amounts of Mo and W in the same family as Cr are determined, if necessary, as a total amount of Mo and W in terms of atomic percent instead of weight percent. The factors described in the foregoing articles (1) and (2) and the determination of the optimum Cr content is quite a novel combination. By satisfying these factors at once, the alloy which has both the intended strength and ductility after long-time heating can be obtained.

More specifically, according to the present invention, there is provided an Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.0 to 3.0 % Al, one or more elements selected from the IVa family and the Va family whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities, wherein Al is an indispensable additive element, and one or more elements selected from Group IVa and Group Va satisfy the following formula by atomic percent:

$$0.45 \leqq Al/(Al+Ti+Zr+Hf+V+Nb+Ta) \leqq 0.75.$$

Preferably, the invention provides an Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.6 to 3.0 % Al, one or more elements selected from the Group IVa and the Group Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities. If necessary, it may include one or both of up to 3 % Mo and up to 3 % W.

More preferably, the invention provides an Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.08 % C, up to 0.5 % Si, up to 1.0 % Mn, 30 to 49 % Ni, 13 to 18 % Cr, 1.6 to 3.0 % Al, 1.5 to 3.0 % Ti, 0.3 to 2.5 % Nb, and balance of Fe and unavoidable impurities. If necessary, it may also include one or both of up to 3 % Mo and up to 3 % W. However, it is more favorable to add up to 3 % Mo alone.

Still more preferably, the invention provides an Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.08 % C, up to 0.2 % Si, up to 0.5 % Mn, 30 to 45 % Ni, 13.5 to 16 % Cr, 0.1 to 1.0 % Mo, 1.8 to 2.4 % Al, 2.0 to 3.0 % Ti and 0.5 to 1.5 % Nb.

If necessary, the alloys may include, by weight, up to 5 % Co in such a range that $Ni+Co \leqq 49$.

Moreover, the above-described alloys preferably contain, by atomic percent, Al which is an indispensable additive element and one or more elements selected from the Group IVa and the Group Va in such a range as to satisfy the following formulas:

$6.5 \leqq Al + Ti + Zr + Hf + V + Nb + Ta \leqq 10.0$
$0.45 \leqq Al/(Al + Ti + Zr + Hf + V + Nb + Ta) \leqq 0.75$

more preferably,

$6.5 \leqq Al + Ti + Zr + Hf + V + Nb + Ta \leqq 8.5$
$0.50 \leqq Al/(Al + Ti + Zr + Hf + V + Nb + Ta) \leqq 0.60$

Furthermore, the foregoing alloys preferably contain, by atomic percent, Cr which is an indispensable additive element and one or both of Mo and W in such a range that $13 \leqq Cr + Mo + W \leqq 18$.

The alloys may include, if necessary, up to 0.015 % B, one or both of up to 0.02 % Mg and up to 0.02 % Ca, and one or both of up to 0.1 % Y and up to 0.1 % rare earth elements (hereinafter referred to as REM).

Some of the alloys having these compositions are characterized in that the U-notch Charpy impact value after heating at 800 ° C for 400 hours is not less than 0.5 MJ/m^2. Further, they are characterized in that the rupture strength in 800 ° C-294 MPa rotary bending fatigue tests after heating at 800 ° C for 400 hours is not less than 0.5×10^6 times. Moreover, engine valves for motor vehicles and knitted mesh supporters for exhaust gas catalyzers for motor vehicles which are made of the above-described Fe-Ni-Cr-base superalloys have excellent properties which have not been observed in the conventional alloys.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a diagram in which the relationship between Al + Ti + Zr + Hf + V + Nb + Ta and Al/-(Al + Ti + Zr + Hf + V + Nb + Ta) of invention alloys, comparative alloys and conventional alloys are plotted.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, a small amount of carbon must be added because carbon combines with Ti and Nb and forms carbides, thereby preventing coarsening of crystal grains and improving the creep rupture ductility. However, excessive addition over 0.15 % causes a large amount of decomposition reactions from MC carbides into $M_{23}C_6$ carbides during long-time heating, and deteriorates the ductility on crystal grain boundaries at a normal temperature. Therefore, up to 0.15 % C is added. Preferably, up to 0.08 % C is added.

Si and Mn are added to an invention alloy as deoxidizing elements. However, excessive addition of either of them results in deterioration of the high-temperature strength. Therefore, the Si content is limited to 1.0 % or less, and the Mn content is limited to 3.0 % or less. Preferably, the Si content is 0.5 % or less, and the Mn content is 1.0 % or less. More preferably, the Si content is 0.2 % or less, and the Mn content is 0.5 % or less.

Ni stabilizes the austenite phase of the matrix and enhances the high-temperature strength. Further, Ni is an indispensable additive element as a constituent of the γ' phase. When the Ni content is below 30 %, precipitation of the γ' phase is insufficient, thereby deteriorating the high-temperature strength. On the other hand, when the Ni content exceeds 49 %, JIS NCF751 as a resource-saving material becomes no longer advantageous in respect of the price. Consequently, the Ni content is limited to 30 to 49 %. Preferably, the Ni content is 30 to 45 %.

Cr is an indispensable element for providing an acid resistance property for an alloy, and at least 10 % Cr is required for ensuring the acid resistance property as heat-resistant parts for a motor vehicle or the like. However, when the Cr content exceeds 18 %, the alloy structure becomes unstable, and harmful embrittlement phases such as the α' phase and the σ phase rich in Cr are generated, thus deteriorating the creep rupture strength and normal-temperature ductility. Therefore, the Cr content is limited to 10 to 18 %. Preferably, the Cr content is 13 to 18 %. More preferably, it is 13.5 to 16 %.

In the invention, Al is an indispensable element for precipitating the stable gamma prime phase, to thereby obtain a desired high-temperature strength, as described above, and at least 1.0 % Al is necessary. However, more than 3.0 % Al deteriorates the hot workability. Therefore, the Al content is limited to 1.0 to 3.0 %. Moreover, such a high Al content serves to increase an amount of generation of Al_2O_3 during high-temperature heating, and contributes to improvement of the acid resistance property. Preferably, the Al content is not less than 1.6 to 3.0 %, more preferably 1.8 to 2.4 %. In the category of Fe-Ni-base superalloys containing less than 50 % Ni and up to 20 % Cr, no alloy having such a high Al content has ever existed, and this is one of the most significant characteristics of the present invention.

As well as Al, elements of the Group IVa and the Va family in an invention alloy combine with Ni and precipitate the gamma prime phase so as to enhance the high-temperature strength. Totally not less than 1.5 % one or more of the elements of the Group IVa and the Group Va must be added. However, when the total additive amount of these elements exceeds 8.0 %, the gamma prime phase becomes unstable during high-temperature long-time heating, and intermetallic compounds of the η phase and the δ phase which do not conform with the γ phase are easily generated, and also, the hot workability is degraded. Consequently, totally 1.5 to 8.0 % one or more of the elements of the IVa family and the Va family are added. Preferably, the total additive amount is 3.0 to 5.0 %.

Among the elements of the Group IVa, Ti is the most favorable element to be added, and preferably, the additive amount of Ti is 1.5 to 3.0 %. More preferably, it is 2.0 to 3.0 %. Zr and Hf have lower solubility into the γ phase than Ti, and can not be added as much as Ti. However, Zr and Hf partially segregate on or around crystal grain boundaries and serve to enhance the grain-boundary strength in a high temperature range.

Among the elements of the Group Va, Nb is the most favorable element to be added, and preferably, the additive amount of Nb is 0.3 to 2.5 %. More preferably, it is 0.5 to 1.5 %. V (vanadium) has a weaker solid-solution strengthening function than Nb and deteriorates the acid resistance property, and consequently, excessive addition of V is not favorable. Ta performs solid-solution strengthening of the γ' phase more than Nb. However, Ta is a rare resource and increases the price by a large degree so that a large amount of Ta can not be added.

Mo and W are elements of the same VIa family as Cr, and both Mo and W perform solid-solution strengthening of the austenite matrix and serve to enhance the high-temperature fatigue strength and high-temperature creep rupture strength. Therefore, if necessary, one or both of 3 % or less Mo and 3 % or less W can be added. However, Mo is preferred in respect of the alloy price and the specific gravity, and the preferable Mo content in this case is 0.1 to 1.0 %. Moreover, precipitation of the α' phase and the σ phase is affected by a total amount of these three elements by atomic percent as well as the additive amount of Cr, and consequently, it is preferable to maintain a predetermined value of the total amount of Mo and W in the same family as Cr in terms of atomic percent instead of weight percent if necessary. Therefore, the amount of Cr + Mo + W expressed by atomic percent is preferably 13 to 18. More preferably, it is 15.0 to 17.5.

Co dissolves in the austenite matrix and promotes solid solution of the γ' phase in a range for hot working, thereby improving the workability. On the other hand, in a practical temperature range, Co increases an amount of precipitation of the γ' phase and enhances the high-temperature strength. Consequently, Co can be added to be substituted for Ni, if necessary, in such a range that $Ni + Co \leqq 49$. However, Co is a more expensive element than Ni so that the upper limit is preferably 5.0 %.

In order to achieve the object of the present invention, Al, the Group IVa elements and the Group Va elements must individually satisfy the foregoing respective ranges. Besides, it is important to realize the total amounts of these elements and the Al rate in proper ranges as the gamma prime constituent elements. As described above, in the γ' phase consisting of $Ni_3(Al,IVa,Va)$, the ratio of Al/(Al + Ti + Zr + Hf + V + Nb + Ta) expressed by atomic percent is increased to stabilize the γ' phase. When this ratio of Al/(Al + Ti + Zr + Hf + V + Nb + Ta) is less than 0.45, the high-temperature strength is easily deteriorated owing to transformation from the γ' phase into the η phase and the δ phase during long-time heating. On the other hand, when this ratio exceeds 0.75, solid-solution strengthening of the γ' phase is not effected sufficiently, and the normal-temperature strength is deteriorated. Therefore, preferably, the ratio of Al/(Al + Ti + Zr + Hf + V + Nb + Ta) is 0.45 to 0.75. More preferably, it is 0.50 to 0.60.

Further, in order to compensate deterioration of the high-temperature strength due to a decrease of the Ni content of the matrix with an increase of the amount of the γ' phase, the amount of (Al + Ti + Zr + Hf + V + Nb + Ta) expressed by atomic percent is preferably controlled in a proper range. When this value is below 6.5 atom. %, the strength is not as high as the strength of the conventional Fe-Ni-Cr-base superalloy having more than 50 % Ni, and when it exceeds 10 atom. %, hot working for engine valves and the like becomes difficult. Therefore, the amount of (Al + Ti + Zr + Hf + V + Nb + Ta) expressed by atomic percent is controlled in a range of 6.5 to 10.0 which is higher than the conventional forging alloy, so as to improve the short-time high-temperature strength. The more preferable range is 7.0 to 8.5 atom. %. Such a high calculated γ' amount has never been realized in a forging alloy for engine valves and the like. In this respect, it is quite a novel invention. In the case of an Ni-base superalloy having 50 % or more Ni, the γ'

phase is stable up to a high temperature, and with this level of γ' amount, hot working for strength of engine valves and the like is difficult.

In the case of an alloy in which the above-mentioned ratio of Al/(Al + Ti + Zr + Hf + V + Nb + Ta) expressed by atomic percent is low, hot working is difficult because of solid-solution strengthening of elements such as Ti, Nb and Ta and an increase of the amount of lattice strain of the γ' phase. Consequently, hot working of an alloy having such a high calculated γ' amount can be conducted only when the Ni content does not exceed 50 % and when the ratio of Al/(Al + Ti + Zr + Hf + V + Nb + Ta) is high. Of the atomic percent values shown in the foregoing formulas, those of the elements which are not added are calculated as zero.

In this invention, B (boron) is effective for enhancing the high-temperature strength and ductility by the grain-boundary strengthening function, and an appropriate amount of B can be added to an invention alloy. The effect starts to take place from addition of a small amount. However, when the additive amount of B exceeds 0.015 %, the solidus temperature during heating is lowered, and the hot workability is degraded. Therefore, the upper limit of B is preferably 0.015 %.

Mg and Ca enhance purification of the alloy as strong deoxidizing, desulfurizing elements, and serve to improve the ductility during high-temperature tension, creep deformation and hot working. Consequently, an appropriate amount of one or both of Mg and Ca can be added. The effect starts to take place from addition of a small amount. However, when the additive amount of each of Mg and Ca exceeds 0.02 %, the solidus temperature during heating is lowered, and the hot workability is degraded. Therefore, the upper limit of each of Mg and Ca is preferably 0.02 %.

In the present invention, Y and REM are effective for enhancing the high-temperature acid resistance property, and an appropriate amount of one or both of Y and REM can be added. The effect starts to take place from addition of a small amount. However, when the additive amount of each of Y and REM exceeds 0.1 %, the solidus temperature during heating is lowered, and the hot workability is degraded. Therefore, the upper limit of each of Y and REM is preferably 0.1 %. It is easy to use an invention alloy as a base and to derive the optimum additive amount of elements of the lanthanoid group so as to enhance the acid resistance property up to the limit, and such an operation does not exceed the range of this invention.

Although not mentioned in the claims, Re dissolves in the austenite matrix to strengthen the same. Also, Re promotes precipitation of the γ' phase, and it advantageously improves the alloy in high-temperature wear resistance property. Therefore, up to 2.0 % Re may be added to the invention alloy. Since Re is a rare resource and increases the alloy price by a large degree, excessive addition is not necessary.

Fe is an effective element for forming the austenite matrix which is inexpensive for a resource-saving alloy. Further, Fe softens the matrix in a higher temperature range than Ni, and consequently, hot working can be conducted even if the alloy includes the above-mentioned amounts of strengthening alloy elements. For the foregoing reasons, Fe is the balance of the composition except unavoidable impurities.

Among the impurities, the following elements may be included in an invention alloy if their additive amounts are within the following ranges:

$P \leqq 0.04$ %, $S \leqq 0.02$ %, $O \leqq 0.02$ %, $N \leqq 0.05$ % more preferably,

$P \leqq 0.02$ %, $S \leqq 0.005$ %, $O \leqq 0.01$ %, $N \leqq 0.01$ %

The above-described Fe-Ni-Cr-base superalloys are subjected to vacuum melting alone or vacuum melting and the subsequent refining process of electroslag remelting, vacuum arc remelting or the like, and the ingots thus obtained are processed through hot forging, hot rolling or the like, and finished as primary products.

These materials are provided for practical use after they are subjected to solid solution heat treatment at 900 to 1100 ° C and aging treatment at 600 to 800 ° C which are generally performed for γ' precipitation strengthening type superalloys. In the case where hot working also serves as solid solution heat treatment, aging treatment may be performed directly after hot working.

Sufficient normal-temperature toughness and ductility can be obtained from these alloys even after they are subjected to long-time heat treatment in which practical use is simulated, for example, long-time heating at 800 ° C for about 400 hours. These are the properties which could not be obtained from the conventional high-Cr Fe-Ni-Cr-base superalloys. As a concrete value, a Charpy impact value of not less than 0.5 MJ/m^2 can be obtained.

These are the properties which have newly taken into consideration because durabilities of the conventional component parts must be improved in accordance with prolongation of the guarantee period of a motor vehicle. If the impact value after heating at 800 ° C for 400 hours as a material for valves of a motor vehicle engine is less than 0.5 MJ/m^2, the valves whose toughness is inadequate might be broken when, for example, the engine after long-term use is quickly rotated up to a high temperature in a cold place. Therefore, if necessary, the impact value of the invention alloy after heating at 800 ° C for 400 hours is preferably limited to 0.5 MJ/m^2 or more.

Similarly, sufficient fatigue strength can be obtained from the invention alloys even after they are heated at 800 °C for 400 hours. In the case of component parts to which cyclic stress is applied at a high temperature, such as engine valves, the most significant factor which shortens the life is fatigue. In order to ensure the performance of the valves in accordance with prolongation of the guarantee period of a motor vehicle, the rotary bending fatigue rupture strength is preferably limited to 0.5×10^6 times or more under the test condition of 800 °C-294 MPa after heating at 800 °C for 400 hours. More preferably, the strength is 2.5×10^6 times or more. The invention alloys can satisfy such fatigue strength under the optimum heat treatment condition.

The invention alloys can realize both the excellent normal-temperature toughness and the high high-temperature fatigue strength after high-temperature long-time heating. This is the performance which could not be achieved by the conventional Fe-Ni-Cr-base superalloys, and the above-mentioned value specifically shows the excellent properties of the invention alloys.

Moreover, hot rolled bars made of the invention alloys are cut into a required size and shaped into engine valves for motor vehicles through hot upset forging or hot extrusion. Such engine valves are inexpensive resource-saving valves which are excellent in high-temperature fatigue strength, high-temperature hardness, stability of alloy structure, the acid resistance property and normal- and high-temperature strength after long-time heating, and which do not require building-up on valve face portions. The engine valves can greatly contribute to the economic aspect of production of motor vehicles. These engine valves can be subjected to various treatments for surface nitrogenization and various kinds of hard plating before practical use. Also, various kinds of heat-resistant steel and high-hardness alloy tool steel are welded on the axial portions of the engine valves, and they can be used as connection valves. Further, when the engine valves are processed in various manners and used as hollow engine valves, their durability is further improved.

Furthermore, hot rolled bars made of the invention alloys after solid solution heat treatment are subjected to cold or warm working and annealing repeatedly, worked into wire having a diameter of about 0.2 mm at the minimum, and shaped into a knitted mesh supporter for supporting a ceramic carrier of exhaust gas catalyzer. This knitted mesh supporter has more excellent acid resistance property and high-temperature strength than stainless steel of SUS310S and so forth which is a conventional knitted mesh material, so that a knitted mesh supporter having higher reliability and excellent durability can be obtained.

Example 1

Alloys of the compositions shown in Table 1 were formed into ingots of 10 kg through vacuum induction melting, and then, the ingots were shaped into bars of 30 mm square through hot working (REM was added as misch metal). The bars were subjected to solid solution heat treatment in which they were maintained at 1050 °C for 30 minutes and then water-cooled, and aging treatment in which they were maintained at 750 °C for 4 hours and then air-cooled. After this normal heat treatment or after maintaining the bars of this condition at 800 °C for 400 hours, normal-temperature hardness, normal-temperature Charpy impact tests, normal-temperature and 800 °C tension tests and rotary bending fatigue tests under the condition of 800 °C-294 MPa were performed. Further, acid resistance properties when the bars were heated at 850 °C for 400 hours were inspected. Normal-temperature hardness was measured by Rockwell hardness meters. The Charpy impact tests were performed at a temperature of 20 °C with 2U-notch test pieces No. 3 in accordance with the JIS method. The tension tests were performed with a parallel-portion diameter of 6.35 mm and an elongation of 4D in accordance with the ASTM method. The rotary bending fatigue tests were performed with test pieces having a parallel-portion diameter of 8 mm at a rotational speed of 3600 in accordance with the JIS Z2274, and the number of testing operations until each test piece was ruptured was counted. Further, in the acid resistance tests, round test bars having a diameter of 10 mm and a length of 20 mm were used, and weights of the test bars were measured before and after heating at 850 °C for 400 hours, thereby evaluating the oxidization weight changes. Results of the various tests are shown in Table 2.

Table 1

	No.	COMPOSITION (WEIGHT %)													
		C	Si	Mn	Ni	Al	IVa			Va			Vla		
							Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
INVENTION ALLOY	1	0.037	0.10	0.14	39.8	1.79	2.18	-	-	-	1.21	-	15.5	0.74	-
	2	0.037	0.08	0.11	41.2	2.00	2.42	-	-	-	1.34	-	15.0	0.74	-
	3	0.035	0.08	0.11	43.1	2.20	2.68	-	-	-	1.47	-	14.3	0.72	-
	4	0.031	0.25	0.10	44.6	2.04	2.33	0.011	-	-	1.25	-	15.1	-	2.50
	5	0.038	0.14	0.16	41.0	1.88	2.40	-	-	-	1.35	-	15.1	-	-
	6	0.013	0.18	0.12	41.3	2.04	2.44	-	-	-	1.31	-	16.3	0.74	-
	7	0.011	0.10	0.92	41.3	2.11	1.74	0.042	0.02	-	2.11	-	14.8	2.50	0.31
	8	0.039	0.09	0.11	45.2	1.94	2.44	-	-	-	1.36	-	16.3	0.76	-
	9	0.037	0.08	0.11	41.5	1.89	2.76	-	-	-	1.35	-	15.0	0.75	-
	10	0.036	0.08	0.12	41.3	2.23	2.11	-	-	-	1.34	-	14.9	0.76	-
	11	0.038	0.11	0.11	41.4	1.99	2.75	-	-	-	0.71	-	14.9	0.75	-
	12	0.035	0.10	0.11	32.3	2.05	2.79	-	-	-	0.70	-	14.2	0.75	-
	13	0.073	0.11	1.53	43.2	2.56	1.75	0.081	-	-	0.75	-	13.5	1.53	-
	14	0.034	0.11	0.25	41.5	2.15	2.05	-	0.06	-	0.75	1.51	15.5	0.71	-
	15	0.024	0.05	0.44	42.2	2.21	2.36	-	-	-	1.29	-	15.8	0.34	-
	16	0.033	0.18	0.21	39.9	2.14	2.38	-	0.11	-	1.44	-	14.9	0.54	2.14
	17	0.025	0.05	0.16	43.3	2.51	2.46	-	-	-	1.47	0.31	14.6	0.31	-
	18	0.024	0.05	0.21	42.4	1.79	2.74	-	-	-	1.54	-	14.8	-	1.44
	19	0.114	0.05	2.15	48.3	2.01	3.61	-	-	-	-	-	11.2	0.35	0.13
	20	0.035	0.62	0.25	46.6	2.02	2.03	0.012	0.03	0.38	1.03	0.54	15.2	-	-
	21	0.042	0.05	0.18	45.6	2.03	2.36	-	-	0.22	-	0.62	16.0	-	-
	22	0.022	0.15	0.35	46.6	1.41	2.55	-	-	-	0.85	0.35	15.0	1.35	0.77
	23	0.009	0.13	0.25	46.8	1.25	2.06	0.008	-	0.15	0.65	0.32	16.2	0.45	0.35
COMPARATIVE ALLOY	31	0.015	0.25	0.35	46.0	2.05	3.62	0.060	0.12	0.35	1.54	2.51	13.2	0.25	-
	32	0.042	0.08	0.12	41.3	2.04	2.45	-	-	-	1.34	-	18.8	0.75	-
	33	0.035	0.11	0.15	41.8	1.22	3.62	-	-	-	1.88	-	15.0	0.74	-
CONVENTIONAL ALLOY	41	0.035	0.16	0.13	59.9	1.07	2.49	0.019	-	-	0.89	-	18.6	-	-

VALUE A = Al+Ti+Zr+Hf+V+Nb+Ta

VALUE B = Al/(Al+Ti+Zr+Hf+V+Nb+Ta)

VALUE C = Cr+Mo+W

NOTE: ATOMIC PERCENT

- Cont'd -

Table 1 (Cont'd)

	COMPOSITION (WEIGHT %)									
	Fe	Co	B	Mg	Ca	Y	REM	CALCULATED VALUE IN ATOMIC PERCENT		
								VALUE A	VALUE B	VALUE C
	Bal.	0.21	0.0045	0.0075	-	-	-	6.91	0.53	16.96
	Bal.	-	0.0045	0.0070	-	-	-	7.69	0.53	16.32
	Bal.	-	0.0048	0.0078	-	-	-	8.47	0.53	15.60
	Bal.	-	0.0094	-	0.0051	0.010	-	7.72	0.55	17.03
	Bal.	-	0.0044	0.0033	-	-	-	7.41	0.52	16.05
	Bal.	-	0.0047	0.0077	-	-	-	7.77	0.54	17.72
	Bal.	2.50	-	0.0035	0.0021	-	0.011	7.73	0.57	17.53
	Bal.	-	0.0048	0.0048	-	-	-	7.61	0.52	17.83
	Bal.	-	0.0045	0.0071	-	-	-	7.87	0.49	16.34
	Bal.	-	0.0051	0.0062	-	-	-	7.79	0.59	16.26
	Bal.	-	0.0043	0.0047	-	-	-	7.65	0.53	16.21
	Bal.	-	0.0043	0.0046	-	-	-	7.78	0.54	15.40
	Bal.	-	-	0.0033	0.0025	0.009	0.015	7.74	0.68	15.19
	Bal.	-	0.0041	-	0.0051	-	-	7.75	0.57	17.00
	Bal.	-	-	-	-	-	-	7.99	0.56	16.94
	Bal.	-	-	-	-	-	-	8.12	0.55	17.00
	Bal.	-	-	-	-	0.010	-	8.93	0.57	15.66
	Bal.	1.50	0.0048	-	-	-	-	7.84	0.47	16.36
	Bal.	-	0.0025	-	-	-	-	8.25	0.50	12.09
	Bal.	-	-	-	0.0065	-	-	7.67	0.54	16.11
	Bal.	-	0.0023	-	-	-	0.008	7.29	0.57	16.96
	Bal.	-	0.0045	0.0082	-	-	-	6.55	0.45	17.24
	Bal.	0.30	0.0062	0.0035	-	0.009	-	5.66	0.46	17.79
	Bal.	-	0.0044	0.0038	-	-	-	10.69	0.40	14.42
	Bal.	-	0.0046	0.0083	-	-	-	7.78	0.54	20.35
	Bal.	-	0.0045	0.0045	-	-	-	7.86	0.32	16.51
	Bal.	-	0.0047	0.0094	-	-	-	5.67	0.39	19.98

Table 2

	No.	HARDNESS (HRC)		NORMAL-TEMPERATURE TENSILE STRENGTH (MPa)		NORMAL-TEMPERATURE TENSILE REDUCTION OF AREA (%)		800°C TENSILE REDUCTION OF AREA (%)	
		NORMAL AGING	OVERAGING	NORMAL AGING	OVERAGING	NORMAL AGING	OVERAGING	NORMAL AGING	OVERAGING
INVENTION ALLOY	1	35.0	33.0	1210	1113	71.6	51.3	574	401
	2	36.0	35.1	1217	1175	50.8	57.6	617	441
	3	38.1	37.4	1233	1216	46.7	29.8	696	470
	4	36.8	35.6	1236	1187	47.3	53.0	626	461
	5	38.4	34.3	1247	1154	44.1	49.5	607	398
	6	37.4	35.2	1235	1195	52.7	41.7	645	446
	7	35.4	34.8	1198	1155	48.8	59.0	608	457
	8	36.7	35.4	1232	1196	49.6	43.7	651	457
	9	37.8	36.9	1248	1209	47.2	38.9	644	462
	10	35.2	33.9	1209	1151	52.5	48.9	600	422
	11	37.1	34.9	1231	1178	48.1	46.2	631	434
	12	33.5	33.4	1162	1107	55.4	46.3	566	405
	13	35.5	33.2	1219	1123	72.0	60.0	579	406
	14	38.0	36.6	1236	1186	44.1	47.6	638	465
	15	33.0	32.8	1137	1099	64.1	58.3	555	424
	16	36.2	35.0	1209	1161	51.4	55.5	597	480
	17	38.9	37.7	1288	1243	40.0	28.8	726	489
	18	38.4	36.0	1265	1200	45.4	38.0	648	451
	19	39.5	35.9	1325	1203	42.4	33.5	688	395
	20	35.8	34.9	1220	1150	45.0	48.0	589	388
	21	35.1	33.2	1215	1120	70.5	52.1	565	415
	22	33.1	31.9	1164	1125	75.2	64.6	548	388
	23	32.5	31.0	1145	1061	78.2	76.3	530	365
COMPARATIVE ALLOY	31	-	-	-	-	-	-	-	-
	32	37.2	36.0	1223	1197	49.7	8.1	638	466
	33	39.9	34.4	1375	1078	34.1	14.4	666	360
CONVENTIONAL ALLOY	41	35.5	31.8	1221	1143	45.8	46.1	610	424

- Cont'd -

Table 2 (Cont'd)

800°C TENSILE REDUCTION OF AREA (%)		CHARPY IMPACT VALUE (MJ/m^2)		800°C-294MPa FATIGUE RUPTURE STRENGTH (x 10^6 TIMES)		OXIDIZATION WEIGHT CHARGE
NORMAL AGING	OVERAGING	NORMAL AGING	OVERAGING	NORMAL AGING	OVERAGING	
7.7	23.4	1.68	1.23	5.34	2.34	0.678
9.9	26.4	1.81	1.10	6.40	4.22	0.687
10.0	15.4	1.58	0.87	4.40	4.78	0.577
8.6	24.4	1.74	1.22	6.91	4.59	0.748
8.9	56.0	1.23	1.21	5.35	3.68	0.602
9.6	28.1	1.86	1.10	7.27	4.35	0.731
10.3	30.0	1.37	0.96	10.55	5.37	1.044
8.2	31.2	1.43	1.05	8.71	3.32	0.712
9.4	36.0	1.45	0.94	5.80	4.14	0.744
13.7	31.1	1.72	1.21	8.04	2.94	0.457
6.5	20.7	1.40	1.01	4.09	3.16	1.028
7.3	53.3	1.84	0.99	10.31	4.84	1.446
12.4	28.4	1.80	1.30	3.35	3.03	1.044
6.9	22.0	1.45	1.22	7.66	5.33	0.700
11.4	38.8	1.82	1.19	5.35	4.21	0.550
11.1	28.4	1.84	1.22	5.98	3.88	0.910
6.6	14.4	1.30	0.86	5.88	4.69	0.619
7.4	30.3	1.31	0.87	3.65	1.08	0.944
8.5	42.1	1.66	1.15	4.11	2.38	1.569
6.8	38.0	1.44	0.81	3.35	1.35	0.594
8.2	25.1	1.85	1.24	4.88	2.25	0.656
14.1	41.4	1.85	1.22	1.43	0.82	1.670
17.3	62.1	1.91	1.45	1.08	0.65	1.920
-	-	-	-	-	-	-
11.2	30.4	1.32	0.16	10.17	14.21	0.742
4.4	44.1	0.84	0.43	1.05	0.33	1.944
5.5	23.6	1.21	1.09	3.24	2.26	0.876

In Table 1, Nos. 1 to 21 are invention alloys, Nos. 31 to 33 are comparative alloys, and No. 41 is a conventional alloy disclosed in JP-B2-4-11613. Values A, B and C appended to the various chemical compositions in Table 1 are, respectively, an amount of Al+Ti+Zr+Hf+V+Nb+Ta, a ratio of Al/(Al+Ti+Zr+Hf+V+Nb+Ta) and an amount of Cr+Mo+W which are expressed by atomic percent. In calculating these values, an atomic weight of La was used as a representative value of the REM content. Further, the relationship between the values A and B is shown in Fig. 1.

The various kinds of mechanical properties and acid resistance properties of the invention alloys were as excellent as or more excellent than those of the conventional alloy No. 41 including 60 % Ni. It was confirmed that the invention alloys were superior resource-saving heat-resistant alloys.

Of the comparative alloys, cracking occurred in No. 31 during hot forging, and evaluation tests were not performed. This was because the sum of the IVa family and the Va family elements in Table 1 was as high as 8.2 %, and because the value A was too high. As shown in Fig. 1, the values A and B of No. 32 were at the same level as those of the invention alloys and had excellent mechanical properties after normal heat treatment. However, the normal-temperature tensile reduction of area and the Charpy impact value after long-time heating were drastically deteriorated. This was because the excessive additive amount of Cr and the excessively high value C resulted in precipitation of the σ phase on crystal grain boundaries. Although No. 33 had excellent mechanical properties after normal heat treatment, the high-temperature tensile strength and the rotary bending fatigue rupture strength after long-time heating were inferior to those of the invention alloys, and the normal-temperature tensile reduction of area and the Charpy impact value were deteriorated by a large degree. This was because the low additive amount of Al and the low value B, as shown in Fig. 1, resulted in coarsening of the γ' phase and transformation from the γ' phase into the η phase during long-time heating.

Example 2

The invention alloy No. 2 shown in Table 1 was further subjected to hot forging and cutting and grinding work, and finished as a round bar having a diameter of 6 mm. Then, one end of this round bar was formed into a shape of an engine valve through hot upset forging. This engine valve and a mass-production engine valve made of the conventional alloy disclosed in JP-B2-4-11613 were subjected to the normal heat treatment described in Example 1, and bench tests were carried out with engine testers for lead-free gasoline. Test conditions as high-speed high-temperature continuous durability tests were selected in such a manner that the maximum temperature of the valve would be 780 to 830 ° C, and continuous operation for 400 hours was performed. After finishing the tests, shape changes and cross-sectional wear states of the engine valves made of the invention alloy and the conventional alloy were observed, and it was confirmed that both the engine valves had such qualities that they could be provided for practical use without any problems.

Example 3

A round bar of 6 mm made of the invention alloy No. 2 in Example 2 was subjected to cold drawing and annealing repeatedly and worked into wire having a diameter of 0.25 mm, and thereafter, the wire is shaped into a knitted mesh supporter of a ceramic carrier for an exhaust gas catalyzer. This catalyzer unit was joined in the bench tests in Example 2, and its performance as the knitted mesh supporter was inspected. Although the temperature of the knitted mesh supporter was higher than that of the valve, the knitted mesh supporter made of the invention alloy did not cause creep deformation nor abnormal oxidization after finishing the tests, and it was found that the invention alloy exhibited an excellent performance in the form of the exhaust gas knitted mesh supporter as well.

As will he apparent from the above, according to the present invention, there can be obtained a resource-saving, inexpensive Fe-Ni-Cr-base superalloy which has excellent stability of alloy structure, excellent normal- and high-temperature tensile properties after long-time heating, a high-temperature acid resistance property, an excellent high-temperature fatigue property and a wear resistance property, and those properties are not inferior to those of an Ni-base superalloy containing 50 % or more Ni which is used for engine valves and the like. When engine valves and knitted mesh supporters for exhaust gas catalyzers which are made of this alloy are used for motor vehicle engines, highly reliable engines which are excellent in cost reduction and durability can be produced.

Claims

1. An Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.0 to 3.0 % Al, one or more elements selected from Groups IVa and Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities,

wherein Al is an indispensable additive element, and one or more elements selected from said Groups IVa and Va satisfy the following formula by atomic percent:

$$0.45 \leqq Al/(Al + Ti + Zr + Hf + V + Nb + Ta) \leqq 0.75.$$

2. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.6 to 3.0 % Al, one or more elements selected from Groups IVa and Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities.

3. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, one or both of up to 3 % Mo and up to 3 % W, 1.6 to 3.0 % Al, one or more elements selected from Groups IVa and Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities.

4. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.08 % C, up to 0.5 % Si, up to 1.0 % Mn, 30 to 49 % Ni, 13 to 18 % Cr, 1.6 to 3.0 % Al, 1.5 to 3.0 % Ti, 0.3 to 2.5 % Nb, and balance of Fe and unavoidable impurities.

5. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.08 % C, up to 0.5 % Si, up to 1.0 % Mn, 30 to 49 % Ni, 13 to 18 % Cr, one or both of up to 3 % Mo and up to 3 % W, 1.6 to 3.0 % Al, 1.5 to 3.0 % Ti, 0.3 to 2.5 % Nb, and balance of Fe and unavoidable impurities.

6. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.08 % C, up to 0.5 % Si, up to 1.0 % Mn, 30 to 49 % Ni, 13 to 18 % Cr, up to 3 % Mo, 1.6 to 3.0 % Al, 1.5 to 3.0 % Ti, 0.3 to 2.5 % Nb, and balance of Fe and unavoidable impurities.

7. An Fe-Ni-Cr-base superalloy according to claim 1, essentially consisting of, by weight, up to 0.08 % C, up to 0.2 % Si, up to 0.5 % Mn, 30 to 45 % Ni, 13.5 to 16 % Cr, 0.1 to 1.0 % Mo, 1.8 to 2.4 % Al, 2.0 to 3.0 % Ti, 0.5 to 1.5 % Nb, and balance of Fe and unavoidable impurities.

8. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 7, further including, by weight, up to 5 % Co in such a range that $Ni + Co \leqq 49$.

9. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 8, wherein Al is an indispensable additive element, and one or more elements selected from said Groups IVa and Va satisfy the following formula by atomic percent:

$$6.5 \leqq Al + Ti + Zr + Hf + V + Nb + Ta \leqq 10.0$$

10. An Fe-Ni-Cr-base superalloy essentially consisting of, by weight, up to 0.15 % C, up to 1.0 % Si, up to 3.0 % Mn, 30 to 49 % Ni, 10 to 18 % Cr, 1.0 to 3.0 % Al, one or more elements selected from Groups IVa and Va whose amount or total amount is 1.5 to 8.0 %, and balance of Fe and unavoidable impurities, wherein

Al is an indispensable additive element, and one or more elements selected from said Groups IVa and Va satisfy the following formulas by atomic percent:

$$6.5 \leqq Al + Ti + Zr + Hf + V + Nb + Ta \leqq 8.5$$
$$0.50 \leqq Al/(Al + Ti + Zr + Hf + V + Nb + Ta) \leqq 0.60.$$

11. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 10, wherein Cr is an indispensable additive element, and one or both of Mo and W are included in such a range that $13 \leqq Cr + Mo + W \leqq 18$ by atomic percent.

12. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 11, further including, by weight, up to 0.015 % B.

13. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 12, further including, by weight, one or both of up to 0.02 % Mg and up to 0.02 % Ca.

14. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 13, further including, by weight, one or both of up to 0.1 % Y and up to 0.1 % REM.

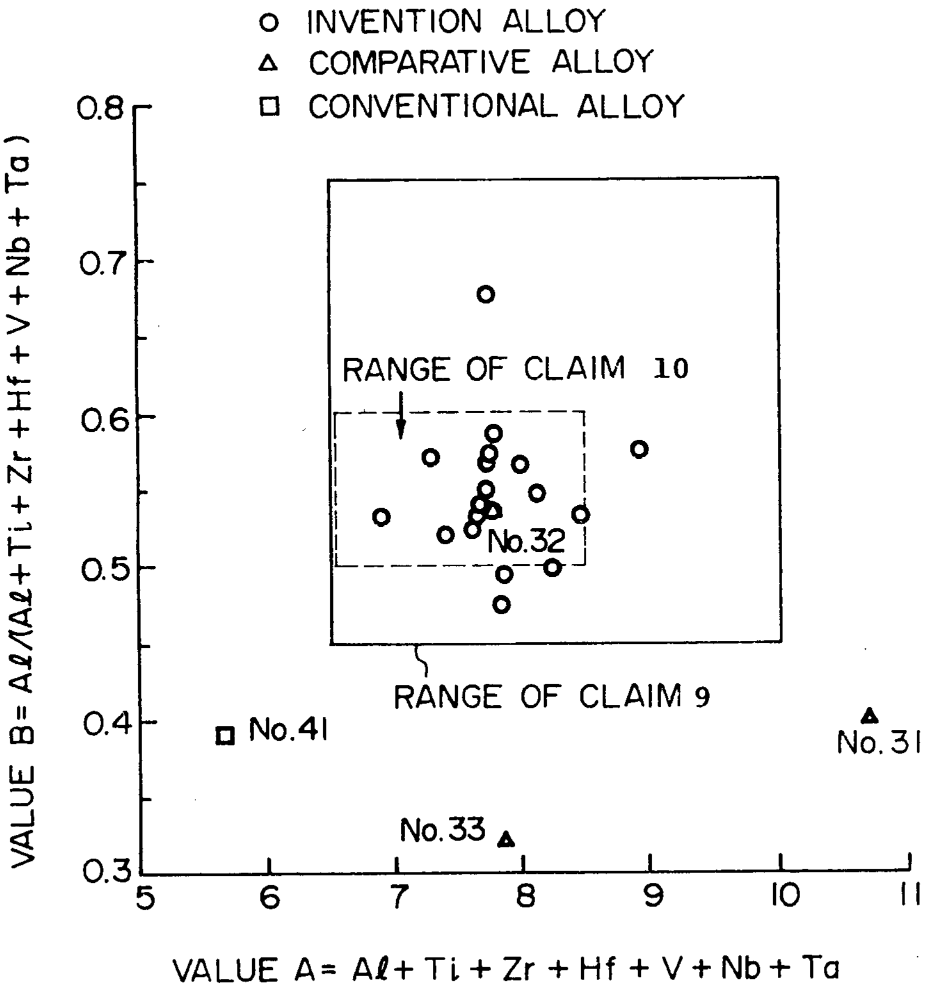
15. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 14, wherein the U-notch Charpy impact value after heating at 800 ° C for 400 hours is not less than 0.5 MJ/m^2.

16. An Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 15, wherein the rupture strength in the 800 °C-294 MPa rotary bending fatigue test after heating at 800 °C for 400 hours is not less than 0.5×10^6 times.

17. An engine valve for a motor vehicle, which is manufactured of an Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 16.

18. A knitted mesh supporter for an exhaust gas catalyzer for a motor vehicle, which is manufactured of an Fe-Ni-Cr-base superalloy according to any one of Claims 1 to 16.

FIG. 1


○ INVENTION ALLOY
△ COMPARATIVE ALLOY
□ CONVENTIONAL ALLOY
VALUE B= Aℓ/(Aℓ+Ti+Zr+Hf+V+Nb+Ta)
0.8
0.7
0.6
0.5
0.4
0.3
RANGE OF CLAIM 10
No.32
RANGE OF CLAIM 9
No.41
No.31
No.33
5
6
7
8
9
10
11
VALUE A= Aℓ+Ti+Zr+Hf+V+Nb+Ta