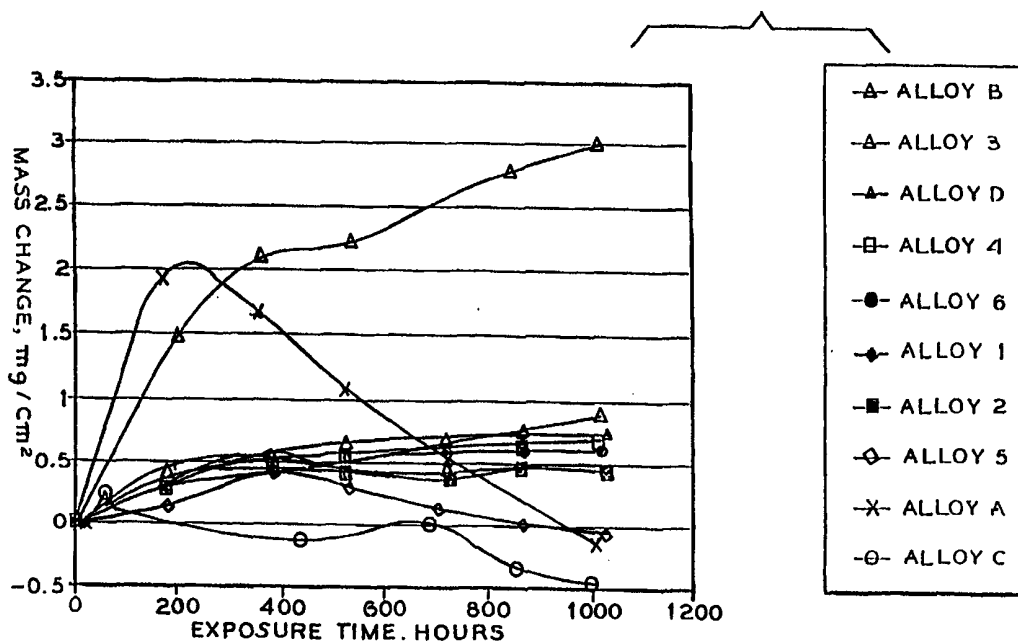




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<p>(21) International Application Number: PCT/US99/19268 (22) International Filing Date: 23 August 1999 (23.08.99) (30) Priority Data: 09/207,240 8 December 1998 (08.12.98) US (71) Applicant: INCO ALLOYS INTERNATIONAL, INC. [US/US]; 3200 Riverside Drive, Huntington, WV 25720 (US). (72) Inventors: SMITH, Gaylord, Darrell; 120 Stamford Park Drive, Huntington, WV 25705 (US). FARR, Norman; 5 Chartwell Road, Hereford (GB). BAKER, Brian, Allen; 63 Private Road #603, Kitts Hill, OH 45645 (US). (74) Agents: BYRNE, Richard, L. et al.; Webb Ziesenheim Logsdon Orkin &amp; Hanson, P.C., 700 Koppers Building, 436 Seventh Avenue, Pittsburgh, PA 15219-1818 (US).</p>		<p>(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: ALLOYS FOR HIGH TEMPERATURE SERVICE IN AGGRESSIVE ENVIRONMENTS



(57) Abstract

An alloy resistant to carburization and high temperature oxidation resistance. The alloy consists essentially of, by weight percent, 27 to 35 chromium, 0 to 7 iron, about 3 to 4.4 aluminum, 0 to 0.4 titanium, 0.2 to 3 niobium, 0.12 to 0.5 carbon, 0 to 0.05 zirconium, 0.002 to 0.05 total cerium and yttrium, 0 to 1 manganese, 0 to 1 silicon, 0 to 0.5 calcium plus magnesium, 0 to 0.1 boron and balance nickel plus incidental impurities.

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**ALLOYS FOR HIGH TEMPERATURE SERVICE**  
**IN AGGRESSIVE ENVIRONMENTS**

**FIELD OF THE INVENTION**

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This invention relates specifically to nickel-chromium alloys having resistance to carburization and high temperature oxidation.

**BACKGROUND OF THE INVENTION**

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Nickel-chromium alloys are known for their capability to afford various degrees of resistance to a myriad of both low temperature and high temperature corrosion environments. For this reason, these alloys are employed in a wide range of industrial and aerospace applications. Of particular utility is the use of nickel-chromium alloys in the thermal processing, chemical and petrochemical applications where high temperatures are essential for technical reasons and economy of operation. Such examples include furnace rollers in annealing furnaces and ceramic kilns, radiant tubes in heating furnaces, conveyor belts in sintering furnaces, muffles and retorts in furnaces and chemical process equipment, tubes for oxidizing titanium compounds to titanium dioxide paint pigment, thermocouple

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protection tubes and hardware for glass manufacture and glass verification of nuclear wastes.

By reason of their strength and corrosion resistance in such environments, alloys such as INCONEL<sup>®</sup> alloys 601, 617 and 690 (INCONEL is a trademark of Inco Alloys International, Inc.) and alloy 602CA are typically used in applications subject to high temperature oxidation. However, the trend towards increasing temperatures, more aggressive environments and the need for longer service life has stretched these alloys beyond their capabilities.

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It is object of this invention to provide an alloy having an improved combination of strength and general corrosion resistance for longer service lives than of existing commercial alloys.

15

It is a further object of this invention to provide an alloy with excellent carburization and oxidation resistance at elevated temperatures.

It is a further object of this invention to provide an alloy with excellent carburization and oxidation resistance under isothermal and cyclic conditions.

20

### SUMMARY OF THE INVENTION

An alloy resistant to carburization and high temperature oxidation resistance. The alloy consists essentially of, by weight percent, 27 to 35 chromium, 0 to 7 iron, 3 to 4.4 aluminum, 0 to 0.4 titanium, 0.2 to 3 niobium, 0.12 to 0.5 carbon, 0 to 0.05 zirconium, 0.002 to 0.05 total cerium and yttrium, 0 to 1 manganese, 0 to 1 silicon, 0 to 0.5 calcium plus magnesium, 0 to 0.1 boron and balance nickel plus incidental impurities.

25

### DESCRIPTION OF THE DRAWING

Figure 1 compares mass change of the alloys in air – 5% H<sub>2</sub>O at a temperature of 1000°C;

30

Figure 2 compares mass change in air for the alloys cycled 15 minutes in and 5 minutes out at a temperature of 1100°C;

Figure 3 compares mass change of the alloys in H<sub>2</sub> - 1% CH<sub>4</sub> at a temperature of 1000°C;

5 Figure 4 compares mass change of the alloys in H<sub>2</sub> - 5.5% CH<sub>4</sub> - 4.5% CO<sub>2</sub> at a temperature of 1000°C; and

Figure 5 compares mass change of the alloys in H<sub>2</sub> - 5.5% CH<sub>4</sub> - 4.5% CO<sub>2</sub> at a temperature of 1100°C.

10

### DESCRIPTION OF PREFERRED EMBODIMENT

It has been discovered that the range of nickel-chromium-aluminum alloys, by virtue of their protective scales and their intrinsic strength, can meet stringent material requirements beyond those of currently available commercial alloys. Specifically, an alloy  
15 range containing controlled percentages of nickel, chromium, aluminum, columbium, iron, manganese, silicon, zirconium, magnesium, boron and cerium plus yttrium provides an excellent combination of carburization and oxidation resistance at elevated temperatures, e.g., 982°-1093°C (1800°-2000°F) under isothermal and cyclic conditions. Furthermore, this alloy has good stress rupture and creep strength at such high temperatures, plus  
20 satisfactory tensile strength and ductility. In this case, high temperature stress rupture strength is defined as greater than about 100 hours or more at a stress of 13.8 MPa (2 ksi) at 982°C (1800°F). Furthermore, this specification describes all compositions in weight percent, unless specifically expressed otherwise.

25 The alloy achieves longer service life by providing an "alloy reservoir" of chromium plus aluminum in an austenitic nickel matrix to maintain a highly protective scale under severe high temperature, corrosive conditions. This alloy reservoir restores protection when spallation or excessive rates of scale formation occurs. Scale adhesion under the most cyclic of conditions is ensured by the addition of at least 20 ppm of cerium plus  
30 yttrium and optionally zirconium. Intermediate strength is achieved through precipitation of gamma prime (Ni<sub>3</sub>Al) as defined by 15 to 20 mole percent of Ni<sub>3</sub>Al at 800°C (1472°F) in this range of alloys. Furthermore, high temperature strength is provided through formation of 2 to 8 mole percent Cr<sub>7</sub>C<sub>3</sub> plus Cr<sub>23</sub>C<sub>6</sub>. High temperature strength and

fabricability are further enhanced by the addition of controlled amounts of zirconium plus boron to strengthen grain boundaries.

In carrying this range of alloys into practice, it is preferred that the chromium content not exceed 35% in order not to detract from high temperature tensile ductility and stress rupture strength. The chromium content can extend down to about 27% with only a minor loss of corrosion resistance. Increasing minimum chromium to 29 or 30% maximizes corrosion resistance. Furthermore, chromium plays a dual role in this alloy range by contributing to the protective nature of the  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  scale and by forming  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_{6,10}$  strengthen the alloy at high temperatures. For these reasons, chromium should be present in the alloy in the optimal range of 29 to 34%.

Aluminum markedly improves carburization and oxidation resistance. It is essential that it be present in amounts of at least 3%. High levels of aluminum detract from toughness after exposure at intermediate temperatures and must to be limited to 4.4% to ensure adequate toughness during service life. Furthermore, aluminum levels above 4.4% adversely impact hot workability. As in the case with chromium, aluminum percentages below 3% fail to develop the protective scale required for long service life. This is exemplified by the oxidation data presented at 1100°C (2000°F) for the commercial alloys cited in Figure 1.

The combination of chromium and aluminum is critical for formation of the stable, highly protective  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  scale. A  $\text{Cr}_2\text{O}_3$  scale, even at 30% chromium in the alloy, does not sufficiently protect the alloy at high temperatures due to vaporization of the scale as  $\text{CrO}_3$  and subspecies of  $\text{Cr}_2\text{O}_3$  – alloy C in Figure 1 exemplifies this. When the alloy contains less than about 3% aluminum, the protective scale fails to prevent internal oxidation of the aluminum – alloy B in Figure 1 exemplifies this. Internal oxidation of aluminum over a wide range of partial pressures of oxygen, carbon and temperature can be avoided by controlling the combination of chromium and aluminum to 30 to 35% chromium and 3 to 4% aluminum. This is also important in ensuring self-healing in the event of mechanical damage to the scale.

Iron may be present in the range of about up to 7%. It is postulated that iron

segregates at the grain boundaries such that carbide morphology is adversely affected and corrosion resistance is impaired. Most advantageously, iron should not exceed 5.5%. But it does lend to the use of ferrochromium. Thus, there is an economic benefit for allowing for the presence of iron.

5

Niobium, in the amount of 0.2 to 3%, contributes to the formation of a stable (Ti, Nb) (C, N) which aids high temperature strength and in small concentrations has been found to enhance oxidation resistance. Excess niobium however can contribute to phase instability and over-aging. Titanium, in the range of 0 to 0.4% acts similarly.

10 Unfortunately, titanium levels above 0.4% decrease the alloy's mechanical properties.

Optionally, zirconium between 0.001 and 0.5% enhances scale adhesion and retards cation diffusion through the protective scale for longer service life. Furthermore, this element acts as a carbonitride former.

15

Carbon at 0.12% is essential in achieving minimum stress rupture life, while carbon contents in excess of 0.5% markedly reduce stress rupture life and lead to intermediate temperature reduction in ductility.

20 Boron is useful as a deoxidizer up to about 0.1% and can be utilized to advantage for hot workability.

Cerium plus yttrium between 20 and 500 ppm play a significant role in ensuring scale adhesion under cyclic conditions. Most advantageously, total cerium and yttrium is at least 40 ppm for excellent scale adhesion. Furthermore, limiting total cerium and yttrium to 400 ppm improves fabricability of the alloy. Optionally, it is possible to add cerium in the form of a misch metal. This introduces lanthanum and other rare earths as incidental impurities. These rare earths can have a small beneficial effect on oxidation resistance.

25  
30

Manganese, used as a sulfur scavenger, is detrimental to high temperature oxidation resistance if present in amounts exceeding about 1%. Silicon in excess of 1% can lead to embrittling grain boundary phases, while minor amounts can lead to improved

oxidation and carburization resistance. Silicon should be held to less than 0.5% however, in order to achieve maximum grain boundary strength.

Nickel and incidental impurities form the balance of the alloy. Advantageously, 52 to 67% nickel form a stable authentic matrix. Maintaining nickel at a minimum of 55% and chromium plus iron at less than 39% minimizes the formation of alpha-chromium to less than 8 mole percent at 800°C (1472°F), thus aiding maintenance of intermediate temperature tensile ductility.

Phosphorus and sulfur should be maintained at the lowest levels consistent with good melting practice. Calcium and magnesium (in addition to cerium) in quantities up to 0.5% serve to tie up sulfur. Most advantageously the alloy contains at least 0.002% calcium plus magnesium. Excess amounts of alkaline earth metal tend to decrease the alloy's strength properties.

Table 1 below summarizes "about" the advantageous ranges of the invention.

**TABLE 1**

	Broad	Intermediate	Narrow
Ni	Bal.*	52 - 67*	55 - 65*
Cr	27 - 35	28 - 34	29 - 34
Fe	0 - 7	0.5 - 6	1 - 5.5
Al	3 - 4.4	3 - 4.2	3 - 4
Ti	0 - 0.4	0.05 - 0.3	0.1 - 0.3
Nb	0.2 - 3	0.3 - 2.5	0.5 - 2
C	0.12 - 0.5	0.12 - 0.4	0.12 - 0.3
Zr	0 - 0.5	0.0002 - 0.3	0.001 - 0.2
Y	**	0.001 - 0.045**	0.0025 - 0.0250***
Ce	**	0.001 - 0.045**	0.0025 - 0.0250***
Mn	0 - 1	0 - 0.7	0 - 0.5
Si	0 - 1	0 - 0.7	0 - 0.5
Ca + Mg	0 - 0.5	0.001 - 0.1	0.002 - 0.05
B	0 - 0.1	0 - 0.05	0 - 0.01

\* Plus Incidental Impurities  
 \*\* Ce + Y = 0.002 to 0.05%  
 \*\*\* Ce + Y = 0.005 to 0.04%



In respect to fabrication, vacuum melting, optionally followed by either electroslag or vacuum arc remelting, is recommended. Because of the composition of the alloy range of this patent application, a dual solution anneal is recommended to maximize solution of the elements -- a single high temperature anneal may only serve to concentrate the  
5 aluminum as a low melting, brittle phase in the grain boundaries. Whereas, an initial anneal in the range of 1100°C (2012°F) to 1150°C (2102°F) serves to diffuse the aluminum away from the grain boundary after which a higher temperature anneal can be used to maximize solution of all elements. Times for this dual step anneal can vary from 1 to 48 hours depending on ingot size and composition.

10

Following solution annealing hot working can be conducted over the range of 982°C (1800°F) to 1150°C (2102°F). Intermediate and final anneals should be performed within the temperature range of about 1038°C (1900°F) to 1204°C (2200°F) depending on desired grain size. Times at temperature of 30 minutes to one hour usually are adequate,  
15 but longer times are easily accommodated.

The alloy range is not intended to be used in the intermediate temperature range where age hardening can occur. However, the alloy can be age hardened in the temperature range of 621 °C (1150°F) to 816°C (1500°F). Conventional double aging treatments may  
20 also be utilized.

The following heats illustrate the benefit achieved with this alloy. A series of six 22.7 kg (50 lb) heats (Alloys 1 through 6) was prepared using vacuum melting. The compositions are given in Table 2. Alloys A through D are examples of commercial alloys  
25 601, 617, 690 and 602CA respectively to illustrate advantages of alloys 1 to 6.

TABLE 2

Nominal Composition															
HEAT	C	Mn	Fe	Si	Ni	Cr	Al	Ti	Mg	Cb	Zr	N	Ce	Y	Other
1	0.10	0.09	5.0	0.18	60.0	30.2	3.21	0.16	0.019	0.977	0.001	0.034	0.005	0.001	
2	0.15	0.10	4.4	0.11	60.3	30.4	3.26	0.15	0.017	0.972	--	0.034	0.010	0.002	
3	0.23	0.10	4.5	0.11	60.0	30.6	3.23	0.15	0.014	0.978	--	0.030	0.008	0.002	
4	0.16	0.10	4.5	0.12	60.1	30.5	3.27	0.15	0.012	0.970	0.089	0.030	0.011	0.002	
5	0.15	0.10	4.5	0.11	60.2	30.5	3.17	0.14	0.013	0.964	0.006	0.036	0.006	0.003	
6	0.23	0.09	4.3	0.12	61.2	30.5	3.17	0.15	0.010	0.046	0.089	0.022	0.001	0.019	
A	0.04	0.2	14	0.2	61.0	23.0	1.4	0.4	--	--	--	0.03	--	--	
B	0.09	--	1.0	0.1	52.0	22.0	1.2	0.4	--	--	--	--	--	--	9.5Mo,12 .5Co
C	0.01	0.1	9.0	0.1	62.0	28.0	--	0.2	--	--	--	--	--	--	
D	0.19	0.10	9.9	0.12	61.9	25.0	2.38	0.17	0.012	--	0.078	0.023	--	0.05	

5 Alloys 1 through 6 were solution annealed 16 hours at 1150°C (2102°F) followed by 4 hours at 1200°C (2192°F) and then hot worked from a 1175°C (2150°F) furnace temperature. The 102 mm (4 in) square x length ingots were forged to 20.4 mm (0.8 in) diameter x length rod and given a final anneal at 1100°C (2012°F) for one hour followed by an air cool. Oxidation, carburization and cyclic oxidation pins [7.65 mm (0.3 in) diameter x 19.1 mm (0.75 in)] were machined and cleaned with acetone. The oxidation pins were exposed for 1000 hours at 1000°C (1832°F) in air plus 5% water vapor with periodic removal from the electrically heated mullite furnace to establish mass change as a function of time. The results are plotted graphically in Figure 1 along with results from some of the commercial alloys. Similarly, cyclic oxidation data are depicted in Figure 2 for alloys 1 to 6 as well as for several of the commercial alloys. The cyclic oxidation testing was conducted in laboratory air with a cycle of 15 minutes in the furnace followed by 5 minutes in air. The test ran for 1200 cycles.

Carburization resistance was established for atmospheres that included: H<sub>2</sub>-1% CH<sub>4</sub> at 1000°C (1832°F) and H<sub>2</sub>-5.5%CH<sub>4</sub> - 4.5%CO<sub>2</sub> at 1000°C (1832°F) and 1100°C (2012°F). Carburization results for alloys 1 to 6 and the commercial alloys are shown in Figures 3 through 5. Figure 3 shows alloys A and C having poor carburization at 1000°C with H<sub>2</sub>-1% CH<sub>4</sub>. Figure 4 illustrates alloy D having poor carburization resistance with H<sub>2</sub> - 5.5% CH<sub>4</sub> - 4.5% CO<sub>2</sub> at a temperature of 1000°C. Finally, Figure 5 demonstrates that alloys A and B have a poor carburization resistance in H<sub>2</sub>-5.5% CH<sub>4</sub> - 4.5% CO<sub>2</sub> at a temperature of 1100°C. In summary, Figures 1 to 5 illustrate that Alloy 1 to 6 have better

general corrosion resistance properties than commercial alloys A to D.

Standard tensile and stress rupture test specimens were machined from the annealed alloy rods. The room temperature tensile properties of alloys 1 through 6 along with those of selected commercial alloys from Table 2 are presented in Table 3 below.

**TABLE 3**

Room Temperature Tensile Data					
Alloy	Yield Strength,		Tensile Strength,		Elongation Percent
	MPa	ksi	MPa	ksi	
1	635	92.1	1068	154.9	30.9
2	625	90.7	1057	153.3	28.6
3	609	88.3	1012	146.8	24.4
4	588	85.3	1021	148.1	31.6
5	618	89.7	1053	152.7	30.4
6	482	69.9	910	132.0	30.5
A	290	42.0	641	93.0	52.0
B	372	54.0	807	117.0	52.0
C	338	49.0	690	100.0	46.0
D	408	59.2	843	122.3	33.9

10

Table 4 presents the 982°C (1800°F) or high temperature strength data for the alloys.

**TABLE 4**

15

982°C (1800°F) Tensile Properties					
Alloy	Yield Strength		Tensile Strength		Elongation Percent
	MPa	ksi	MPa	ksi	
1	45.0	6.5	71.7	10.4	85.3
2	46.0	6.7	80.0	11.6	56.2
3	40.0	5.8	70.3	10.2	98.4
4	45.0	6.5	70.3	10.2	100.2
5	44.0	6.4	71.7	10.4	99.3
6	39.0	5.7	68.3	9.9	144.2
A	69.0	10	75.8	11	100
B	96.5	14.0	186	27.0	92.0
C	--	--	--	--	--
D	41.0	6.0	80.7	11.7	52.6

The data from Tables 3 and 4 indicate that this alloy has mechanical properties acceptable for most high strengths applications at room and elevated temperatures.

5 Table 5 below provides the stress rupture data for the alloy.

**TABLE 5**

982°C (1800°F) Stress Rupture Properties Specimens Annealed 1100°C (2012°F)/30 Minutes/Air Cooled Test Conditions: 13.8 MPa (2 ksi)/982°C (1800°F)		
Alloy	Time to Failure, Hours	Elongation, Percent
2	511	94
	758	158
3	101	115
4	210	138
5	132	206
	154	189
C	65	--

10

With regard to the stress rupture results presented in Table 5, it is observed that alloys 1 to 6 exceeded the desired minimum stress rupture life of 100 hours at 982°C (1800°F) and 13.8 MPa (2 ksi). Analysis of the data show that carbon levels between 0.12 and 0.16% yield the longest stress rupture lives, but at values to 0.23 and greater alloys are

15 satisfactory.

20

The data in Figures 1 through 5 illustrate of the improvement in carburization and oxidation resistance characteristic of the alloy's compositional range. Resistance to spallation under thermal cycling conditions is attributed in great measure to the critical presence of cerium plus yttrium and optionally zirconium. In addition, the alloy's reservoir of chromium and aluminum give the alloy a self-healing scale. The commercial alloys however, lacking adequate chromium plus aluminum, tend to internally oxidize and fail to perform similarly.

25

While the present patent application has been described with reference to specific embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the patent application, as those skilled in the art will readily understand. Such modifications and variations are considered to be within

the purview and scope of the patent application and appended claims. A given percentage range for an element can be used within a given range for the other constituents. The term "balance nickel" or "balance nickel and incidental impurities" used in referring to the nickel content of the alloy range does not exclude the presence of other elements in amounts  
5 which do not adversely affect the basic characteristics of the range of alloys, including deoxidizers and rare earth metals. It is considered that, in addition to the wrought form, this alloy range can be used in the cast condition or fabricated using powder metallurgy techniques.

1. An alloy resistant to carburization and high temperature oxidation consisting essentially of, by weight percent, about 27 to 35 chromium, about 0 to 7 iron, about 3 to 4.4 aluminum, about 0 to 0.14 titanium, about 0.2 to 3 niobium, about 0.12 to 0.5 carbon, about 0 to 0.05 zirconium, about 0.002 to 0.05 total cerium and yttrium,  
5 about 0 to 1 manganese, about 0 to 1 silicon, about 0 to 0.5 calcium plus magnesium, about 0 to 0.1 boron and balance nickel plus incidental impurities.
2. The alloy of claim 1 containing about 28 to 34 chromium, about 0.5 to 6 iron, about 3 to 4.2 aluminum, about 0.05 to 0.3 titanium and about 0.3 to 2.5 niobium.
3. The alloy of claim 1 containing about 0.0002 to 0.3 zirconium, about 0.001 to 0.045 cerium, about 0.001 to 0.045 yttrium and total of about 0.002 to 0.05 cerium plus yttrium.
4. The alloy of claim 1 having a stress rupture life of at least 100 hours at a stress of 13.8 MPa and a temperature of 982°C.
5. An alloy resistant to carburization and high temperature oxidation consisting essentially of, by weight percent, about 52 to 67 nickel, about 28 to 34 chromium, about 0.5 to 6 iron, about 3 to 4.2 aluminum, about 0.05 to 0.3 titanium, about 0.3 to 2.5 niobium, about 0.12 to 0.4 carbon, about 0.0002 to 0.3 zirconium, about  
5 0.001 to 0.045 cerium, about 0.001 to 0.045 yttrium, about 0.002 to 0.05 total cerium and yttrium, about 0 to 0.7 manganese, about 0 to 0.7 silicon, about 0.001 to 0.1 calcium plus magnesium, about 0 to 0.05 boron and incidental impurities.
6. The alloy of claim 5 containing about 29 to 34 chromium, about 1 to 5.5 iron, about 3 to 4 aluminum, about 0.1 to 0.3 titanium and about 0.5 to 2 niobium.

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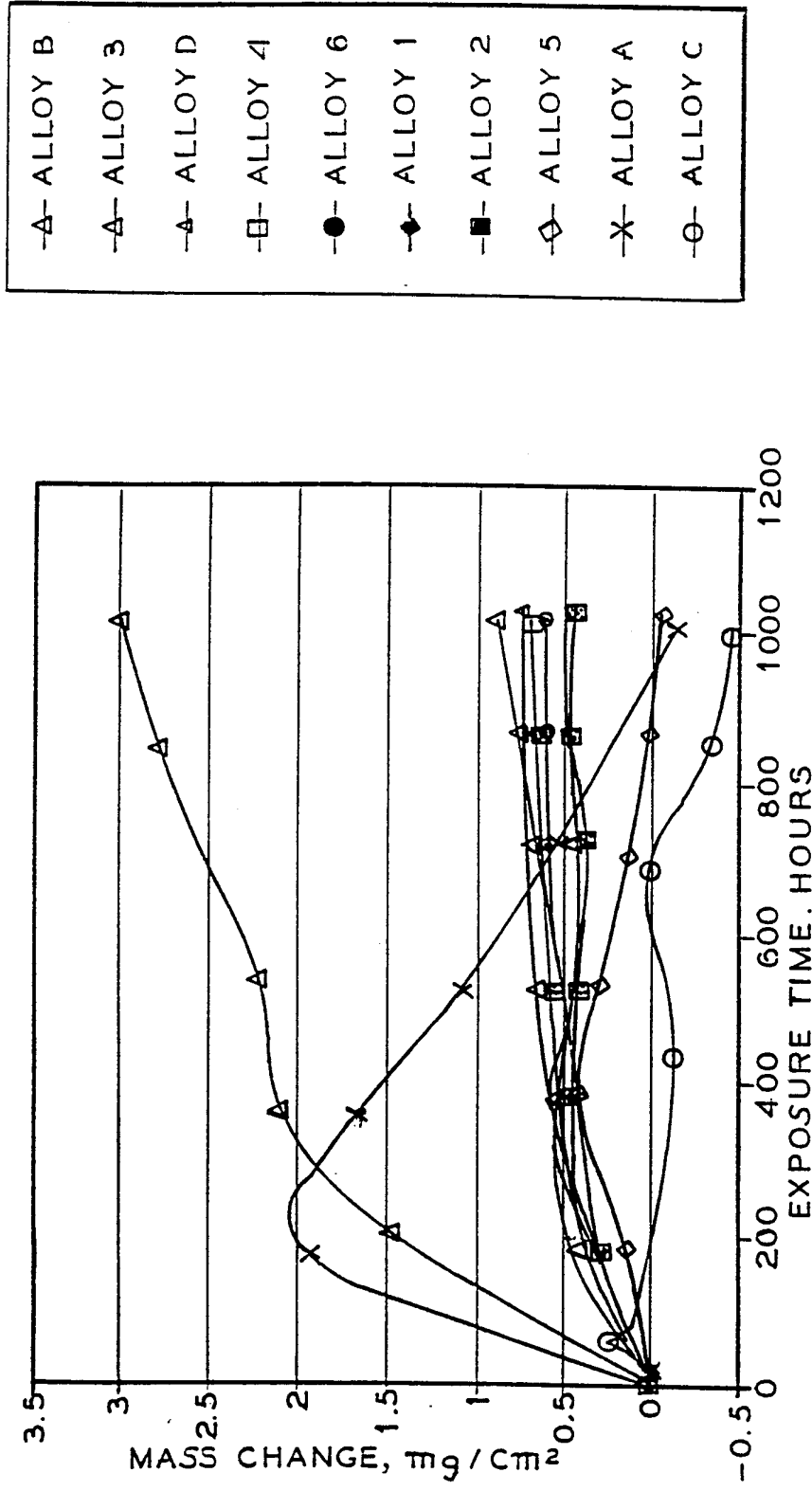
7. The alloy of claim 5 containing about 0.001 to 0.2 zirconium, about 0.0025 to 0.025 cerium, about 0.0025 to 0.025 yttrium and total of about 0.005 to 0.04 cerium plus yttrium.

8. The alloy of claim 5 having a stress rupture life of at least 100 hours at a stress of 13.8 MPa and a temperature of 982°C.

9. An alloy resistant to carburization and high temperature oxidation consisting essentially of, by weight percent, about 55 to 65 nickel, about 29 to 34 chromium, about 1 to 5.5 iron, about 3 to 4 aluminum, about 0.1 to 0.3 titanium, about 0.5 to 2 niobium, about 0.12 to 0.3 carbon, about 0.001 to 0.2 zirconium, about 0.0025 to 0.025 cerium, about 0.0025 to 0.025 yttrium, about 0.005 to 0.04 total cerium and yttrium, about 0 to 0.5 manganese, about 0 to 0.5 silicon, about 0.002 to 0.05 calcium plus magnesium, about 0 to 0.01 boron and incidental impurities.

10. The alloy of claim 9 having a stress rupture life of at least 100 hours at a stress of 13.8 MPa and a temperature of 982°C.

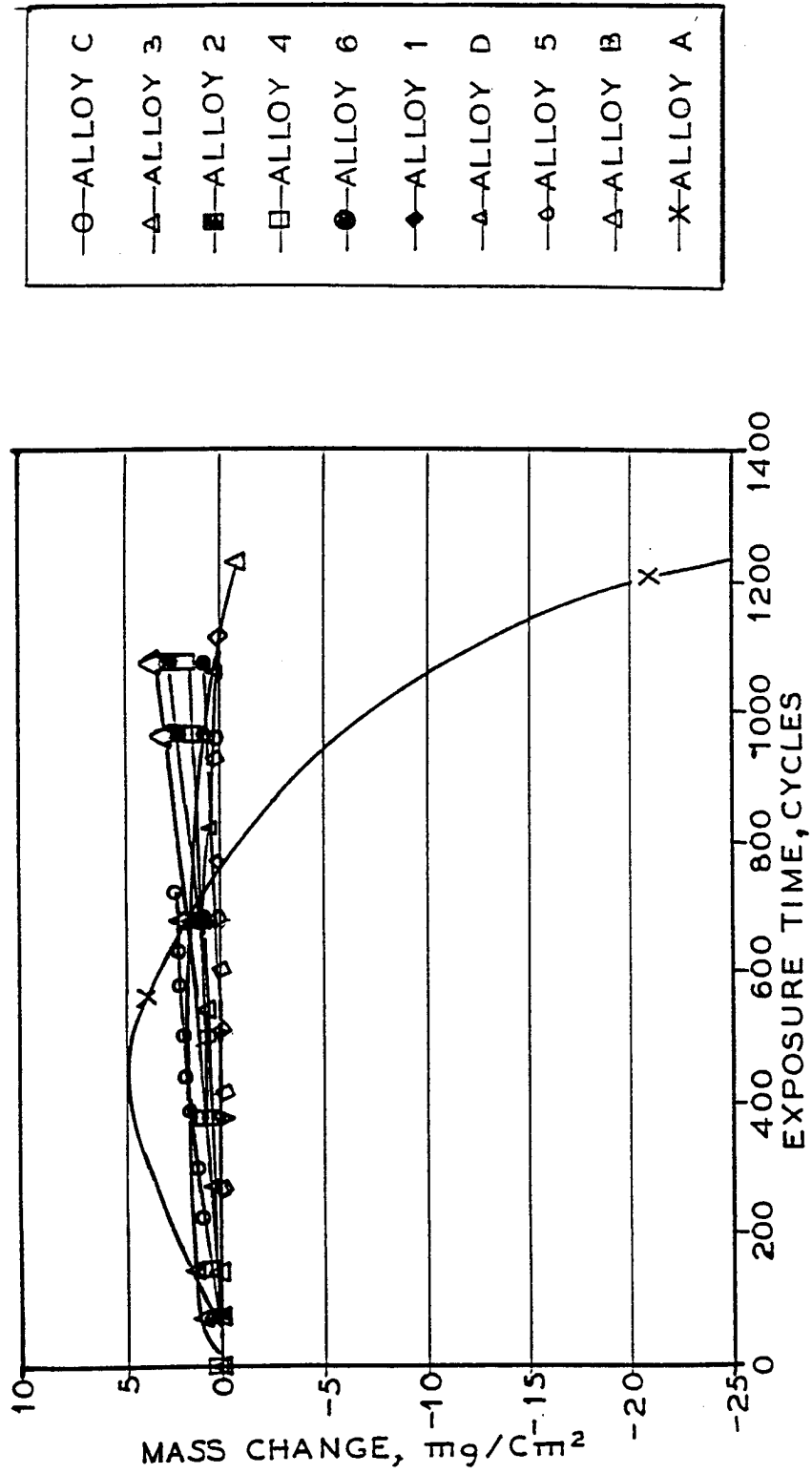
FIG.1



- △- ALLOY B
- △- ALLOY 3
- △- ALLOY D
- ALLOY 4
- ALLOY 6
- ◆- ALLOY 1
- ALLOY 2
- ◇- ALLOY 5
- X- ALLOY A
- ALLOY C



FIG. 2



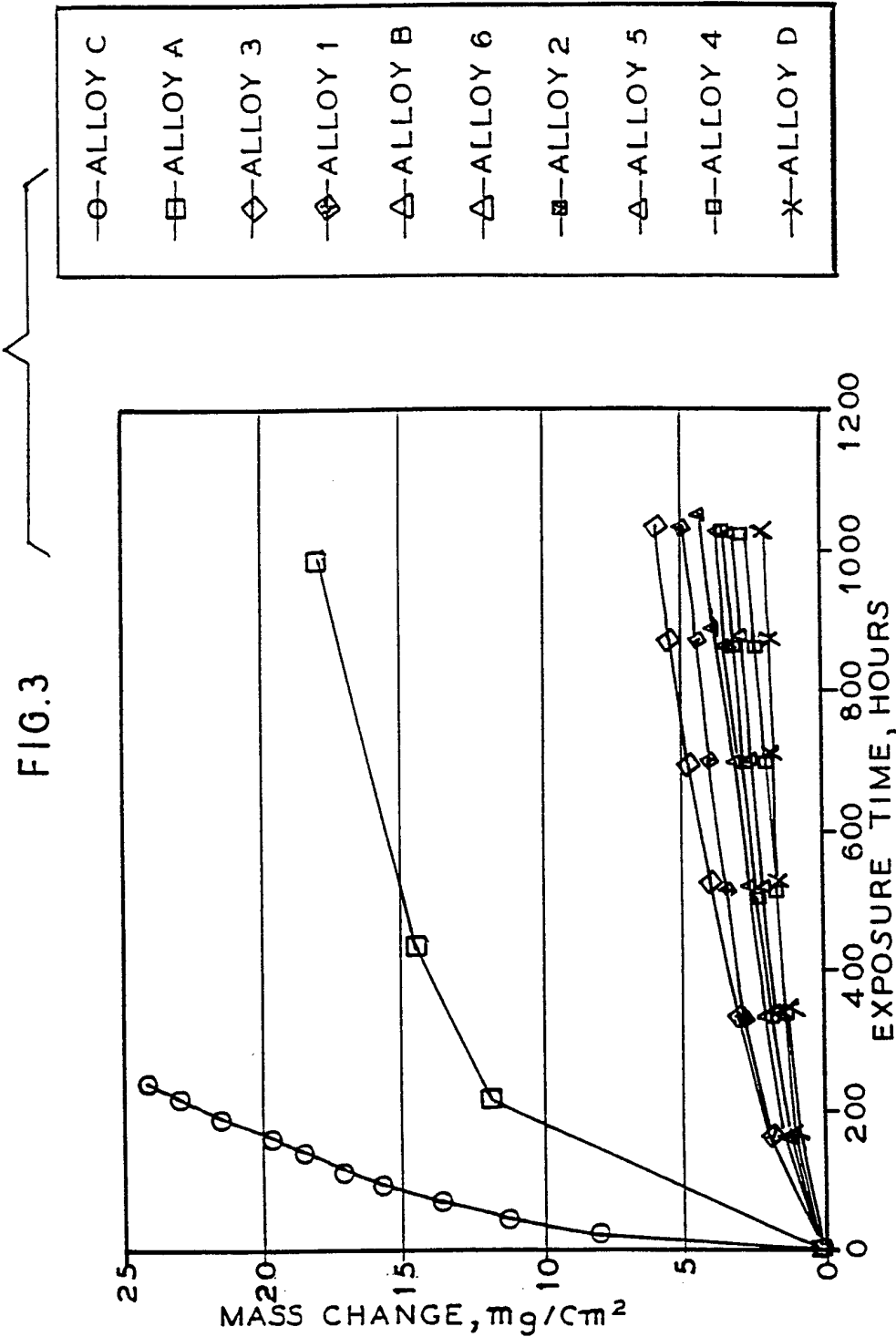
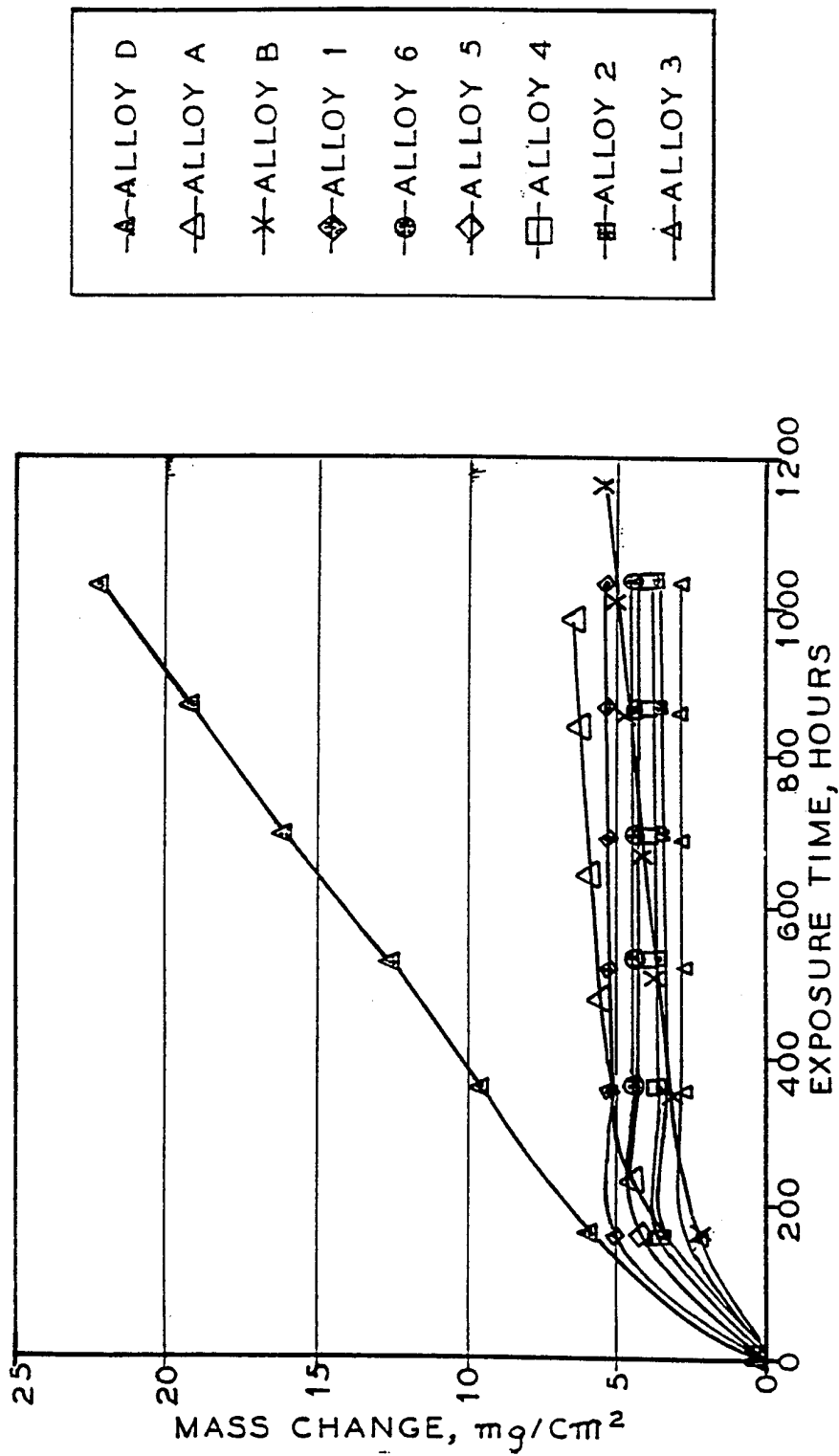
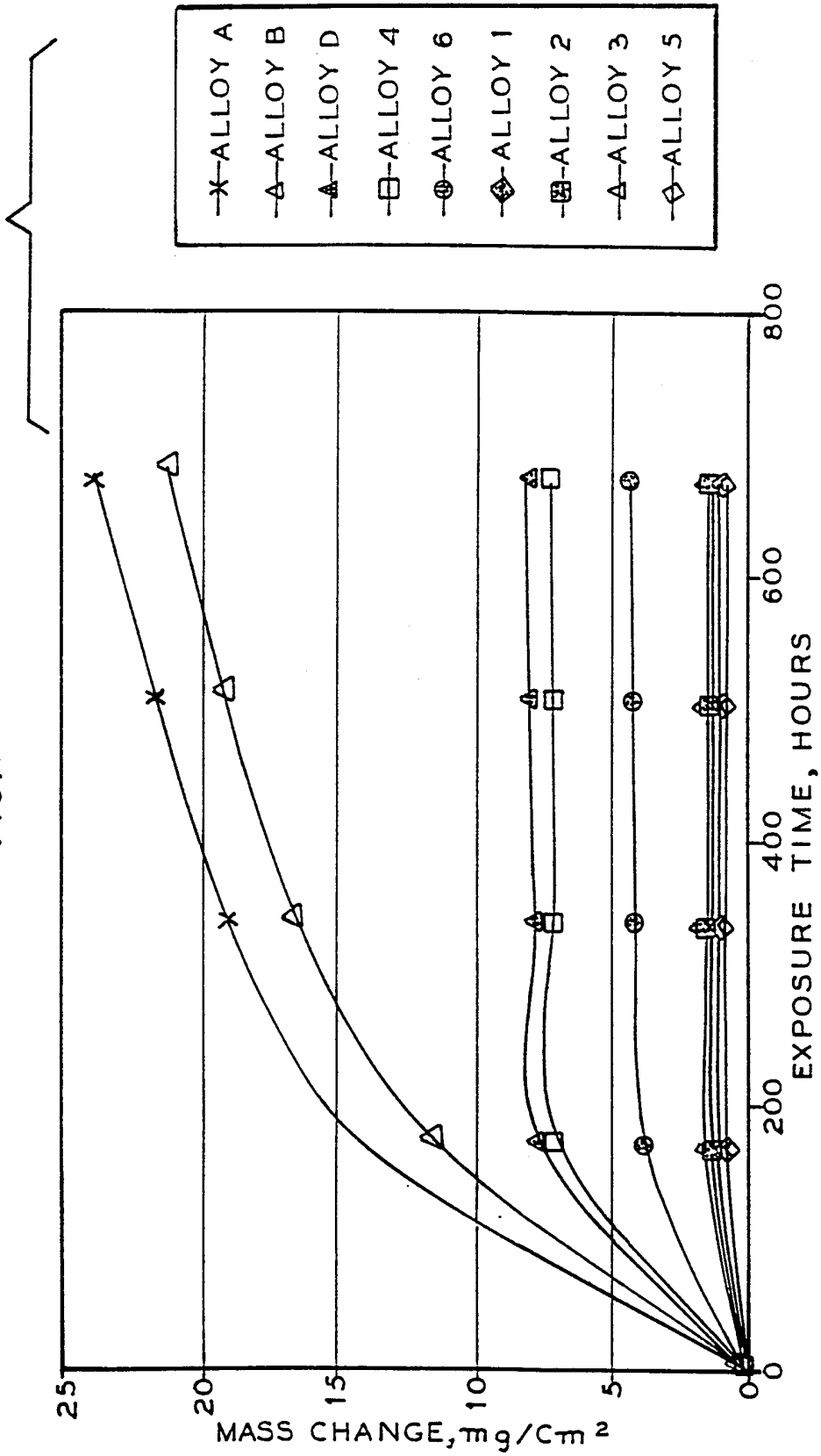


FIG. 4



- ▲-ALLOY D
- △-ALLOY A
- X-ALLOY B
- ◇-ALLOY 1
- ⊙-ALLOY 6
- ◇-ALLOY 5
- ALLOY 4
- ⊞-ALLOY 2
- △-ALLOY 3

FIG. 5



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/19268

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C22C19/05

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 338 574 A (INCO ALLOYS INT) 25 October 1989 (1989-10-25) the whole document examples 2,3,10,12,14; tables I,III ---	1-10
Y	DE 41 11 821 C (VDM NICKEL-TECHNOLOGIE AG) 28 November 1991 (1991-11-28) page 3, line 35 - line 42 page 3, line 61 - line 65 ---	1-10
A	EP 0 752 481 A (KRUPP VDM GMBH) 8 January 1997 (1997-01-08) page 3, line 40 - line 47; claim 1; table 1 --- -/-	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 May 2000

Date of mailing of the international search report

15/05/2000

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/19268

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DE 32 40 188 A (TOKYO SHIBAURA ELECTRIC CO) 11 May 1983 (1983-05-11) page 9, line 1 - line 8; claim 1 -----	1-10

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