EUROPEAN PATENT APPLICATION

(71) Applicant: DAIDO TOKUSHUKO KABUSHIKI KAISHA
No. 66, Aza Kuridashi Hoshizaki-cho
Minami-ku
Nagoya-shi Aichi-ken(JP)

(72) Inventor: Isobe, Susumu Lions Mansion
Irinaka Garden 508
No. 122-1, Takigawa-cho Showa-ku
Nagoya-city Aichi-prefecture(JP)
Inventor: Imamura, Motoaki
No. 3-18, Aigigaoka
Kani-city Gifu-prefecture(JP)

(74) Representative: Palmer, Roger et al
Page, White and Farrer 5 Plough Place New
Fetter Lane
London EC4A 1HY(GB)

(54) Heat resistant alloys.

(57) An Fe-Ni based heat resistant alloy having high strength, high toughness and excellent high-temperature corrosion resistance is disclosed, which comprises 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM, and the remainder being E and inevitable impurity. This alloy is suitable as a material for heat resistant components in internal combustion engine.
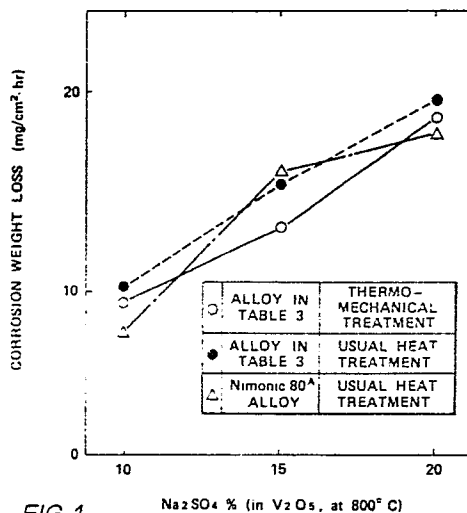
EP 0 244 520 A1

FIG. 1   Na2SO4 % (in V2O5, at 800°C)

HEAT RESISTANT ALLOYS

This invention relates to an Fe-Ni based heat resistant alloy having an excellent high-temperature corrosion resistance, and high toughness and strength, and more particularly to a high strength Fe-Ni based heat resistant alloy useful as a material for heat resistant components in internal combustion engine such as exhaust valve, heat resistant spring, heat resistant bolt and the like.

5 Lately, the interest to diesel engines having an improved fuel consumption is gradually raised, so that the service condition of exhaust valve in the diesel engines becomes more severer, and consequently requirements in the material for the exhaust valve are severer. In a part of the diesel engines, therefore, high-grade materials such as Ni based heat resistant alloy and the like are used without surface hardening at a valve face. However, the Ni based resistant alloy is expensive, so that the reduction of the cost is 10 strongly demanded, and particularly Fe-Ni based heat resistant alloy is developed in view of the Ni-saving.

The reinforcing mechanism of this Fe-Ni based heat resistant alloy is due to the precipitation of γ'-phase [Ni_3(Al, Ti)] likewise in case of the Ni based heat resistant alloy. However, the precipitation at grain boundary of η-phase [Ni_3Ti] not contributing to the reinforcement is liable to occur in the Fe-Ni based heat resistant alloy, so that the reduction of strength and ductility is not avoided. In fact, the addition amount of 15 Al, Ti or the like as a reinforcing element is limited to a relatively narrow range from a viewpoint of the structure stability.

The addition of B is effective for restraining the grain boundary precipitation of η-phase, but in this case, it is required to add a great amount of B. However, B considerably reduces the incipient melting temperature of the grain boundary, so that the addition of the great amount of B causes a problem of 20 damaging hot workability. Therefore, the addition amount of B is restricted to an extent of causing no damage of hot warkability.

On the other hand, it has been confirmed that the increase of Al amount is effective for restraining the grain boundary precipitation of η-phase. In the Fe-Ni based heat resistant alloy, the reinforcing action based on the precipitation of γ'-phase is produced by strain energy based on the difference in crystal lattice 25 constant between the precipitated γ'-phase and matrix, so that it is necessary to increase the lattice constant of γ'-phase as far as possible in order to provide a large strength. For this purpose, it is effective to make a large ratio of Ti/Al by decreasing the Al amount. Therefore, the increase of Al does not quite contribute to the reinforcement of the Fe-Ni based heat resistant alloy, so that the amount of Al becomes limited low.

30 The inventors have made various studies in order to provide Fe-Ni based heat resistant alloys which can restrain the precipitation of η-phase by adding proper amounts of B and Al and to improve the strength even if the Al amount is limited low, and further to improve high-temperature corrosion resistance, and as a result, the invention has been accomplished.

According to the invention, there is the provision of a hith strength, high toughness, high corrosion 35 resistant Fe-Ni based heat resistant alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM (at least one rare earth element), and if necessary,0.003-0.05% of N, and further at least one of 0.005-0.05% of Zr, 0.05-1% of V, 0.05-3% of Nb + Ta (inclusive of a case that either is zero), 0.05-3% of Mo and 0.05-3% of W, and the remainder being Fe and inevitable impurities. 40 In the preferred embodiment of the invention, the heat resistant alloy having a high strength and a remarkably excellent high-temperature corrosion resistance is provided without the damage of the toughness by subjecting the alloy of the above chemical composition to a solid solution treatment at a temperature of not less than 1050°C as a usual heat treatment and further to an age hardening treatment at 650-850 °C, and if necessary, subjecting to a working heat treatment wherein the homogenization is carried 45 out at a high temperature of not less than 1050 °C and residual strain is given by working at a temperature of not more than 1000 °C and an age hardening treatment is carried out at 650-850 °C, whereby the precipitation in grain of γ'-phase [(Ni_3(Al, Ti)] is promoted and the precipitation of harmful η-phase [Ni_2Ti] is restrained.

The present invention will now be described in greater detail by way of example only with reference to 50 the accompanying drawing. in which:-

Fig. 1 is a graph showing experimantal results on high-temperature corrosion resistance in Examples according to the invention.

The reason why the chemical composition of the high strength. high toughness, high corrosion resistant Fe-Ni based heat resistant alloy in this invention is limited to the above ranges (weight %) is as follows.

C: 0.01-0.2%

C is an effective element for enhancing high-temperature strength by bonding with Cr and Ti to form carbides. In order to obtain such an effect, it is necessary to add not less than 0.01% of C. However, if the amount is too large, the toughness and ductility are degraded and if it is applied, for example, to an exhaust valve, the performances are deteriorated, so that the upper limit should be 0.2%.

Si: not more than 2%

Si is mainly added as a deoxidizer in melting process. However, if the amount is too large, the toughness and ductility lower, so that it is limited to not more than 2%.

Mn: not more than 2%

Mn is added as a deoxidizer likewise Si and desulfurizer in melting. However, if the amount is too large, the oxidation resistance at high temperature lowers, so that it is limited to not more than 2%.

Ni: 25-50%

Ni is an element required for stabilizing austenite structure and simultaneously forming γ'-phase [Ni_3(Al, Ti)]. When the amount is less than 25%, brittle phase such as σ-phase or the like is formed in use at high temperature to degrade high-temperature properties, while when it is too large, the improvement of high-temperature properties is not so expected and the cost is rather increased, so that the Ni amount is limited to 25-50%.

Cr: 13-23%

Cr is an effective element for ensuring corrosion resistance and oxidation resistance required in the heat resistant alloy. In order to obtain such an effect, it is necessary to add not less than 13% of Cr. However, if the amount is too large, σ-phase is formed to degrade toughness and ductility, so that it is limited to not more than 23%.

Ti: 1.5-3.5%

Ti is an element necessary for bonding with Ni and Al to form γ'-phase [Ni_2 (Al, Ti)] effective for the increase of high-temperature strength. For this purpose, not less than 1.5% of Ti is added. However, if the amount is too large, η-phase [Ni_3 Ti] is precipitated to degrade high-temperature properties, so that it is limited to not more than 3.5%.

Al: 0.1-0.7%

Al is an element necessary for the formation of γ'-phase likewise Ti. For this purpose, not less than 0.1% of Al is added. However, if the amount is too large, the ratio of Ti/Al decreases and the strength is reduced, so that it is limited to not more than 0.7%.

B: 0.001-0.05%

B is an effective element for restraining the precipitation of η-phase. In order to obtain such an effect, it is necessary to add not less than 0.001% of B. However, if the amount is too large, local melting temperature of grain boundary is considerably reduced and hot workability is damaged, so that it should be limited to not more than 0.05%.

Ca: 0.001-0.01%

Ca is an effective element for fixing S to enhance hot workability and controlling distribution form of carbides to enhance toughness and ductility, and contributes to enhance the strength even if the Al amount is limited low. For this purpose, not less than 0.001% of Ca is added. However, if the amount is too large, the workability lowers, so that it should be limited to not more than 0.01%.

REM (at least one earth element): 0.001-0.1%

REM is an element for considerably improving adhesion property of oxide film, and is effective for the improvement of high-temperature corrosion resistance. Particularly, the effect by the addition of REM is considerably developed when the variation of service temperature is large. In order to obtain such an effect, not less than 0.001% of REM is added. However, when the REM amount exceeds 0.1%, the hot workability is apt to be degraded.

At least one of Zr: 0.005-0.05%, V: 0.05-1%, Nb + Ta(inclusive of a case that either is zero): 0.05-3%, Mo: 0.05-0.3%, and W: 0.05-3%

Zr, V, Nb, Ta, Mo and W are effective elements for forming carbides to enhance high-temperature strength and toughness, and among them, Zr is also an effective element for reinforcing grain boundary. If necessary, at least one of Zr, V, Nb, Ta Mo and W may be added for obtaining the above effect. However, if the amount is too large, the toughness and hot workability are degraded, so that it should be limited to the above defined range.

N: 0.003-0.05%

Since N is an element effective for controlling the growth of crystal grains to make the structure fine, not less than 0.003% of N may be added, if necessary. However, if the amount is too large, stringers due to agglomeration of nitride are formed to degrade ductility, so that it should be limited to not more than 0.05%.

According to the invention, Fe-Ni based heat resistant alloys having high strength, high toughness and improved high-temperature corrosion resistance have a chemical composition as defined above. It has been found that it is more desirable that the above chemical composition alloy is subjected to a solid solution treatment at a temperature of not less than 1050 C as a usual heat treatment and further to an age hardening treatment at 650-850 °C. Furthermore, it has been confirmed that the above treated alloy is homogenized at a high temperature of not less than 1050 °C. subjected to a working strain at a temperature of not more than 1000 °C, and then age-hardened at a temperature of 650-850 °C. Thus. the precipitation of γ'-phase in grain is promoted, and the precipitation of harmful η-phase is restrained to thereby provide high strength and considerably improve high-temperature corrosion resistance without the damage of toughness.

The following examples are given in illustration of the invention and are not intended as limitations thereof.

Example 1

An alloy having a chemical composition as shown in the following Table 1 was melted in a high frequency induction furnace of 50kg capacity to form an ingot of 30kg. Then, the ingot was subjected to a homogenization treatment at 1150°C for 16 hours, and forged to to a billet of 40mm square.

In order to examine hot workability of the alloy steel to be tested, a speciment of 15mm in diameter and 20mm in length was cut out from the billet and heated to 900-1150 °C conduct an upset test in mechanical press. whereby a limit reduction ratio producing cracks on free surface was measured The measured results of the upset test at 1100 °C which a typical working temperature are shown in the following Table 2.

4

Then, a part of the billets was subjected to a thermo-mechanical treatment, and the remaining billets were subjected to the usual heat treatment (solid solution and aging), to measure mechanical properties thereof. In this case, the conditions of the thermo-mechanical treatment were as follows. That is, the billet was soaked at 1000°C and rapidly forged to a reduction ratio of 50% through an air hammer, and immediately quenched, and then subjected to an aging at 750 °C for 16 hours. On the other hand, the usual heat treatment was carried out by subjecting to a solid solution treatment at 1000°C for 1 hour, quenching, and aging at 750 °C for 16 hours. The thus measured results are also shown in Table 2.

5

10

15

20

25

30

35

40

45

50

55

Table 1

Kind of alloy	Chemical composition (wt%)												Remarks
	C	Si	Mn	Ni	Cr	Ti	Al	B	Ca	REM	Others	Fe	
A	0.04	0.30	0.65	41.73	20.03	2.92	0.56	–	–	–	–	remainder	Comparative Example
B	0.04	0.20	0.67	40.56	19.47	2.88	0.70	0.004	0.002	0.005	–	″	Example
C	0.09	0.38	1.49	27.05	15.06	1.57	0.25	0.003	0.002	0.005	Nb:1.76 Zr:0.05	″	″
D	0.05	0.30	0.42	41.22	19.86	2.11	0.66	0.003	0.004	0.007	Mo:2.38 Zr:0.01	″	″
E	0.10	0.46	0.33	37.50	21.95	3.04	0.35	0.007	0.007	0.006	W :2.86 Zr:0.01	″	″
F	0.05	0.35	0.72	40.32	20.75	2.68	0.55	0.005	0.005	0.008	N :0.02 V :0.07 Zr:0.02	″	″

Table 2

Kind of alloy	Hot workability: Limit reduction ratio producing cracks in upset test at 1100°C (%)	Mechanical properties							
		Thermo-mechanical treatment 1000°C / 50% + 750°C×16hr				Usual heat treatment 1000°C×1hr water cooling + 750°C×16hr			
		0.2% yield stress kgf/mm²	tensile strength kgf/mm²	elongation %	reduction of area %	0.2% yield stress kgf/mm²	tensile strength kgf/mm²	elongation %	reduction of area %
A	47	94.5 / 91.8	127.6 / 122.4	19.8 / 18.9	31.4 / 37.5	85.1 / 83.8	115.8 / 114.2	25.7 / 27.4	36.7 / 35.5
B	67	93.5 / 92.7	128.0 / 125.3	20.3 / 19.5	33.1 / 30.7	83.5 / 84.8	114.2 / 115.9	27.5 / 26.3	37.2 / 35.8
C	70	75.8 / 78.3	110.2 / 112.4	21.3 / 20.5	34.0 / 30.8	64.3 / 65.7	98.5 / 97.7	26.7 / 28.3	32.4 / 31.6
D	72	88.6 / 89.2	123.0 / 121.6	20.7 / 19.0	29.3 / 28.6	76.4 / 77.6	110.2 / 108.7	26.6 / 24.5	36.7 / 34.0
E	63	97.1 / 99.4	130.0 / 129.2	17.6 / 17.8	25.4 / 26.5	86.7 / 88.1	118.6 / 117.2	22.4 / 21.7	30.2 / 29.5
F	60	94.6 / 96.2	129.5 / 130.7	20.6 / 22.3	32.5 / 33.0	85.5 / 84.8	110.3 / 112.8	28.5 / 26.4	31.7 / 33.2

As seen from Table 2, the limit reduction ratio producing cracks is only 47% in the comparative alloy A, but is as high as 60-72% in the alloys B-F according to the invention, from which it is apparent that the addition of Ca is effective.

As to the mechanical properies, the alloys B-F according to the invention are superior in the strength and toughness to the comparative alloy A. Particularly, it has been found that the thermo-mechanically treated alloys are higher in the strength as compared with the usually heat treated alloy, and are sufficiently high in the toughness.

Example 2

An alloy having a chemical composition as shown in the following Table 3 was melted in an electric furnace to form an ingot of 1 ton, which was drawn by forging into a billet of 180mm in diameter, from which an exhaust valve for large vessel was manufactured. In this case, the forging of the exhaust valve was divided into the forging of shaft and the shaping of valve head. The forging of the shaft was conducted by heating at 1000 °C with 3 heat cycles so as to render the diameter into 70mm, wherein the forging ratio at the third heat cycle was 30%, and the finish temperature was about 900 °C. Then, the forging of the valve head was conducted to a diameter of about 300mm by heating at 1000°C at one heat, wherein the finish temperature was about 850°C, at the valve face, and about 900 °C at teh central part in the top of the valve head. And also, the forging ratio of the valve face was about 60% at maximum.

Then, the valve was subjected to an age hardening treatment at 750°C for 16 hours as a thermo-mechanical treatment, or to a usual heat treatment wherein the valve was solid soluted at 1000 °C for 1 hour, cooled with water, and aged at 750 °C for 16 hours. Thereafter, the tensile properties of the shaft and the hardness of the vave face were examined and the results obtained are shown in Table 4.

Table 3

Chemical composition (wt%)

C	Si	Mn	Ni	Cr	Ti	Al	B	Ca	REM	Others	Fe
0.04	0.20	0.72	40.21	19.65	2.90	0.65	0.005	0.002	0.006	Zr:0.01	remainder

Table 4

Heat treating conditions	Tensile properties (shaft portion)				Hardness of valve face H v
	0.2% yield stress (kgf / mm²)	tensile strength (kgf / mm²)	elongation (%)	reduction of area (%)	H v
Thermo-mechanical treatment					
1000 °C shape forging	92.8	128.9	13.5	31.4	420 ~ 410
750 °C × 16hr air cooling	93.5	126.3	19.7	38.0	
Usual heat treatment					
1000 °C × 1hr water cooling	80.6	118.3	24.5	35.0	328 ~ 319
750 °C × 16hr air cooling	78.3	110.0	27.6	36.7	

As apparently from the results of Table 4. the valves after the thermo-mechanical treatment are better than the usual heat treatment. Especially. when the thermo-mechanicaly treated valve is compared with the usual heat treated valve. the tensile strength and yield stress of the shaft portion and the hardness of the valve face are superior, and the ductility of the shaft portion is sufficient in practical use.

Experiment

The actual exhaust valve is required to not only be excellent in the strength and toughness, but also have a resistance against high -temperature corrosion induced by V and S compounds in the fuel residue from a viewpoint of the performance of the exhaust valve. Further, even if the change of the service temperture as in the exhaust valve is remarkable, it is required to have a considerably excellent adhesion of oxide film. Therefore, vanadium attack test was made with respect to a specimen cut out from the face of the exhaust valve in Example 2.

In this test, the specimen was immersed in a molten mixed salt of vanadium pentoxide and sodium sulfate held at 800 °C, and then the corrosion weight loss was measured to obtain results as shown in the figure 1. As seen from this figure, the exhaust valve after the thermo-mechanical treatment of the alloy in Table 3 has an excellent high-temperature corrosion resistance substantially equal to that of the usual heat treated valve, which is almost equal to that of Nimonic 80A as the usually used expensive Ni based heat resistant alloy.

As mentioned above, the Fe-Ni based heat resistant alloy comprises, on a wight ratio, of 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM (at least one rare earth element), and if necessary, 0.003-0.05% of N, and further at least one of 0.005-0.05% of Zr, 0.05-1% of V, 0.05-3% of Nb + Ta (inclusive of a case that either is zero), 0.05-3% of Mo and 0.05-3% of W, and the remainder being Fe and inevitable impurities. In this case, the addition of Ni and Cr improves the heat resistance and corrosion resistance, and the addition of Ti and Al produces the formation of γ'-phase effective for the improvement of high-temperature strength, and the addition of B and Al restrains the precipitation of η -phase, and the addition of Ca improves the hot workability, and the addition of REM improves high-temperature corrosion resistance, and if necessary, the addition of Zr, V, Nb, Ta, Mo and W more improves the strength, and further the addition of N makes the structure finer. Furthermore, since the alloy is used by subjecting to the usual heat treatment or the thermo-mechanical treatment, the precipitation of γ'-phase effective for the improvement of high-temperature strength is promoted in the crystal grains, and also the precipitation in grain boundary of η-phase harmful for the strength and notch susceptibility can be restrained , so that the strength and toughness become higher, and the high-temperature corrosion resistance is considerably excellent. Consequently, the invention can provide Fe-Ni based heat resistant alloys cheaper than Ni based heat resistant alloy, and has a remarkable merit that the alloy is suitable as a material for heat resistant components in internal combustion engine such as exhaust valve, heat resistant spring, heat resistant bolt and so on.

Claims

1. A high strength FE-Ni based heat resistant alloy comprising, on a weight ratio. 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM, and the remainder being Fe and inevitable impurities.

2. A high strength Fe-Ni based heat resistant alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B. 0.001-0.01% of Ca, 0.001-0.1% of REM, and at least one of 0.005-0.05% of Zr, 0.05-1% of V, 0.05-3% of Nb + Ta, 0.05-3% of Mo and 0.05-3% of W, and the remainder being Fe and inevitable impurities.

3. A high strength Fe-Ni based heat resistant alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca. 0.001-0.1% of REM, 0.003-0.05% of N, and at least one of 0.005-0.05% of Zr, 0.05-1% of V. 0.05-3% of Nb + Ta, 0.05-3% of Mo and 0.05-3% of W. and the remainder being Fe and inevitable impurities

4. A process of producing a high strength Fe-Ni based heat resistant alloy, the process comprising providing an alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si. not more than 2% of Mn. 25-50% of Ni, 13-23% of Cr. 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca. 0.001-0.1% of REM, and the remainder being FE and inevitable impurities: subjecting the alloy to a solid solution treatment at a temperature of not less than 1050°C and further to an age hardening treatment of 650-850°C.

5. A process of producing a high strength Fe-Ni based heat resistant alloy, the process comprising providing an alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si. not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM, and at least one of 0.005-0.05% of Zr, 0.05-1% of V, 0.05-3% of Nb + Ta, 0.05-3% of Mo and 0.05-3% of W, and the remainder being Fe and inevitable impurities; subjecting the alloy to a solid solution treatment at a temperature of not less than 1050°C and further to an age hardening treatment of 650-850°C.

6. A process of producing a high strength Fe-Ni based heat resistant alloy, the process comprising providing an alloy comprising, on a weight ratio, 0.01-0.2% of C, not more than 2% of Si, not more than 2% of Mn, 25-50% of Ni, 13-23% of Cr, 1.5-3.5% of Ti, 0.1-0.7% of Al, 0.001-0.05% of B, 0.001-0.01% of Ca, 0.001-0.1% of REM, 0.003-0.05% of N, and at least one of 0.005-0.05% of Zr, 0.05-1% of V, 0.05-3% of Nb + Ta, 0.05-3% of Mo and 0.05-3% of W, and the remainder being Fe and inevitable impurities; subjecting the alloy to a solid solution treatment at a temperature of not less than 1050°C and further to an age hardening treatment of 650-850°C.

7. A process according to any one of Claims 4 to 6 further comprising the step of subjecting the alloy to a working strain at a temperature of not more than 1000°C, the working step being carried out between the solid solution treatment and the age hardening treatment.
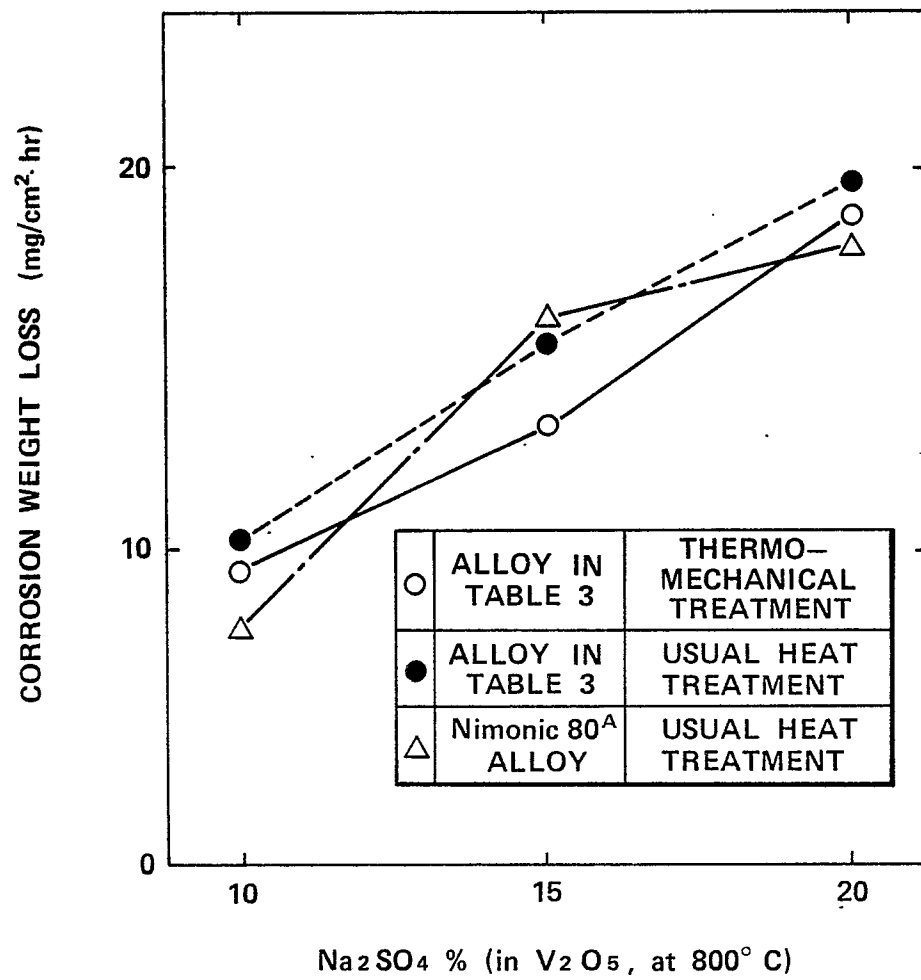
FIG. 1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 092 623 (WESTINGHOUSE ELECTRIC CORP.) * Claims 1,2,5,6,8 *	1-3	C 22 C 38/50 C 22 C 38/54 C 22 C 19/05
Y	US-A-3 575 734 (MUZYKA et al.) * Claims 1,2,4,5; column 7, lines 37-65; column 8, lines 33-53; column 8, line 54 - column 9, line 4 *	1-3	
A	DE-B-1 082 739 (NYBY BRUKS AKTIEBOLAG) * Claims 1,3 *	1	
A	* Claims 4-7 *	4-7	
A	GB-A- 999 439 (ALLEGHENY LUDLUM STEEL CORP.) * Claims 1-14 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 22 C 19 C 22 C 38
Y	US-A-3 865 581 (SEKINO et al.) * Claims 1-3; column 3, line 65 - column 4, line 30 *	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-01-1987	LIPPENS M.H.