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(11) **EP 0 765 950 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**17.10.2001 Bulletin 2001/42**

(51) Int Cl.7: **C22C 38/08**

(21) Application number: **96306099.1**

(22) Date of filing: **21.08.1996**

(54) **High strength low thermal expansion alloy**

Hochfeste Legierung mit niedrigem Ausdehnungskoeffizient

Alliage à haute résistance et à coefficient d'expansion thermique faible

(84) Designated Contracting States:  
**DE ES FR GB**

• **Moore, Melissa Ann**  
**Littleton, CO 80127 (US)**

(30) Priority: **25.08.1995 US 519678**  
**14.08.1996 US 696487**

(74) Representative: **Hedley, Nicholas James Matthew**  
**Kilburn & Strode**  
**20 Red Lion Street**  
**London WC1R 4PJ (GB)**

(43) Date of publication of application:  
**02.04.1997 Bulletin 1997/14**

(73) Proprietor: **Inco Alloys International, Inc.**  
**Huntington West Virginia 25720 (US)**

(56) References cited:  
**EP-A- 0 075 416**                      **CH-A- 404 965**  
**DE-A- 1 558 714**                      **FR-A- 2 139 424**

(72) Inventors:  
• **Smith, John Scott**  
**Proctorville, Ohio 45669 (US)**  
• **Hillis, LaDonna Sheree**  
**Orlando, Florida 32835 (US)**

• **PATENT ABSTRACTS OF JAPAN vol. 16, no. 490**  
**(C-994), 12 October 1992 & JP-A-04 180542**  
**(HITACHI METALS LTD.), 26 June 1992,**  
• **PATENT ABSTRACTS OF JAPAN vol. 95, no. 6 &**  
**JP-A-07 166298 (TOSHIBA CORP.), 27 June 1995,**

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**Description****Field of Invention**

5 **[0001]** This invention relates to low expansion alloys. In particular, this invention relates to low expansion iron alloys containing about 40.5 to about 48 weight percent nickel.

**Background of the Art and Problem**

10 **[0002]** The nickel-containing alloy tooling or fixtures used for curing graphite-epoxy composites must have very low thermal expansion coefficients. The low coefficients of thermal expansion are necessary to decrease stresses arising from thermal expansion mismatch that occurs during heating of resin-containing tooling to curing temperatures. The low-expansion alloy system of 36 to 42 weight percent nickel and balance of essentially iron has been commercially used for these tooling applications. These iron-base alloys are, however, inherently soft, difficult to weld in large sections, lack dimensional stability after thermomechanical processing, and are difficult to machine. For example, the knives used to remove graphite epoxy composites from the tooling routinely cut into and mar the tooling's surface. Another problem with these iron-base low expansion alloys is its general corrosion that accelerates during the curing of graphite epoxy tooling.

15 **[0003]** Structural graphite epoxy composites have CTEs that are highly variable with orientation. Typically graphite-epoxy composites have CTEs that range from  $1.8$  to  $9.0 \times 10^{-6}$  m/m/°C ( $1.0$  to  $5.0 \times 10^{-6}$  in/in/°F) depending upon orientation. The mean CTE of this composite is about  $5.4 \times 10^{-6}$  m/m/°C ( $3.0 \times 10^{-6}$  in/in/°F). The alloys used for this tooling have a lower CTE than the composite being cured. The low CTE tooling provides a constant and uniform compressive force during heating of the composites from room to curing temperatures. This compressive force reduces porosity, permits tight tolerances (e.g.,  $\pm 0.0051$  cm or  $\pm 0.002$  in or less), and provides high quality composite surfaces. To achieve these goals, CTE of the alloy must be  $4.9 \times 10^{-6}$  m/m/°C ( $2.7 \times 10^{-6}$  in/in/°F) or less.

20 **[0004]** It is an object of this invention to provide a low CTE alloy having good resistance to marring.

25 **[0005]** It is a further object of this invention to provide a low CTE alloy having good dimensional stability and strength after thermomechanical processing.

30 **[0006]** It is a further object of this invention to provide a low CTE alloy having relatively good weldability and corrosion resistance.

**[0007]** It is a further object of this invention to provide an alloy particularly suited for curing graphite-epoxy resins.

**Summary of the Invention**

35 **[0008]** The alloy of the invention provides a low coefficient of thermal expansion alloy having a CTE of about  $4.9 \times 10^{-6}$  m/m/°C or less at 204°C and a relatively high strength is defined in the accompanying claims. Alloys of the invention may be aged to a Rockwell C hardness of at least about 30.

**Description of the Drawing**

40 **[0009]**

Figure 1 is a three dimensional plot of coefficient of thermal expansion versus nickel and aluminum content at 400°F (204°C);

45 Figure 2 is a two dimensional graph of coefficient of thermal expansion versus nickel and aluminum content at 400°F (204°C); and

50 Figure 3 is a graph of coefficient of thermal expansion versus total niobium plus tantalum content at 204 °C (400°F),

**Description of Preferred Embodiment**

**[0010]** It has been discovered that niobium and titanium may be used in combination to provide an age hardenable alloy while maintaining a relatively low CTE. The alloys of the invention are readily aged to produce a hardness of at least 30 on the Rockwell "C" (RC) scale. For comparative purposes, NILO® alloy 36 typically only has a hardness of 71 on the Rockwell "B" (RB) scale (NILO is a trademark of the Inco family of companies). The alloys of the invention are uniquely characterized by a relatively low CTE in combination with excellent marring resistance.

**[0011]** The alloys of Table 1 were prepared for testing.

Table 1

HEAT	C	MIN	FE	S	SI	NI	CR	AL	TI	MG	CO	MO	NIB	TA	NIB + TA
1*	0.004	0.2	56.7	0.001	0.1	38.17	<0.1	0.33	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
2*	0.005	0.2	54.9	0.001	0.1	40.09	<0.1	0.12	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
3*	0.018	0.2	54.8	0.001	0.1	40.24	<0.1	0.30	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
4*	0.003	0.2	54.8	0.001	0.1	40.07	<0.1	0.32	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
5*	0.005	0.2	54.4	0.001	0.1	40.06	<0.1	0.51	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
6*	0.004	0.2	52.7	0.001	0.1	41.93	<0.1	0.32	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
7	0.009	0.2	50.8	0.001	0.1	43.97	<0.1	0.33	1.5	<0.1	<0.1	<0.1	2.9	0.001	2.9
8 <sup>(1)</sup>	0.011	0.31	Bal.	0.001	0.08	43.80	0.08	0.12	1.25	<0.1	0.01	0.01	3.21	0.004	3.21
9	<.01	0.2	Bal.	0.001	0.11	43.76	0.01	0.16	1.45	<0.1	0.001	<0.1	3.45	0.001	3.45
10	<.01	0.19	Bal.	0.001	0.12	43.77	0.03	0.11	1.48	<0.1	0.001	<0.1	2.93	0.001	2.93
11	0.026	0.31	50.9	<0.001	0.08	43.70	0.04	0.18	1.45	<0.1	0.28	<0.1	3.03	0.003	3.03
12	0.02	0.31	51.1	<0.001	0.08	43.77	0.03	0.08	0.95	<0.1	0.20	<0.1	3.38	<0.01	3.38
13	0.005	0.19	51.2	0.002	0.12	43.33	0.08	0.14	1.42	<0.1	<0.1	<0.1	3.46	0.001	3.46
A <sup>(2)</sup>	0.01	0.01	Bal.	0.009	<0.01	43.61	N/A	0.17	1.48	N/A <sup>(3)</sup>	N/A	N/A			3.94
B <sup>(4)</sup>	0.035	0.40	63.3	0.001	0.06	36.05	0.06	0.15	0.07	<0.1	<0.1	<0.1	0.03	0.001	0.03
C <sup>(4)</sup>	0.021	0.40	63.0	0.002	0.04	36.16	0.01	0.20	0.08	<0.1	<0.1	<0.1	<0.01	0.001	<0.01
D <sup>(4)</sup>	0.026	0.38	63.0	0.002	0.05	36.21	0.01	0.21	0.08	<0.1	<0.1	<0.1	<0.01	0.001	<0.01

Note: N/A = Not Analyzed

(1) Contains 0.007 P and 0.05 Cu

(2) Corresponds to alloy A of U.S. Pat. No. 3,514,284 (For comparative purposes only)

(3) None Added

(4) Comparative alloys B, C & D correspond to commercially available low CTE alloy 36

(5) Only analyzed in combination

\* Heats 1-6 are comparative alloys

[0012] The data of Table 1 are expressed in weight percent. For purpose of this specification, all alloy compositions are expressed in weight percent.

[0013] Table 2 below provides coefficient of thermal expansion and hardness data for alloys that were warm worked and aged at 1200°F (649°C) for 8 hours then air cooled.

TABLE 2

HEAT	CTE at 400°F (204°C)		Hardness (RC)
	in/in/°F x 10 <sup>-6</sup>	m/m/°C x 10 <sup>-6</sup>	
1	5.91	10.6	40
2	3.06	5.51	39
3	3.62	6.52	40
5	4.56	8.21	37
6	2.58	4.64	39
7	2.52	4.53	36

[0014] For comparison purposes, the CTE of graphite-epoxy composites at 360°F (182°C) is 3.1 x 10<sup>-6</sup> in/in/°F (5.6 x 10<sup>-6</sup> m/m/°C).

[0015] Figures 1 and 2 illustrate that CTE reaches a minimum above about 42.3% nickel. Advantageously, alloys of the invention contain sufficient nickel to provide a relatively low CTE of less than or equal to about 4.9 x 10<sup>-6</sup> m/m/°C (2.7 x 10<sup>-6</sup> in/in/°F) at 204°C (400°F). Most advantageously, the CTE is less than or equal to about (4.5 x 10<sup>-6</sup> m/m/°C (2.5 x 10<sup>-6</sup> in/in/°F) at 204°C (400°F). At 204°C (400°F), coefficient of thermal expansion may be estimated by the following:

$$\begin{aligned} \text{CTE (m/m/°C)} &= 441.52 \times 10^{-6} - 20.27 \times 10^{-6} (\text{Ni}) \\ &+ 0.23 \times 10^{-6} (\text{Ni}^2) + 6.79 \times 10^{-6} (\text{Al}) \end{aligned}$$

$$\begin{aligned} \text{CTE (in/in/°F)} &= 245.29 \times 10^{-6} - 11.26 \times 10^{-6} (\text{Ni}) \\ &+ 0.13 \times 10^{-6} (\text{Ni}^2) + 3.77 \times 10^{-6} (\text{Al}) \end{aligned}$$

[0016] Figure 3 illustrates that total niobium and tantalum must be limited to about 3.7 weight percent to maintain a CTE less than 4.9 x 10<sup>-6</sup> m/m/°C. At total niobium plus tantalum concentrations above about 3.5 weight percent, the 204°C (400°F) CTE of the alloy dramatically increases.

[0017] Most advantageously, tantalum is maintained at concentrations below about 0.25 weight percent. Tantalum concentrations above about 0.25 weight percent are believed to be detrimental to weldability and phase segregation. Alloys containing less than 0.25 weight percent tantalum may be readily formed into large sections free of both macro- and micro-segregation. Furthermore, an optional addition of at least about 0.15 weight percent manganese facilitates hot working of the alloy. In addition, boron may optionally be added to the alloy in quantities up to about 0.01 weight percent.

[0018] Table 3 below illustrates that CTE increases dramatically with niobium plus tantalum compositions above 3.45 at temperatures between 142°C and 315°C.

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**TABLE 3**  
Age Hardenable Ni-Fe Alloys, wt%

Heat	Coefficient of Thermal Expansion											Nb + Ta (wt%)
	200°F (x10 <sup>-6</sup> /°F)	142°C (x10 <sup>-6</sup> /°C)	400°F (x10 <sup>-6</sup> /°F)	204°C (x10 <sup>-6</sup> /°C)	500°F (x10 <sup>-6</sup> /°F)	260°C (x10 <sup>-6</sup> /°C)	600°F (x10 <sup>-6</sup> /°F)	315°C (x10 <sup>-6</sup> /°C)	800°F (x10 <sup>-6</sup> /°F)	427°C (x10 <sup>-6</sup> /°C)		
9	2.17	3.91	2.33	4.19	2.56	4.61	3.28	5.90	4.6	8.28		3.45
10	2.17	3.91	2.34	4.21	2.53	4.55	NT	NT	NT	NT		2.93
A	2.9	5.22	2.8	5.04	3.1	5.58	3.7	6.66	4.8	8.64		3.94

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**[0019]** Table 4 below provides hardness of the alloys in the Rockwell "B" scale for various annealing conditions.

TABLE 4

ANNEAL		HEAT					
(°F)/(hr)	(°C)/(hr)	1	2	3	5	6	7
1600/1	871/1	91	88	86	90	88	85
1650/1	915/1	89	86	86	96	84	82
1700/1	926/1	86	85	85	84	84	84
1750/1	954/1	84	82	82	85	82	82
1800/1	982/1	84	83	83	84	83	83
1850/1	1010/1	82	82	82	82	84	80
1900/1	1038/1	82	82	82	82	81	80
1950/1	1066/1	82	81	81	82	80	79
AR	AR	94	95	95	97	95	96

AR = As warm rolled

**[0020]** Table 5 below provides hardness in the Rockwell "C" scale for alloys treated with various isothermal aging heat treatments directly after warm working the alloys.

TABLE 5

AGE		HEAT					
(°F)/(hr)	(°C)/(hr)	1	2	3	5	6	7
1150/4	621/4	36	34	35	35	35	32
1150/8	621/8	39	38	35	37	36	36
1200/4	649/4	36	38	34	38	37	36
1200/8	649/8	38	41	38	41	40	38
1250/4	677/4	34	39	37	40	37	35
1250/8	677/8	38	37	37	39	35	37
1300/4	704/4	35	34	36	37	35	35
1300/8	704/8	35	35	35	38	35	37
1350/4	732/4	34	31	31	30	33	32
1350/8	732/8	31	26	29	33	29	30
1400/4	760/4	28	25	29	31	31	28
1450/4	788/4	23	21	24	25	24	25
1500/4	815/4	19	18	17	18	17	18

**[0021]** Table 6 below provides hardness data for annealed and aged alloys of the invention. The alloy of Table 6 were all annealed at 1700°F (927°C) prior to aging.

TABLE 6

HEAT	AGING TEMPERATURE / TIME							
	1150/8 (°F)/(hr)	621/8 (°C)/(hr)	1200/8 (°F)/(hr)	649/8 (°C)/(hr)	1250/4 (°F)/(hr)	677/4 (°C)/ (hr)	1250/8 (°F)/(hr)	677/8 (°C)/ (hr)
1	31		35		32		35	

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TABLE 6 (continued)

HEAT	AGING TEMPERATURE / TIME							
	1150/8 (°F)/(hr)	621/8 (°C)/(hr)	1200/8 (°F)/(hr)	649/8 (°C)/(hr)	1250/4 (°F)/(hr)	677/4 (°C)/ (hr)	1250/8 (°F)/(hr)	677/8 (°C)/ (hr)
2	29		35		32		37	
3	29		34		33		35	
5	34		33		35		36	
6	30		36		34		36	
7	28		32		32		33	

[0022] Tables 4-6 illustrate that the alloys of the invention may be readily age hardened to hardness levels at least as high as about 30 on the Rockwell C scale. Most advantageously, alloys are aged to a hardness of at least about 35 on the Rockwell C scale. Advantageously, the alloys are aged at a temperature between 1000 and 1400°F (538 and 760°C). Most advantageously, alloys are aged at a temperature between about 1100 and 1300°F (593 to 704°C) for optimum age hardening. It has been discovered that thermomechanical processing followed by an aging heat treatment further optimizes hardness of the alloy.

[0023] Table 7 below compares oxidation resistance of alloys of the invention to alloy 36 Ni-Fe after exposure to air at 371°C for 560 hours.

TABLE 7

HEAT	CHANGE IN WEIGHT GAIN, MILLIGRAMS/SQUARE CENTIMETER
8	0.082
9	0.136
11	0.133
12	0.133
13	0.150
B (Alloy 36)	0.248
C (Alloy 36)	0.220

Alloys 8 to 13 of Table 7 were annealed then aged as follows:

[0024] Anneal - 871°C for one hour, air cooled to room temperature.

[0025] Age - 677°C for four hours, furnace cooled at a rate of 55°C per hour to 621°C, 621°C for four hours and air cooled to room temperature.

[0026] Alloys B, C and D of Table 7 were all annealed as follows:

[0027] Anneal - 871°C for one hour and air cooled to room temperature -- these alloys are not age hardenable.

[0028] The data of Table 7 illustrate that alloy 36 oxidizes nearly twice as rapidly as alloys of the invention at typical curing temperature for graphite-epoxy composites. Although these alloys lack the oxidation resistance of chromium-containing alloys, the increased oxidation resistance of the invention significantly reduces tooling maintenance. For example, facing plates require less grinding, polishing or pickling to maintain a smooth metal surface.

[0029] Table 8 below demonstrates the dimensional stability of alloys of the invention in comparison to 36 Ni-Fe alloys.

TABLE 8

HEAT	CREEP STRENGTH, MPa
11	>690
12	>690
D (Alloy 36)	55

[0030] Heat D was annealed prior to testing. Heats 11 and 12 were annealed and aged as above. The age hardened alloys of the invention provide at least a ten-fold increase in creep resistance. This increase in creep resistance provides

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excellent dimensional stability that effectively resists deformation during curing. The alloys dimensional stability allows significant reductions of the size and amount of materials necessary to produce durable tooling.

**[0031]** The alloy of the invention is described by alloys having the composition of Table 9 below.

TABLE 9

	BROAD	INTERMEDIATE	NARROW	NOMINAL
Ni	42.3-48	42.3-46	42.3-45	43.5
Nb	2-3.7	2.5 - 3.6	3-3.5	3.3
Ti	0.75-2	0.9-1.9	1-1.8	1.4
Al	0-1	0.05-0.8	0.05-0.6	0.2
C		0-0.1	0-0.05	0.01
Mn		0-1	0-0.5	0.3
Si		0-1	0-0.5	-
Cu		0-1	0.5	-
Cr		0-1	0-0.5	-
Co		0-5	0-2	-
B		0-0.01	0-0.005	-
W, V		0-2	0-1	-
Ta			0-0.25	
Mg, Ca, Ce (Total)		0-0.1	0-0.05	-
Y, Rare Earths (Total)		0-0.5	0-0.1	-
S		0-0.1	0-0.05	-
P		0-0.1	0-0.05	-
N		0-0.1	0-0.05	-
Fe	Balance + Incidental Impurities	Balance + Incidental Impurities	Balance + Incidental Impurities	Balance + Incidental Impurities
Total Nb + Ta	≤ 3.7	≤ 3.6	≤3.5	3.3

**[0032]** The alloy of the invention provides alloys having a coefficient of thermal expansion of  $2.7 \times 10^{-6}$  in/in/°F ( $5.5 \times 10^{-6}$  m/m/°C) or less with a minimum hardness of RC 30. With a hardness above RC 30, composite tooling alloys provide excellent resistance to scratching and marring. In addition, age hardening increases the yield strength of the alloy and machinability of the alloy. The alloy has tested to be excellent with the drop weight and bend tests. The alloy may be readily welded with NILO® filler metals 36 and 42. Finally, the alloys of the invention provide improved oxidation resistance and dimensional stability over conventional iron-nickel low coefficient of thermal expansion alloys.

**[0033]** The alloys of the invention provides an especially useful material for tooling that are used to fabricate graphite-epoxy composites or other low CTE composites under compression. In addition, the alloys of the invention are expected to be useful for high strength electronic strips, age hardenable lead frames and mask alloys for tubes.

### Claims

1. A high strength low coefficient of thermal expansion alloy having a CTE of  $4.9 \times 10^{-6}$ m/m/°C or less at 204°C, consisting of, by weight percent, 42.3 to 48 nickel, 2 to 3.7 niobium, 0.75 to 2 titanium, 3.7 or less total niobium plus tantalum, 0 to 1 aluminium, 0 to 0.1 carbon, 0 to 1 manganese, 0 to 1 silicon, 0 to 1 copper, 0 to 1 chromium, 0 to 5 cobalt, 0 to 0.01 boron, 0 to 2 tungsten, 0 to 2 vanadium, 0 to 0.1 total magnesium, calcium and cerium, 0 to 0.5 total yttrium and rare earths, 0 to 0.1 sulfur, 0 to 0.1 phosphorous, 0 to 0.1 nitrogen, and balance iron and incidental impurities.

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2. The alloy of claim 1 comprising 42.3 to 46 nickel, 2.5 to 3.6 niobium, 0.9 to 1.9 titanium and 0.05 to 0.8 aluminium.
3. The alloy of claim 1 having a hardness of at least 30 on the Rockwell C scale.
- 5 4. A high strength low coefficient of thermal expansion alloy having a CTE of  $4.9 \times 10^{-6} \text{m/m/}^\circ\text{C}$  or less at  $204^\circ\text{C}$ , consisting of, by weight percent, 42.3 to 46 nickel, 2.5 to 3.6 niobium, 0.9 to 1.9 titanium, 0.05 to 0.8 aluminium, 0 to 0.1 carbon, 0 to 1 manganese, 0 to 1 silicon, 0 to 1 copper, 0 to 5 cobalt, 0 to 0.01 boron, 0 to 2 tungsten, 0 to 2 vanadium, 0 to 0.5 total yttrium and rare earths, 0 to 0.1 sulfur, 0 to 0.1 phosphorous, 0 to 0.1 nitrogen, 3.6 or less total niobium plus tantalum and balance iron and incidental impurities.
- 10 5. The alloy of claim 4 comprising 42.3 to 45 nickel.
6. The alloy of claim 4 comprising 3 to 3.5 niobium, 1 to 1.8 titanium and 0.05 to 0.6 aluminium.
- 15 7. The alloy of claim 4 comprising 0 to 0.05 carbon, 0 to 0.5 manganese, 0 to 0.5 silicon, 0 to 0.5 copper, 0 to 0.5 chromium, 0 to 2 cobalt, 0 to 0.005 boron, 0 to 1 tungsten, 0 to 1 vanadium, 0 to 0.05 total magnesium, calcium and cerium, 0 to 0.1 total yttrium and rare earths, 0 to 0.5 sulfur, 0 to 0.05 phosphorous, less than 0.25 tantalum and 0 to 0.05 nitrogen.
- 20 8. The alloy of claim 4 having a hardness of at least 30 on the Rockwell C scale.
9. A high strength low coefficient of thermal expansion alloy having a CTE of  $4.9 \times 10^{-6} \text{m/m/}^\circ\text{C}$  or less at  $204^\circ\text{C}$ , consisting of, by weight percent 42.3 to 45 nickel, 3 to 3.5 niobium, 1 to 1.8 titanium, 0.05 to 0.6 aluminium, 0 to 0.05 carbon, 0 to 0.5 manganese, 0 to 0.5 silicon, 0 to 0.5 copper, 0 to 2 cobalt, 0 to 0.005 boron, 0 to 1 tungsten,
- 25 0 to 1 vanadium, 0 to 0.1 total yttrium and rare earths, 0 to 0.05 sulfur, 0 to 0.05 phosphorous, 0 to 0.05 nitrogen, 3.5 or less total niobium plus tantalum, 0 to 0.25 tantalum and balance iron and incidental impurities.
10. The alloy of claim 9 having a hardness of at least 30 on the Rockwell C scale.
- 30 11. Use of an alloy as defined in any one of claims 1 to 10 for the manufacture of tooling for the fabrication of low CTE (coefficient of thermal expansion) composites, e.g. graphite-epoxy composites, or for the manufacture of electronic strips, age hardenable lead frames or mask alloys for tubes.

### 35 Patentansprüche

1. Hochfeste Legierung mit niedrigem Ausdehnungskoeffizienten von höchstens  $4,9 \times 10^{-6} \text{m/m/}^\circ\text{C}$  bei  $204^\circ\text{C}$ , die sich aus 42,3 bis 48 Gew.% Nickel, 2 bis 3,7 Gew.% Niob, 0,75 bis 2 Gew.% Titan, höchstens 3,7 Gew.% Gesamtgehalt an Niob plus Tantal, 0 bis 1 Gew.% Aluminium, 0 bis 0,1 Gew.% Kohlenstoff, 0 bis 1 Gew.% Mangan, 0 bis 1 Gew.% Silicium, 0 bis 1 Gew.% Kupfer, 0 bis 1 Gew.% Chrom, 0 bis 5 Gew.% Cobalt, 0 bis 0,01 Gew.% Bor, 0 bis 2 Gew.% Wolfram, 0 bis 2 Gew.% Vanadium, 0 bis 0,1 Gew.% Gesamtgehalt an Magnesium, Calcium und Cer, 0 bis 0,5 Gew.% Gesamtgehalt an Yttrium und seltenen Erden, 0 bis 0,1 Gew.% Schwefel, 0 bis 0,1 Gew.% Phosphor, 0 bis 0,1 Gew.% Stickstoff und als Restmaterial Eisen und geringfügigen Verunreinigungen zusammensetzt.
- 40 2. Legierung nach Anspruch 1, die 42,3 bis 40 Gew.% Nickel, 2,5 bis 3,6 Gew.% Niob, 0,9 bis 1,9 Gew.% Titan und 0,05 bis 0,8 Gew.% Aluminium aufweist.
3. Legierung nach Anspruch 1 mit einer Rockwellhärte C von mindestens 30.
- 50 4. Hochfeste Legierung mit niedrigem Ausdehnungskoeffizient von höchstens  $4,9 \times 10^{-6} \text{m/m/}^\circ\text{C}$  bei  $204^\circ\text{C}$ , die sich aus 42,3 bis 46 Gew.% Nickel, 2,5 bis 3,6 Gew.% Niob, 0,9 bis 1,9 Gew.% Titan, 0,05 bis 0,8 Gew.% Aluminium, 0 bis 0,1 Gew.% Kohlenstoff, 0 bis 1 Gew.% Mangan, 0 bis 1 Gew.% Silicium, 0 bis 1 Gew.% Kupfer, 0 bis 5 Gew.% Cobalt, 0 bis 0,01 Gew.% Bor, 0 bis 2 Gew.% Wolfram, 0 bis 2 Gew.% Vanadium, 0 bis 0,5 Gew.% Gesamtgehalt an Yttrium und seltenen Erden, 0 bis 0,1 Gew.% Schwefel, 0 bis 0,1 Gew.% Phosphor, 0 bis 0,1 Gew.% Stickstoff,
- 55 höchstens 3,6 Gew.% Gesamtgehalt an Niob plus Tantal und als Restmaterial Eisen und geringfügigen Verunreinigungen zusammensetzt.
5. Legierung nach Anspruch 4, die 42,3 bis 45 Gew.% Nickel aufweist.

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6. Legierung nach Anspruch 4, die 3 bis 3,5 Gew.% Niob, 1 bis 1,8 Gew.% Titan und 0,05 bis 0,6 Gew.% Aluminium aufweist.
- 5 7. Legierung nach Anspruch 4, die 0 bis 0,05 Gew.% Kohlenstoff, 0 bis 0,5 Gew.% Mangan, 0 bis 0,5 Gew.% Silicium, 0 bis 0,5 Gew.% Kupfer, 0 bis 0,5 Gew.% Chrom, 0 bis 2 Gew.% Cobalt, 0 bis 0,005 Gew.% Bor, 0 bis 1 Gew.% Wolfram, 0 bis 1 Gew.% Vanadium, 0 bis 0,05 Gew.% Gesamtgehalt an Magnesium, Calcium und Cer, 0 bis 0,1 Gew.% Gesamtgehalt an Yttrium und seltenen Erden, 0 bis 0,5 Gew.% Schwefel, 0 bis 0,05 Gew.% Phosphor, höchstens 0,25 Gew.% Tantal and 0 bis 0,05 Gew.% Stickstoff aufweist.
- 10 8. Legierung nach Anspruch 4 mit einer Rockwellhärte C von mindestens 30.
9. Hochfeste Legierung mit niedrigem Ausdehnungskoeffizient von höchstens  $4,9 \times 10^{-6}$  m/m/°C bei 204°C, die sich aus 42,3 bis 45 Gew.% Nickel, 3 bis 3,5 Gew.% Niob, 1 bis 1,8 Gew.% Titan, 0,05 bis 0,6 Gew.% Aluminium, 0 bis 0,05 Gew.% Kohlenstoff, 0 bis 0,5 Gew.% Mangan, 0 bis 0,5 Gew.% Silicium, 0 bis 0,5 Gew.% Kupfer, 0 bis 2 Gew.% Cobalt, 0 bis 0,005 Gew.% Bor, 0 bis 1 Gew.% Wolfram, 0 bis 1 Gew.% Vanadium, 0 bis 0,1 Gew.% Gesamtgehalt an Yttrium und seltenen Erden, 0 bis 0,05 Gew.% Schwefel, 0 bis 0,05 Gew.% Phosphor, 0 bis 0,05 Gew.% Stickstoff, höchstens 3,5 Gew.% Gesamtgehalt an Niob plus Tantal, 0 bis 0,25 Gew.% Tantal und als Restmaterial Eisen und geringfügigen Verunreinigungen zusammensetzt.
- 15 10. Legierung nach Anspruch 9 mit einer Rockwellhärte C von mindestens 30.
- 20 11. Verwendung nach einem der vorangehenden Ansprüche 1 bis 10 zur Herstellung von Formungswerkzeugen für Verbundwerkstoffe mit niedrigem Ausdehnungskoeffizienten, zum Beispiel Graphit-Epoxid-Verbundwerkstoffe, oder zur Herstellung von Elektronikstreifen, alterungshärtbaren Leiterrahmen oder Maskenlegierungen für Röhren.
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### Revendications

- 30 1. Un alliage à haute résistance et à faible coefficient de dilatation thermique, CTE, de  $4,9 \times 10^{-6}$  m/m.°C ou moins à 204°C, constitué, exprimé en pourcentage en poids, de 42,3 à 48 % de nickel, 2 à 3,7 % de niobium, 0,75 à 2 % de titane, 3,7 ou moins pour le total du niobium plus le tantale, 0 à 1 % d'aluminium, 0 à 0,1 % de carbone, 0 à 1 de manganèse, 0 à 1 % de silicium, 0 à 1 % de cuivre, 0 à 1 % de chrome, 0 à 5 % de cobalt, 0 à 0,01 % de bore, 0 à 2 % de tungstène, 0 à 2 % de vanadium, 0 à 0,1 % du total du magnésium, calcium et cérium, 0 à 0,5 % du total de l'yttrium et de terres rares, de 0 à 0,1 % de soufre, 0 à 0,1 % de phosphore, 0 à 0,1 % d'azote et le reste étant du fer et d'éventuelles impuretés.
- 35 2. L'alliage selon la revendication 1, comprenant de 42,3 à 46 % en poids de nickel, 2,5 à 3,6 % de niobium, 0,9 à 1,9 de titane et 0,05 à 0,8 % d'aluminium.
- 40 3. L'alliage selon la revendication 1 ayant une dureté d'au moins 30 sur l'échelle Rockwell C.
4. Un alliage à haute résistance et à faible coefficient de dilatation thermique, CTE, de  $4,9 \times 10^{-6}$  m/m.°C ou moins à 204°C, constitué, exprimé en pourcentage en poids, de 42,3 à 46 % de nickel, 2 à 3,6 % de niobium, 0,9 à 1,9 % de titane, 0,05 à 0,8 % d'aluminium, 0 à 0,1 % de carbone, 0 à 1 % de manganèse, 0 à 1 % de silicium, 0 à 1 % de cuivre, 0 à 5 % de cobalt, 0 à 0,01 % de bore, 0 à 2 % de tungstène, 0 à 2 % de vanadium, 0 à 0,5 % du total de l'yttrium et de terres rares, 0 à 0,1 % de soufre, 0 à 0,1 % de phosphore, 0 à 0,1 % d'azote, 3,6 % ou moins du total du niobium plus le tantale, et le reste étant du fer et d'éventuelles impuretés.
- 45 5. L'alliage selon la revendication 4, comprenant de 42,3 à 45 % en poids de nickel.
- 50 6. L'alliage selon la revendication 4, comprenant de 3 à 3,5 % en poids de niobium, 1 à 1,8 % en poids de titane et 0,05 à 0,6 % en poids d'aluminium.
- 55 7. L'alliage selon la revendication 4, comprenant de 0 à 0,05 % en poids de carbone, 0 à 0,5 % de manganèse, 0 à 0,5 % de silicium, 0 à 0,5 % de cuivre, 0 à 0,5 % de chrome, 0 à 2 % de cobalt, 0 à 0,005 de bore, 0 à 1 % de tungstène, 0 à 1 % de vanadium, 0 à 0,05 % du total du magnésium, calcium et cérium, 0 à 0,01 % total de l'yttrium et des terres rares, 0 à 0,5 % de soufre, 0 à 0,05 % de phosphore, moins de 0,25 % en poids de tantale et de 0 à 0,05 % en poids d'azote.

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8. L'alliage selon la revendication 4, ayant une dureté d'au moins 30 sur l'échelle Rockwell C.

5 9. Un alliage à haute résistance et à faible coefficient de dilatation thermique, CTE, de  $4,9 \times 10^{-6} \text{m/m} \cdot ^\circ\text{C}$  ou moins à  $204^\circ\text{C}$ , constitué, exprimé en pourcentage en poids, de 42,3 à 45 % de nickel, 3 à 3,5 % de niobium, 1 à 1,8 % de titane, 0 à 0,6 % d'aluminium, 0 à 0,05 % de carbone, 0 à 0,5 de manganèse, 0 à 0,5 % de silicium, 0 à 0,5 % de cuivre, 0 à 2 % de cobalt, 0 à 0,005 % de bore, 0 à 1 % de tungstène, 0 à 1 % de vanadium, 0 à 0,1 % du total de l'yttrium et de terres rares, 0 à 0,05 % de soufre, 0 à 0,05 % de phosphore, 0 à 0,05 % d'azote, 3,5 % ou moins du total du niobium plus le tantale, 0 à 0,25 % de tantale et le reste étant du fer et d'éventuelles impuretés.

10 10. L'alliage selon la revendication 9 ayant une dureté d'au moins 30 sur l'échelle Rockwell C.

15 11. Utilisation d'un alliage, telle que définie sur l'une quelconque des revendications 1 à 10 pour la fabrication d'outillage destiné à la fabrication, à faible coefficient de dilatation thermique CTE, de composites, graphite-epoxy, ou pour la fabrication de bandes électroniques, de châssis conducteurs durcissables par le vieillissement, ou bien d'alliages de masques pour des tubes.

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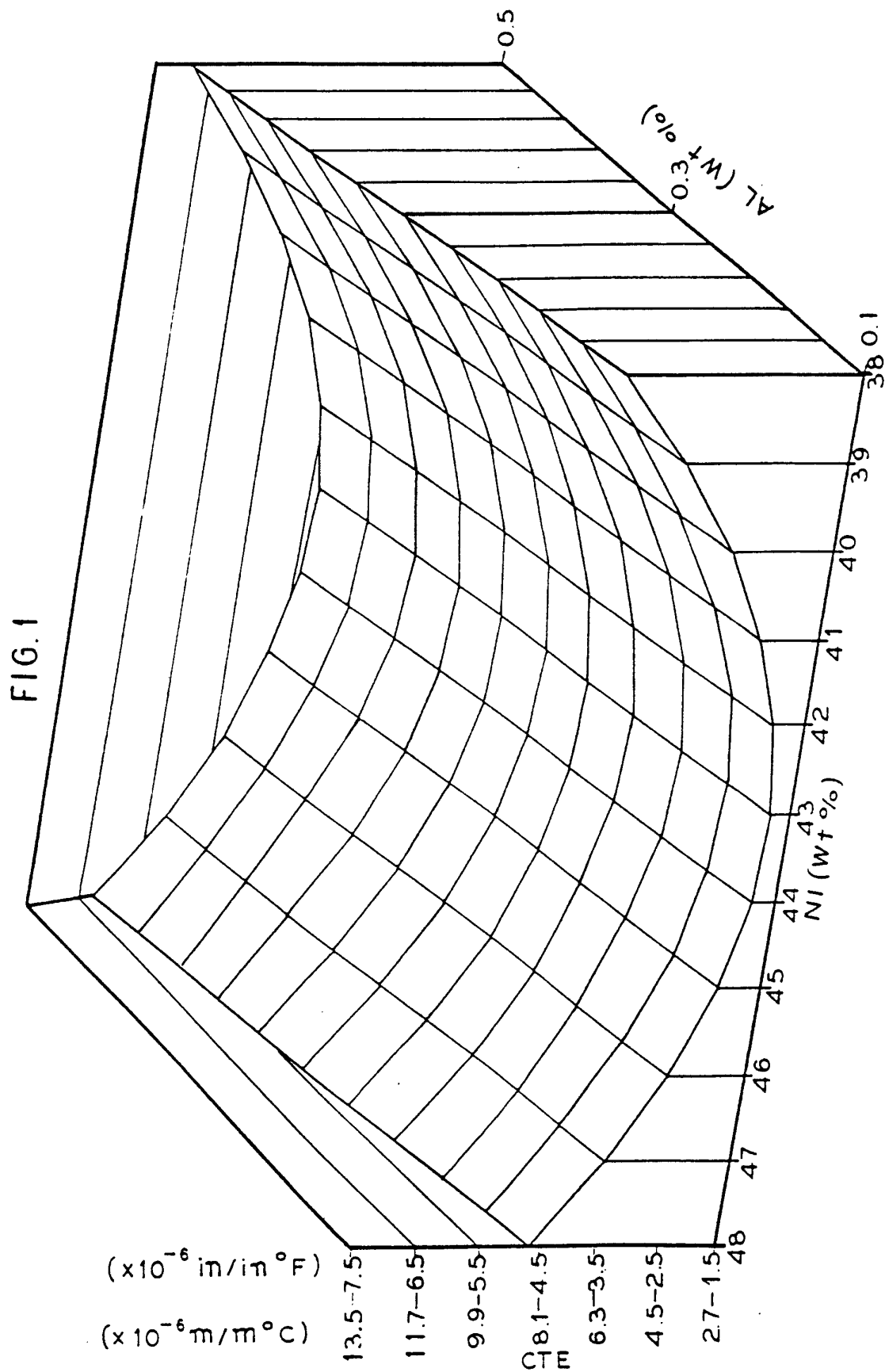


FIG. 2

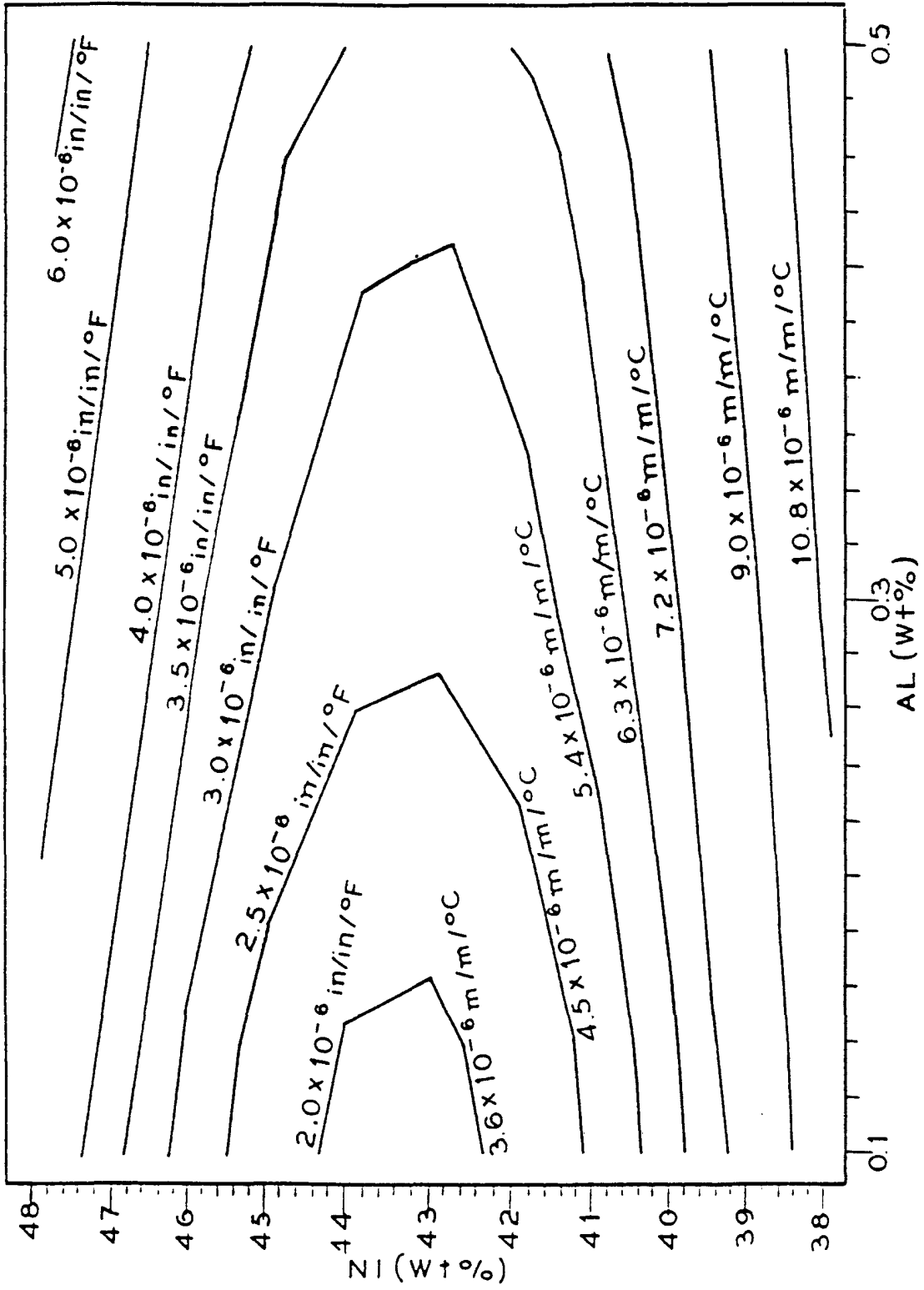


FIG. 3

