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(54) **Hot corrosion resistant single crystal nickel-based superalloys**

(57) This invention relates to a hot corrosion resistant nickel-based superalloy comprising the following elements in percent by weight: from about 14.2 to about 15.5 percent chromium, from about 2.0 to about 4.0 percent cobalt, from about 0.30 to about 0.45 percent molybdenum, from about 4.0 to about 5.0 percent tungsten, from about 4.5 to about 5.8 percent tantalum, from about 0.05 to about 0.25 percent columbium, from about 3.2

to about 3.6 percent aluminum, from about 4.0 to about 4.4 percent titanium, from about 0.01 to about 0.06 percent hafnium, and the balance nickel plus incidental impurities, the superalloy having a phasial stability number N_{V3B} less than about 2.45. Single crystal articles can be suitably made from the superalloy of this invention. The article can be a component for a gas turbine engine and, more particularly, the component can be a gas turbine blade or gas turbine vane.

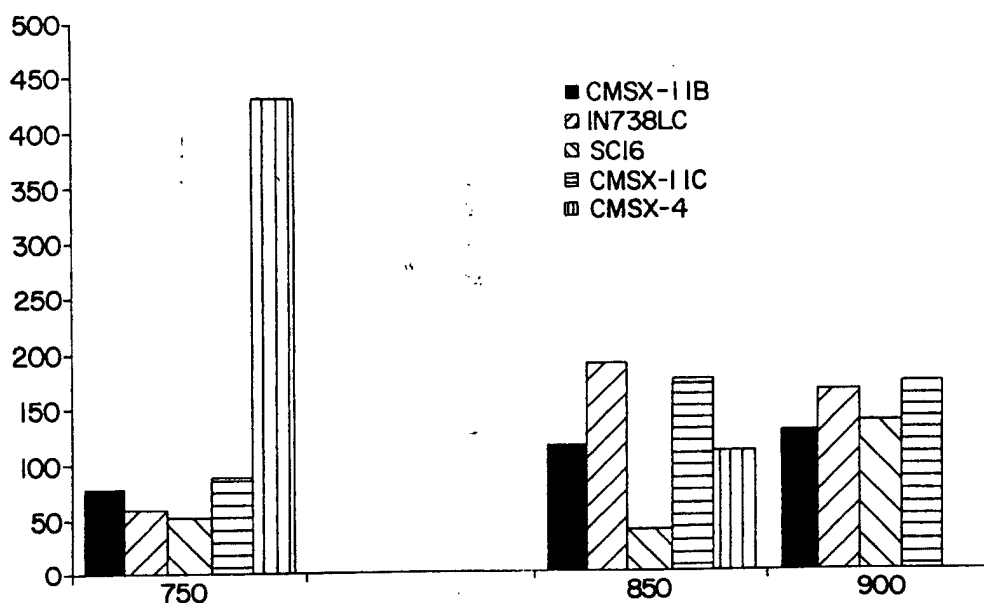


FIG. 1

Description**BACKGROUND OF THE INVENTION**

1. Field of the Invention

[0001] This invention relates to single crystal nickel-based superalloys and, more particularly, single crystal nickel-based superalloys and articles made therefrom having increased resistance to bare hot corrosion for use in gas turbine engines.

2. Description of the Prior Art

[0002] Advances over recent years in the metal temperature and stress capability of single crystal articles have been the result of the continuing development of single crystal superalloys, as well as improvements in casting processes and engine application technology. These single crystal superalloy articles include rotating and stationary turbine blades and vanes found in the hot sections of gas turbine engines. Gas turbine engine design goals have remained the same during the past decades. These goals include the desire to increase engine operating temperature, rotational speed, fuel efficiency, and engine component durability and reliability.

[0003] Prior art attempts to provide alloys to help achieve these design goals for industrial gas turbine engine applications include U.S. Patent No. 4,677,035, Fiedler et al., which discloses a nickel-base single crystal alloy composition consisting essentially of, in percent by weight, 8.0-14.0% chromium, 1.5-6.0% cobalt, 0.5-2.0% molybdenum, 3.0-10.0% tungsten, 2.5-7.0% titanium, 2.5-7.0% aluminum, 3.0-6.0% tantalum, and the balance nickel. However, the alloy compositions taught by this reference, while possessing relatively high strength at prolonged or repeated exposure to high temperatures, are susceptible to the accelerated corrosive effect of the hot gas environment in which components fabricated from the alloys are exposed to when used in gas turbines.

[0004] Also, U.K. Patent Application Publication No. 2153848A discloses nickel-base alloys having a composition within the range of 13-15.6% chromium, 5-15% cobalt, 2.5-5% molybdenum, 3-6% tungsten, 4-6% titanium, 2-4% aluminum, and the balance essentially nickel without intentional additions of carbon, boron or zirconium, which are fabricated into single crystals. Although the alloys taught by this reference claim an improvement in hot corrosion resistance accompanied by an increase in creep rupture properties, the need remains in the art for single crystal superalloys for industrial gas turbine applications having a superior combination of increased hot corrosion resistance, oxidation resistance, mechanical strength, large component castability and adequate heat treatment response.

[0005] Single crystal articles are generally produced having the low-modulus (001) crystallographic orientation parallel to the component dendritic growth pattern or blade stacking axis. Face-centered cubic (FOC) superalloy single crystals grown in the (001) direction provide extremely good thermal fatigue resistance relative to conventionally cast polycrystalline articles. Since these single crystal articles have no grain boundaries, alloy design without grain boundary strengtheners, such as carbon, boron and zirconium, is possible. As these elements are alloy melting point depressants, their essential elimination from the alloy design provides a greater potential for high temperature mechanical strength achievement since more complete gamma prime solution and microstructural homogenization can be achieved relative to directionally solidified (DS) columnar grain and conventionally cast materials, made possible by a higher incipient melting temperature.

[0006] These process benefits are not necessarily realized unless a multi-faceted alloy design approach is undertaken. Alloys must be designed to avoid tendency for casting defect formation such as freckles, slivers, spurious grains and recrystallization, particularly when utilized for large cast components. Additionally, the alloys must provide an adequate heat treatment "window" (numeric difference between an alloy's gamma prime solvus and incipient melting point) to allow for nearly complete gamma prime solutioning. At the same time, the alloy compositional balance should be designed to provide an adequate blend of engineering properties necessary for operation in gas turbine engines. Selected properties generally considered important by gas turbine engine designers include: elevated temperature creep-rupture strength, thermo-mechanical fatigue resistance, impact resistance, hot corrosion and oxidation resistance, plus coating performance. In particular, industrial turbine designers require unique blends of hot corrosion and oxidation resistance, plus good long-term mechanical properties.

[0007] An alloy designer can attempt to improve one or two of these design properties by adjusting the compositional balance of known superalloys.

[0008] However, it is extremely difficult to improve more than one or two of the design properties without significantly or even severely compromising some of the remaining properties. The unique superalloy of the present invention provides an excellent blend of the properties necessary for use in producing single crystal articles for operation in industrial and marine gas turbine engine hot sections.

SUMMARY OF THE INVENTION

[0009] This invention relates to a hot corrosion resistant nickel-based superalloy comprising the following elements in percent by weight: from about 14.2 to about 15.5 percent chromium, from about 2.0 to about 4.0 percent cobalt, from about 0.30 to about 0.45 percent molybdenum, from about 4.0 to about 5.0 percent tungsten, from about 4.5 to about 5.8 percent tantalum, from about 0.05 to about 0.25 percent columbium, from about 3.2 to about 3.6 percent aluminum, from about 4.0 to about 4.4 percent titanium, from about 0.01 to about 0.06 percent hafnium, and the balance nickel plus incidental impurities, the superalloy having a phasial stability number N_{V3B} less than about 2.45.

[0010] Advantageously, the sum of aluminum plus titanium in this superalloy composition is from 7.2 to 8.0 percent by weight. Also, it is advantageous to have a Ti:Al ratio greater than 1 and a Ta:W ratio greater than 1 in the composition of the present invention. Although incidental impurities should be kept to the least amount possible, the superalloy can also be comprised of from about 0 to about 0.05 percent carbon, from about 0 to about 0.03 percent boron, from about 0 to about 0.03 percent zirconium, from about 0 to about 0.25 percent rhenium, from about 0 to about 0.10 percent silicon, and from about 0 to about 0.10 percent manganese. In all cases, the base element is nickel. This invention provides a single crystal superalloy having an increased resistance to hot corrosion, an increased resistance to oxidation, and increased creep-rupture strength.

[0011] Single crystal articles can be suitably made from the superalloy of this invention. The article can be a component for a gas turbine engine and, more particularly, the component can be a gas turbine blade or gas turbine vane.

[0012] The superalloy compositions of this invention have a critically balanced alloy chemistry which results in a unique blend of desirable properties, including an increased resistance to hot corrosion, which are particularly suitable for industrial and marine gas turbine applications. These properties include: excellent bare hot corrosion resistance and creep-rupture strength; good bare oxidation resistance; good single crystal component castability, particularly for large blade and vane components; good solution heat treatment response; adequate resistance to cast component recrystallization; adequate component coatability and microstructural stability, such as long-term resistance to the formation of undesirable, brittle phases called topologically close-packed (TCP) phases.

[0013] Accordingly, it is an object of the present to provide superalloy compositions and single Crystal articles made therefrom having a unique blend of desirable properties, including increased hot corrosion resistance. It is a further object of the present invention to provide superalloys and single crystal articles made therefrom for use in industrial and marine gas turbine engines. These and other objects and advantages of the present invention will be apparent to those skilled in the art upon reference to the following description of the preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a chart of hot corrosion test results performed at three exposure temperatures on one embodiment of this invention and on four other alloys.

[0015] FIG. 2 is a graphical comparison of hot corrosion data from tests performed at 732°C (1350°F) on one embodiment of this invention and on two other alloys.

[0016] FIG. 3 is a graphical comparison of hot corrosion data from tests performed at 899°C (1650°F) on one embodiment of this invention and on two other alloys.

[0017] FIG. 4 is a graphical comparison of alloy strength and hot corrosion data from tests performed on one embodiment of this invention and on six other alloys.

[0018] FIG. 5 is a graphical comparison of oxidation data from tests performed at 1000°C (1832°F) on one embodiment of this invention and on two other alloys.

[0019] FIG. 6 is a graphical comparison of oxidation data from tests performed at 1010°C (1850°F) on one embodiment of the present invention and on two other alloys.

[0020] FIG. 7 is a graphical comparison of alloy strength and oxidation data from tests performed on one embodiment of this invention and on six other alloys.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The hot corrosion resistant nickel-based superalloy of the present invention comprises the following elements in percent by weight:

Chromium	about 14.2-15.5
Cobalt	about 2.0-4.0
Molybdenum	about 0.30-0.45
Tungsten	about 4.0-5.0

(continued)

Tantalum	about 4.5-5.8
Columbium	about 0.05-0.25
Aluminum	about 3.2-3.6
Titanium	about 4.0-4.4
Hafnium	about 0.01-0.06
Nickel + Incidental impurities	balance

This superalloy composition also has a phasial stability number N_{V38} less than about 2.45. Further, this invention has a critically balanced alloy chemistry which results in a unique blend of desirable properties useful for industrial and marine gas turbine engine applications. These properties include a superior blend of bare hot corrosion resistance and creep-rupture strength relative to prior art single crystal superalloys for industrial and marine gas turbine applications, bare oxidation resistance, single crystal component castability, and microstructural stability, including resistance to TCP phase formation under high stress, high temperature conditions.

[0022] Superalloy chromium content is a primary contributor toward attaining superalloy hot corrosion resistance. The superalloys of the present invention have a relatively high chromium content since alloy hot corrosion resistance was one of the primary design criteria in the development of these alloys. The chromium is about 14.2-15.5% by weight. Advantageously, the chromium content is from 14.3% to 15.0% by weight. Although chromium provides hot corrosion resistance, it may also assist with the alloys' oxidation capability. Additionally, this superalloys' tantalum and titanium contents, as well as its Ti:Al ratio being greater than 1, are beneficial for hot corrosion resistance attainment. However, besides lowering the alloys' gamma prime solvus, chromium contributes to the formation of Cr and W-rich TCP phase and must be balanced accordingly in these compositions.

[0023] In one embodiment of the present invention, the cobalt content is about 2.0-4.0% by weight. In another embodiment of the present invention, the cobalt content is from 2.5% to 3.5% by weight. The chromium and cobalt levels in these superalloys assist in making the superalloy solution heat treatable, since both elements tend to decrease an alloy's gamma prime solvus. Proper balancing of these elements in the present invention in tandem with those which tend to increase the alloy's incipient melting temperature, such as tungsten and tantalum, result in superalloy compositions which have desirable solution heat treatment windows (numerical difference between an alloy's incipient melting point and its gamma prime solvus), thereby facilitating full gamma prime solutioning. The cobalt content is also beneficial to the superalloy's solid solubility.

[0024] The tungsten content is about 4.0-5.0% by weight and, advantageously, the amount of tungsten is from 4.2% to 4.8% by weight. Tungsten is added in these compositions since it is an effective solid solution strengthener and it can contribute to strengthening the gamma prime. Additionally, tungsten is effective in raising the alloy's incipient melting temperature.

[0025] Similar to tungsten, tantalum is a significant solid solution strengthener in these compositions, while also contributing to enhanced gamma prime particle strength and volume fraction. The tantalum content is about 4.5-5.8% by weight and, advantageously, the tantalum content is from 4.8% to 5.4% by weight. In these compositions, tantalum is beneficial since it helps to provide bare hot corrosion and oxidation resistance, along with aluminide coating durability. Additionally, tantalum is an attractive single crystal alloy additive in these compositions since it assists in preventing "freckle" defect formation during the single crystal casting process. Particularly when present in greater proportion than tungsten (i.e., the ratio is greater than 1). Furthermore, tantalum is an attractive means of strength attainment in these alloys since it is believed not to directly participate in TCP phase formation.

[0026] The molybdenum content is about 0.30-0.45% by weight. Advantageously, molybdenum is present in an amount of from 0.35% to 0.43% by weight. Molybdenum is a good solid solution strengthener, but it is not as effective as tungsten and tantalum, and it tends to be a negative factor toward hot corrosion capability. However, since the alloy's density is always a design consideration, and the molybdenum atom is lighter than the other solid solution strengtheners, the addition of molybdenum is a means of assisting control of the overall alloy density in the compositions of this invention. It is believed that the relatively low molybdenum content is unique in this class of bare hot corrosion resistant nickel-based single crystal superalloys.

[0027] The aluminum content is about 3.2-3.6% by weight. Furthermore, the amount of aluminum present in these compositions is advantageously from 3.3% to 3.5% by weight. Aluminum and titanium are the primary elements comprising the gamma prime phase, and the sum of aluminum plus titanium in the present invention is from 7.2 to 8.0 percent by weight. These elements are added in these compositions in a proportion and ratio consistent with achieving adequate alloy castability, solution heat treatability, phasial stability and the desired blend of high mechanical strength and hot corrosion resistance. Aluminum is also added to these alloys in proportions sufficient to provide oxidation resistance.

[0028] The titanium content is about 4.0-4.4% by weight. Advantageously, titanium is present in this composition in an amount from 4.1% to 4.3% by weight. These alloys' titanium content is relatively high and, therefore, is beneficial

to the alloys' hot corrosion resistance. However, it can also have a negative effect on oxidation resistance, alloy castability and alloy response to solution heat treatment. Accordingly, it is critical that the titanium content is maintained within the stated range of this composition and the proper balancing of the aforementioned elemental constituents is maintained. Furthermore, maintaining the alloys' Ti:Al ratio greater than 1 is critical in achieving the desired bare hot corrosion resistance in these compositions.

[0029] The columbium content is about 0.05%-0.25% by weight and, advantageously, the columbium content is from 0.05% to 0.12% by weight. Columbium is a gamma prime forming element and it is an effective strengthener in the nickel-based superalloys of this invention. Generally, however, columbium is a detriment to alloy oxidation and hot corrosion properties, so its addition to the compositions of this invention is minimized. Moreover, Columbium is added to this invention's compositions for the purpose of getting carbon, which can be chemisorbed into component surfaces during non-optimized vacuum solution heat treatment procedures. Any carbon pick-up will tend to form columbium carbide instead of titanium or tantalum carbide, thereby preserving the greatest proportion of titanium and/or tantalum for gamma prime and/or solid solution strengthening in these alloys. Furthermore, it is critical that the sum of columbium plus hafnium is from 0.06 to 0.31 percent by weight in these compositions in order to enhance the strength of these superalloys.

[0030] The hafnium content is about 0.01%-0.06% by weight and, advantageously, hafnium is present in an amount from 0.02% to 0.05% by weight. Hafnium is added in a small proportion to the present compositions in order to assist with coating performance and adherence. Hafnium generally partitions to the gamma prime phase.

[0031] The balance of this invention's superalloy compositions is comprised of nickel and small amounts of incidental impurities. Generally, these incidental impurities are entrained from the industrial process of production, and they should be kept to the least amount possible in the composition so that they do not affect the advantageous aspects of the superalloy. For example, these incidental impurities may include up to about 0.05 percent carbon, up to about 0.03 percent boron, up to about 0.03 percent zirconium, up to about 0.25 percent rhenium, up to about 0.10 percent silicon, and up to about 0.10 percent manganese. Amounts of these impurities which exceed the stated amounts could have an adverse effect upon the resulting alloy's properties.

[0032] Not only does the superalloy of this invention have a composition within the above specified ranges, but it also has a phase stability number N_{V3B} less than about 2.45. As can be appreciated by those skilled in the art, N_{V3B} is defined by the PWA N-35 method of nickel-based alloy electron vacancy TCP phase control factor calculation. This calculation is as follows

EQUATION 1

[0033] Conversion for weight percent to atomic percent:

$$\text{Atomic percent of element } i = P_i = \frac{W_i/A_i}{\sum_i (W_i/A_i)} \times 100$$

where:

W_i = weight percent of element i

A_i = atomic weight of element i

EQUATION 2

[0034] Calculation for the amount of each element present in the continuous matrix phase:

Element	Atomic amount R_{ii} remaining
Cr	$R_{Cr} = 0.97P_{Cr} - 0.375P_B - 1.75P_C$
Ni	$R_{Ni} = P_{Ni} + 0.525P_B - 3(P_{Al} + 0.03P_{Cr} + P_{Ti} - 0.5P_C + 0.5P_V + P_{Ta} + P_{Cb} + P_{Rf})$
Ti, Al, B, C, Ta, Cb, Hf	$R_i = 0$
V	$R_V = 0.5P_V$
W	$R_{(W)} = P_W - 0.167P_C \frac{P_W}{P_{Mo} + P_W}$
Mo	$R_{(Mo)} = P_{(Mo)} - 0.75P_B - 0.167P_C \frac{P_{Mo}}{(P_{Mo} + P_W)}$

EQUATION 3

[0035] Calculation of N_{V3B} using atomic factors from Equations 1 and 2 above:

$$N_i^i = \frac{R_i}{\sum_i R_i} \quad \text{then} \quad N_{v38} = \sum_i N_i (N_v)_i$$

where:

i = each individual element in turn.

N_i = the atomic factor of each element in matrix.

$(N_v)_i$ = the electron vacancy No. of each respective element.

This calculation is exemplified in detail in a technical paper entitled "PHACOMP Revisited", by H. J. Murphy, C. T. Sims and A. M. Beltran, published in Volume 1 of International Symposium on Structural Stability in Superalloys (1968), the disclosure which is incorporated by reference herein. As can be appreciated by those skilled in the art, the phasial stability number for the superalloys of this invention is critical and must be less than the stated maximum to provide a stable microstructure and capability for the desired properties under high temperature, high stress conditions. The phasial stability number can be determined empirically, once the practitioner skilled in the art is in possession of the present subject matter.

[0036] The superalloys of this invention can be used to suitably make single crystal articles, such as components for industrial and marine gas turbine engines. Preferably, these superalloys are utilized to make a single crystal casting to be used under high stress, high temperature conditions characterized by an increased resistance to hot corrosion (sulfidation) under such conditions, particularly high temperature conditions involving corrosive atmospheres containing sulfur, sodium and vanadium contaminants, up to about 1922°F (1050°C). While these superalloys can be used for any purpose requiring high strength castings produced as a single crystal, their particular use is in the casting of single crystal blades and vanes for industrial and marine gas turbine engines.

[0037] The single crystal components made from this invention's compositions can be produced by any of the single crystal casting techniques known in the art. For example, single crystal directional solidification processes can be utilized, such as the seed crystal process and the choke process.

[0038] The single crystal castings made from the superalloys of the present invention can be aged at a temperature of from about 1800°F (982°C) to about 2125°F (1163°C) for about 1 to about 50 hours. However, as can be appreciated by those skilled in the art, the optimum aging temperature and time for aging depends on the precise composition of the superalloy.

[0039] This invention provides superalloy compositions having a unique blend of desirable properties. These properties include: excellent bare hot corrosion resistance and creep-rupture strength; good oxidation resistance; good single crystal component castability, particularly for large blade and vane components; good solution heat treatment response; adequate resistance to cast component recrystallization; adequate component coatability and microstructural stability, such as long-term resistance to the formation of undesirable, brittle phases called topologically close-packed (TCP) phases.

As noted above, this superalloy has a precise composition with only small permissible variations in any one element if the unique blend of properties is to be maintained.

[0040] In order to more clearly illustrate this invention and provide a comparison with representative superalloys outside the claimed scope of the invention, the examples set forth below are presented. The following examples are included as being illustrations of the invention and its relation to other superalloys and articles, and should not be construed as limiting the scope thereof.

EXAMPLES

[0041] Test materials were prepared to investigate the compositional variations and ranges for the superalloys of the present invention. One of the alloy compositions tested and reported below falls outside the claimed scope of the present invention, but is included for comparative purposes to assist in the understanding of the invention. Representative alloy chemistries of materials tested are reported in Table 1 below.

TABLE 1

AIM CHEMISTRIES				
ELEMENT	CMSX-11C	CMSX-11C'	CMSX-11C"	CMSX-11B
C	Lap	Lap	Lap	Lap
Cr	14.5	14.5	14.4	12.5
Co	3.0	2.5	2.9	6.0
Mo	.40	.35	.40	0.55
W	4.4	4.6	4.5	5.0
Ta	4.95	5.1	5.1	5.15
Cb	.10	.08	.10	0.20
Al	3.40	3.40	3.4	3.60
Ti	4.20	4.15	4.2	4.20
Hf	.04	.03	.04	0.040
Ni	BAL	BAL	BAL	BAL
N _{v3B}	2.41	2.40	2.42	2.42
NOTE: Chemistries are in wt. %.				

[0042] Test materials defined by the CMSX® -11C aim chemistry shown in Table 1 were initially produced by mixing 15 lbs. of the heat R2D2 alloy (see Table 2 below) with 8 lbs. of virgin materials, melting and subsequently pouring the melt into a ceramic shell mold. (CMSX is a registered trademark of Cannon-Muskegon Corporation, assignee of the present application).

[0043] Nineteen (19) each $\frac{3}{8}$ " diameter x 6" long test bars plus three (3) each solid turbine blades were investment cast with the resulting blended product. Specimen inspection revealed satisfactory grain yield with only one test bar rejectable for mis-orientation. No freckles were apparent. Furthermore, a test-bar chemistry check indicated that the CMSX-11C aim composition was attained.

[0044] Further test materials were obtained with alloy product which was VIM produced in 250 -270 lb. (113-122 kg.) quantities. The VIM heats that were produced and their respective chemistries are reported in Table 2 below.

TABLE 2
VIM FURNACE HEAT CHEMISTRIES

ELEMENT													
Heat #/Alloy Designation	ppm	C	Cr	Co	Mo	W	Ta	Co	Al	Ti	Hf	Ni	N ₂₃₈
VF 952/R2D2	10	11.0	4.9	.49	.49	2.5	5.0	<.01	3.39	3.76	.05	BAL	1.92
VF 998/CMSX-11C	14	14.6	3.0	.41	.41	4.4	4.95	.10	3.4	4.18	.03	BAL	2.42
VG 33/CMSX-11C	11	14.4	3.0	.40	.40	4.4	4.9	.10	3.46	4.15	.03	BAL	2.41
VG 110/CMSX-11C'	16	14.4	2.4	.35	.35	4.6	5.0	.07	3.4	4.1	.03	BAL	2.37
VG 113/CMSX-11C'	12	14.6	2.4	.36	.36	4.6	5.1	.09	3.4	4.1	.04	BAL	2.41
VG 148/CMSX-11C'	15	14.4	2.4	.35	.35	4.6	5.1	.08	3.4	4.1	.03	BAL	2.38
VG 175/CMSX-11C"	15	14.4	2.9	.40	.40	4.5	5.1	.10	3.4	4.2	.04	BAL	2.42

NOTE: Chemistries in wt. % unless otherwise indicated.

EP 1 127 948 A2

[0045] Small quantities of these materials were re-melted and precision investment cast into both bar and blade configurations.

[0046] Grain and orientation inspections for product that was investment cast yielded satisfactory results. Generally, the aim compositions reported in Table 1 above, resulting in product reported in Table 2, yielded SX cast parts which were single crystal, void of spurious grain and/or sliver indications, free of apparent freckles, possessed orientations generally within 10° of the desired primary (001) crystallographic orientation, and met the compositional requirements.

[0047] Some of the test specimens produced were used to develop appropriate solution heat treatment procedures, with the results reported in Table 3 below. Complete coarse γ' and eutectic γ - γ' solutioning was achieved with a peak solution temperature of 2309°F (1265°C) applied. But variable levels of test specimen recrystallization, occurring during solution heat treatment, was observed. This problem was alleviated by reducing the CMSX-11C alloy peak solution temperature to 2289°F (1254°C), where full γ' solutioning still prevailed.

[0048] Similarly, the other two compositional variants listed in Table 1 (CMSX-11C' and CMSX-11C") were solution treated to a peak temperature of 2289°F (1254°C) with similar results.

[0049] All test specimens were further heat treated by aging initially at 2050°F (1121°C) to encourage a desirable γ' morphology and distribution, followed by secondary ages at 1600°F (871°C) and 1400°F (760°C), respectively (see Table 3 below).

TABLE 3

HEAT TREATMENT			
ALLOY	PEAK SOLUTION TEMP. °F (°C)	% SOLUTIONING	AGING TREATMENT
CMSX-11C	2309 (1265)	100	2050°F/5 Hrs/AC 1600°F/24 Hrs/AC 1400°F/30 Hrs/AC
	and *2289(1254)	100	2050°F/5 Hrs/AC 1600°F/24 Hrs/AC 1400°F/30 Hrs/AC
CMSX-11C' and CMSX-11C"	2289 (1254)	100	2050°F/5 Hrs/AC 1600°F/24 Hrs/AC 1400°F/30 Hrs/AC

NOTE:

* Lower solution temperature chosen to reduce tendency toward SX cast product recrystallization during solution heat treatment.

[0050] Differential Thermal Analysis (DTA) of the VIM heats (reported in Table 2 above) produced respective alloy solidus and liquidus data. The DTA detail is reported in Table 4 below.

TABLE 4

DTA DATA		
HEAT	SOLIDUS °F (°C)	LIQUIDS °F(°C)
VF 998	2296 (1258)	2404 (1318)
VG 33	2298 (1259)	2403 (1317)
VG 110	2305 (1263)	2408 (1320)
VG 113	2300 (1260)	2402 (1317)
VG 148	2302 (1261)	2414 (1323)
VG 175	2306 (1263)	2412 (1322)

[0051] Following heat treatment, test bars were machined and low-stress ground to ASIM standard proportional specimen dimension for subsequent stress - and creep-rupture testing at various conditions of temperature and stress, according to standard ASTM procedure. Specimens removed from solid turbine blades were prepared similarly.

[0052] Table 5 below shows the results of stress - and creep-rupture tests undertaken with the CMSX-11C alloy specimens. The tests were performed at conditions ranging 1400-1900°F (760-1038°C).

[0053] Most of the tests reported in Table 5 were undertaken with alloy originating from the previously detailed heat

EP 1 127 948 A2

R2D2/virgin material blending along with product from heat VF 998. Test results for materials produced with heat VG 33 product are highlighted in Table 5. No rupture tests were performed with product originating from the remaining VIM heats listed in Table 2 above.

TABLE 5

STRESS - AND CREEP-RUPTURE DATA							
CMSX-11C Alloy							
TEST CONDITION	RUPTURE TIME HRS	EL %	RA %	FINAL CREEP READING FINAL CREEP READING		TIME IN HRS TO REACH	
				T, HRS	% DEFORMATION	1.0%	2.0%
1400°F/95.0 ksi (760°C/655 MPa)	681.8	10.8	15.7	681.1	10.331	56.6	215.8
	+627.6	14.3	17.8	-	-	-	-
	+677.4	14.4	17.8	-	-	-	-
	++220.9	5.5	8.0	-	-	-	-
	++321.6	5.5	7.8	-	-	-	-
1600°F/50.0 ksi (871°C/345 MPa)	418.4	8.9	10.7	417.1	7.842	100.8	232.6
	317.7	11.3	17.0	316.5	10.405	97.8	182.2
	977.1	9.2	13.1	975.8	8.550	264.6	553.8
	+294.7	10.6	12.5	-	-	-	-
	+621.3	15.9	16.2	-	-	-	-
1600°F/55.0 ksi (871°C/379 MPa)	++314.3	8.4	9.2	-	-	-	-
	++366.4	5.5	9.2	-	-	-	-
	251.6	7.4	10.8	251.3	6.278	116.6	198.7
	228.6	9.2	18.0	227.3	5.902	123.7	190.9
	**461.8	9.0	13.4	461.1	7.858	154.9	330.1
1650°F/45.0 ksi (899°C/310 MPa)	702.8	11.5	18.9	701.1	9.421	162.7	337.8
	+564.1	12.4	17.6	-	-	-	-
	+645.9	12.7	11.6	-	-	-	-
	++481.9	11.2	12.6	-	-	-	-
	++442.2	9.5	11.4	-	-	-	-
1650°F/45.0 ksi (899°C/310 MPa)	295.2	5.9	10.6	295.1	4.918	186.9	262.7
	336.4	9.6	16.4	334.8	7.288	176.5	275.2
	281.2	8.5	11.8	279.9	6.100	92.9	213.8
	**524.5	9.1	13.8	523.9	6.779	203.2	405.5

+ Machined From Blade Specimen (Airfoil)

++ Machined From Blade Specimen (Transverse Root)

** Heat VG 33 Test Results

EP 1 127 948 A2

TABLE 5 (continued)

STRESS - AND CREEP-RUPTURE DATA							
CMSX-11C Alloy							
TEST CONDITION	RUPTURE TIME HRS	EL %	RA %	FINAL CREEP READING FINAL CREEP READING		TIME IN HRS TO REACH	
				T, HRS	% DEFORMATION	1.0%	2.0%
1652°F/ 21.76 ksi (900°C/150 MPa)	9921.2	7.5	14.8	9912.5	6.107	6329.2	8374.9
	12373.1	8.3	14.7	12366.0	6.474	8976.2	10885.1
1700°F/36.0 ksi (927°C/248 MPa)	871.4	11.2	16.1	869.2	9.409	179.6	451.4
	+ 696.6	16.7	32.3	-	-	-	-
	+745.1	15.6	23.1	-	-	-	-
	++592.3	12.6	13.8	-	-	-	-
	++513.9	12.9	16.4	-	-	-	-
	302.3	11.4	22.1	301.3	7.376	203.5	260.4
	290.8	9.8	21.9	290.6	8.061	197.7	255.8
	**487.6	8.4	15.2	487.5	7.203	263.6	417.4
1750°F/30.0 ksi (954°C/207 MPa)	+473.6	11.8	23.4	-	-	-	-
	+770.6	18.1	30.8	-	-	-	-
	++ 419.3	-	13.8	-	-	-	-
	++526.7	14.1	13.8	-	-	-	-
	1124.8	10.4	11.0	1124.5	7.049	529.5	924.3
	279.5	10.6	23.6	278.1	7.173	190.0	246.5
	** 615.8	5.8	8.9	615.3	5.000	301.1	539.9
	458.4	-	-	-	-	-	-
1750°/ 20.0/30.0 ksi* (954°C/ 138/207 MPa)	2057.9	13.1	26.7	2057.1	11.892	1748.1	1905.7
	1082.1	12.1	32.2	1081.5	9.769	268.4	870.9
1800°F/25.0 ksi (982°C/172 MPa)	+599.7	15.3	29.6	-	-	-	-
	+447.8	16.3	30.4	-	-	-	-
	++367.3	10.7	13.1	-	-	-	-
	++366.6	10.3	14.5	-	-	-	-
	1511.6	4.3	11.6	1511.4	3.403	908.5	1449.1
	577.0	7.8	18.3	575.6	6.239	331.8	524.9

+ Machined From Blade Specimen (Airfoil)

++ Machined From Blade Specimen (Transverse Root)

** Heat VG 33 Test Results

EP 1 127 948 A2

TABLE 5 (continued)

STRESS - AND CREEP-RUPTURE DATA							
CMSX-11C Alloy							
TEST CONDITION	RUPTURE TIME HRS	EL %	RA %	FINAL CREEP READING FINAL CREEP READING		TIME IN HRS TO REACH	
				T, HRS	% DEFORMATION	1.0%	2.0%
1850°F/15.0 ksi (1010°C/172 MPa)	479.2	6.4	14.5	477.7	5.057	266.2	438.1
	571.2	-	-	-	-	-	-
	**1060.8	7.0	19.7	1059.4	5.354	333.9	979.1
	891.4	-	-	-	-	-	-
	Running at 620 Hrs						
	5381.8	7.2	24.8	5381.2	4.066	4671.9	5293.3
	** Running at 3798.8 Hrs., 1.250% Deformation						2134.0
1850°F/25.0 ksi (1010°C/172 MPa)	510.5	6.1	31.3	509.1	4.770	88.3	442.4
	446.2	7.4	32.0	445.1	5.031	57.8	367.2
	518.1	8.1	36.1	579.6	6.184	109.0	457.5
	**734.4	6.7	27.6	733.7	4.302	80.5	662.4
1900°F/18.0 ksi (1038°C/124 MPa)	1904.9	4.9	20.8	1904.6	2.877	1160.2	1888.0
	1981.0	5.9	18.1	1974.9	2.493	104.7	1946.4
	1714.0	4.0	9.4	1711.4	2.875	377.4	1633.7
	**2097.7	5.0	16.4	2094.2	2.412	727.7	2087.0

** Heat VG 33 Test Results

[0054] Selected rupture test specimens were reviewed metallographically following testing. None of the ruptured specimens which were reviewed exhibited any observable signs of undesirable microstructural instability, ie., formation of Topologically-Close-Packed (TCP) phases such as sigma, mu or others.

[0055] Additionally, two test bars were exposed to 1600°F/39.2 ksi (870°C/270 MPa) condition for 200 hours. The respective bar gage sections were then reviewed and no sign of deleterious phase formation was observed.

[0056] Initial Low Cycle Fatigue (LCF) test results are reported in Table 6 below. The results of the strain-controlled tests undertaken at 1112°F (600°C) are compared to the typical capabilities of selected other alloys, such as single crystal CMSX-2 alloy, DS and equiaxed CM 247 LC® alloy and DS René 80 H alloy.

TABLE 6

PLAIN LOW CYCLE FATIGUE	
1112° F (600°C) ; Strain-controlled ($\epsilon_{TOTAL} = 1.106$); R = 0; 0.25 Hz	
Alloy	Cycles to Failure
CMSX-11C	12,130; 7,980
CMSX-2	10,000

EP 1 127 948 A2

TABLE 6 (continued)

PLAIN LOW CYCLE FATIGUE	
1112° F (600°C) ; Strain-controlled ($\epsilon_{TOTAL} = 1.106$); R = 0; 0.25 Hz	
Alloy	Cycles to Failure
DS CM 247 LC d	5,000
DS RENÉ 80 H	1,500
CC CM 247 LC	90

[0057] Concurrent to the previously detailed evaluations, fully heat treated CMSX-11C test specimens were subjected to bare oxidation and hot corrosion testing.

[0058] The results of hot corrosion tests performed are reported in Table 7 below. The tests were undertaken at 1292°F (700°C) and 1472°F (800°C) in a laboratory furnace utilizing an artificial ash plus SO₂. Metal loss data are reported as mean and maximum values, as well as a percentage loss of the test pin employed. Data are reported for intervals of 100, 576 and 1056 hours for the 1292°F (700°C) test, and 100, 576, 1056 and 5000 hours for the 1472°F (800°C) test.

TABLE 7

CMSX-11C HOT CORROSION (crucible test with synthetic slag)			
TEST TEMPERATURE: 700°C (1292°F)			
EXPOSURE TIME (HRS.)	METAL LOSS (microns)		PERCENTAGE METAL LOSS
	MEAN	MAXIMUM	
100	34.5	39	2.70
576	90.5	102	7.05
1056	120.5	143.5	9.27
TEST TEMPERATURE: 800°C (1472°F)			
100	56.5	112.5	4.41
576	366.5	394.5	26.97
1056	2520	2520	100.00
5000	2520	2520	100.00

[0059] Similarly, Figure 1 illustrates the results of additional hot corrosion tests undertaken with CMSX-11C alloy and other alloys to 500 hours exposure in synthetic slag (GTV Type) plus .03 volume percent SO_x in air. The 500 hour tests were undertaken at 1382, 1562, 1652°F, (750, 850 and 900°C). The results indicate that the CMSX-11C alloy provides extremely good corrosion resistance at all three test temperatures.

[0060] Subsequent testing utilizing an alternative slag, type FW, with test temperatures of 1472°F and 1652°F (800, 900°C), was also undertaken. The 500 hour test results are reported in Table 8 below and illustrate a performance benefit derived from the CMSX-11C alloys having a higher chromium content compared to the 12.5% - containing CMSX-11B alloy.

TABLE 8

CMSX-11C Alloy vs. IN 738 LC Alloy vs. CMSX-11B Alloy Hot Corrosion		
Results presented represent depth of penetration after 500 hours exposure in synthetic slag (type FVV) plus 0.03% SO _x in air.		
• Test Temperature - 800°C (1472°F)		
Alloy	Maximum Penetration	Average Penetration
CMSX-11C	160 µm	140 µm

EP 1 127 948 A2

TABLE 8 (continued)

CMSX-11C Alloy vs. IN 738 LC Alloy vs. CMSX-11B Alloy Hot Corrosion		
• Test Temperature - 800°C (1472°F)		
Alloy	Maximum Penetration	Average Penetration
CMSX-11B	350 µm	170 µm
• Test Temperature — 900°C (1652°F)		
Alloy	Maximum Penetration	Average Penetration
CMSX-11C	150 µm	130 µm
IN 738 LC	-	190 µm
CMSX-11B	220 µm	150 µm

[0061] Additional laboratory furnace, crucible type, artificial ash hot corrosion tests were performed. The results of these tests, undertaken at 1350°F (732°C) and 1650°F (899°C), are illustrated in Figures 2 and 3, respectively. In these tests, the specimens were coated with 1 mg./cm² Na₂SO₄ every 100 cycles and were cycled 3 times per day. Both tests were run to about 2400 hours. These results further demonstrate an improved level of hot corrosion resistance obtained with the CMSX-11C alloy vs. the CMSX-11B material.

[0062] Further hot corrosion tests were performed with the CMSX-11C alloy, along with other materials for comparative purposes. In contrast to the aforementioned tests, these hot corrosion evaluations were performed in burner rigs, which is usually a preferred method of testing since the results achieved in burner rig tests generally give more representative indications of the way materials will perform in a gas turbine engine.

[0063] The burner rig tests were performed at 1652°F (900°C) and 1922°F (1050°C), and the test results are reported below in Tables 9 and 10, respectively. The .35 in. (9 mm) diameter x 3.9 in. (100 mm) long test pins utilized were mounted in a rotating cylindrical jig and exposed to a high speed gas stream. Other test conditions were as specified in the respective Tables.

TABLE 9

900°C (1652°F) HOT CORROSION (BURNER RIG.)					
		Weight Loss In Grams As a Function of Time			
ALLOY Hrs.	100	200	300	400	500
CMSX-11B **	.005	.015	.01	-.01	.03
CMSX-11C **	-.04	.005	-.015	-.045	.013
FSX 414 *	.015	.045	.04	.04	.085
RENÉ 80 H *	.075	.275	.365	.46	.495
IN 738 LC *	.015	.08	.10	.15	.195
IN 939 *	-.07	-.09	-.14	-.15	-.06
CM 186 LC *	.08	.195	.30	.395	.44

* DS Columnar

** Single Crystal

CONDITIONS		
1	temperature, time	900°C - 500 hrs (max)
2	burning gas flow rate	6 Nm ³ /min.
3	petroleum flow rate	9 ℓ/hr.
4	salt water	6 cc/min.
5	sulfuric oil	6 cc/min.

TABLE 10

1050°C (1922°F) HOT CORROSION (BURNER RIG.)					
	Weight Loss In Grams As a Function of Time				
ALLOY Hrs.	100	200	300	400	500
CMSX-11B **	0.1	0.7	1.15	2.5	-
CMSX-11C **	0.04	0.05	1.22	1.55	1.65
FSX 414 *	0.2	0.39	0.5	0.65	0.9
RENÉ 80 H *	0.18	0.38	0.47	1.45	1.68
IN 738 LC *	0.1	0.43	1.35	2.09	2.33
IN 939 *	0.1	0.22	0.26	0.45	0.65
CM 186 LC *	0.6	2.9	-	-	13.7

* DS Columnar

** Single Crystal

CONDITIONS				
1	temperature, time	1050° C - 500 hrs (max)		
2	burning gas flow rate	6 Nm ³ /min	SO _x	:257 - 287 ppm
3	petroleum flow rate	18 ℓ/min	NaCl	:17.8 - 18.2 mg/m ³
4	NaCl solution	6 cc/min	Na ₂ SO ₄	:<0.5 mg/m ³
5	sulphuric oil	7 cc/min		

[0064] The results of the tests indicate that the CMSX-11C alloy provided much better hot corrosion resistance than the IN 738 LC alloy at both test temperatures, and also performed superior to the CMSX-11B alloy.

Furthermore, Figure 4 illustrates that CMSX-11C alloy provides an attractive blend of strength and hot corrosion resistance at 1922°F (1050°C), and most notably, outperforms the commercially, widely used DS René 80 H alloy. It is believed that a similar analysis at 900°C would illustrate an even greater blend of capability.

[0065] CMSX-11C alloy oxidation tests were performed concurrent to the hot corrosion tests. Table 11 below reports the results of a crucible oxidation test performed at 1742°F (950°C) for 1000 hour duration within a laboratory furnace. Mean and maximum oxidation depth plus weight gain measurements recorded at 100 and 500 hour intervals are reported, as well as at test completion.

TABLE 11

CMSX-11C HOT OXIDATION			
TEST TEMPERATURE: 950°C (1742°F)			
EXPOSURE TIME (HRS.)	OXIDATION DEPTH (microns)		WEIGHT GAIN (GRAMS)
	MEAN	MAXIMUM	
100	3.6	14.7	1.30E-03
500	5.6	11.9	2.40E-03
1000	8.7	19.6	3.10E-03
5000			

[0066] Slightly higher temperature oxidation test results are presented in Figure 5. The data illustrated are the result of oxidation tests run at 1832°F (1000°C) and to as long as 3000 hour duration. The tests were performed in an air atmosphere, and measured test specimen weight change as a function of time. The test temperature was cycled to room temperature on a once-per-hour basis. The test results indicate that the CMSX-11C alloy provides much better oxidation resistance than IN 738 LC, an alloy which is widely used throughout the industrial turbine industry.

[0067] Further oxidation test results are illustrated in Figure 6. In this particular test, the pins were cycled to room temperature 3 times per day from the 1850°F (1010°C) test temperature, and weight change measured as a function

of time. The test was run to about 2400 hours and the results indicate that the CMSX-11C material provides much better oxidation resistance than the alloy IN 738 LC.

[0068] Burner rig oxidation testing was undertaken at 2192°F (1200°C), with the results presented in Table 12 below. Various alloys were tested within the same rotating carousel. Specimen weight loss was measured at intervals of 100, 200, 300, 400 and 500 hours. Additional test conditions are provided in the Table.

TABLE 12

1200°C (2192°F) OXIDATION (BURNER RIG.)					
	Weight Loss In Grams As a Function of Time				
ALLOY	100	200	300	400	500 Hrs.
CMSX-11R **	.002	.005	.011	.012	.026
CMSX-11C **	.002	.005	.009	.01	.022
FSX 414 *	.02	.077	.085	.12	.125
RENÉ 80 H *	.002	.005	.014	.20	.35
IN 738 LC *	.005	.034	.049	.064	.095
IN 939 *	.016	.038	.064	.077	.113
CM 186 LC *	.002	.01	.01	.015	.013

* DS Columnar

** Single Crystal

CONDITIONS		
1	temperature, time	1200°C - 500 hrs (max)
2	burning gas flow rate	6 Nm ³ /min
3	petroleum flow rate	18 - 20 ℓ/min
4	burning pressure	11 kgf/cm ²

[0069] The burner rig oxidation test results illustrate that the CMSX-11C material provides extremely good 2192°F (1200°C) oxidation resistance in comparison to widely used industrial turbine blade and vane materials.

[0070] An alloy strength and 2192°F (1200°C) oxidation comparrison is illustrated in Figure 7. This Figure illustrates that the CMSX-11C alloy blended capability is superior to directional solidified alloys such as René 80 H, FSX 414, IN 939 and IN 738 LC alloys.

[0071] While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. the appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

Claims

1. A hot corrosion resistant nickel-based superalloy comprising the following elements in percent by weight:

Chromium	about 14.2-15.5
Cobalt	about 2.0-4.0
Molybdenum	about 0.30-0.45
Tungsten	about 4.0-5.0
Tantalum	about 4.5-5.8
Columbium	about 0.05-0.25
Aluminum	about 3.2-3.6
Titanium	about 4.0-4.4
Hafnium	about 0.01-0.06
Nickel + Incidental Impurities	balance

said superalloy having a phasial stability number N_{V3B} less than about 2.45.

2. The superalloy of Claim 1 further comprising the following elements in percent by weight:

Carbon	about 0-0.05
Boron	about 0-0.03
Zirconium	about 0-0.03
Rhenium	about 0-0.25
Silicon	about 0-0.10
Manganese	about 0-0.10

3. The superalloy of Claim 1 wherein the sum of columbium plus hafnium is from 0.06 to 0.31 percent by weight.

4. The superalloy of Claim 1 wherein the Ti:Al ratio is greater than 1.

5. The superalloy of Claim 1 wherein the sum of aluminum plus titanium is from 7.2 to 8.0 percent by weight.

6. The superalloy of Claim 1 wherein Ta:W ratio is greater than 1.

7. The superalloy of Claim 1 wherein said superalloy has an increased resistance to oxidation.

8. A single crystal article made from the superalloy of Claim 1.

9. The single crystal article of Claim 7, wherein the article is a component for a turbine engine.

10. The article of Claim 11, wherein the component is a gas turbine blade or gas turbine vane.

11. A single crystal casting characterized by an increased resistance to hot corrosion, said casting being made from a nickel-based superalloy comprising the following elements in percent by weight:

Chromium	14.3-15.0
Cobalt	2.5-3.5
Molybdenum	0.35-0.43
Tungsten	4.2-4.8
Tantalum	4.8-5.4
Columbium	0.05-0.12
Aluminum	3.3-3.5
Titanium	4.1-4.3
Hafnium	0.02-0.05
Nickel + Incidental Impurities	balance

said superalloy having a phasial stability number N_{V3B} less than about 2.45.

12. The single crystal casting of Claim 10 further comprising the following elements in percent by weight:

Carbon	0-0.05
Boron	0-0.03
Zirconium	0-0.03
Rhenium	0-0.25
Silicon	0-0.10
Manganese	0-0.10.

13. The single crystal casting of Claim 10 wherein the sum of columbium plus hafnium is from 0.06 to 0.31 percent by weight.

EP 1 127 948 A2

14. The single crystal casting of Claim 10 wherein the sum of aluminum plus titanium is from 7.2 to 8.0 percent by weight.

15. The single crystal casting of Claim 10 wherein both the Ti:Al ratio and the Ta:W ratio are greater than 1.

16. The single crystal casting of Claim 10 wherein said casting has an increased resistance to oxidation.

17. The single crystal casting of Claim 10 wherein said casting has an increased creep-rupture strength.

18. The single crystal casting of Claim 10 wherein said casting is a gas turbine blade or gas turbine vane.

19. A single crystal casting characterized by an increased resistance to hot corrosion, said casting being made from a nickel-based superalloy comprising the following elements in percent by weight:

Chromium	about 14.5
Cobalt	about 3.0
Molybdenum	about 0.40
Tungsten	about 4.4
Tantalum	about 4.95
Columbium	about 0.10
Aluminum	about 3.40
Titanium	about 4.2
Hafnium	about 0.04
Carbon	about 0-0.05
Boron	about 0-0.03
Zirconium	about 0-0.03
Rhenium	about 0-0.25
Silicon	about 0-0.10
Manganese	about 0-0.10
Nickel	balance

said superalloy having a phasial stability number N_{V3B} less than about 2.45, wherein the sum of columbium plus hafnium is from 0.06 to 0.31 percent by weight, the sum of aluminum plus titanium is from 7.2 to 8.0 percent by weight, the Ti:Al ratio is greater than 1, and the Ta:W ratio is greater than 1.

20. The single crystal casting of Claim 18 wherein said casting is a gas turbine blade or gas turbine vane.

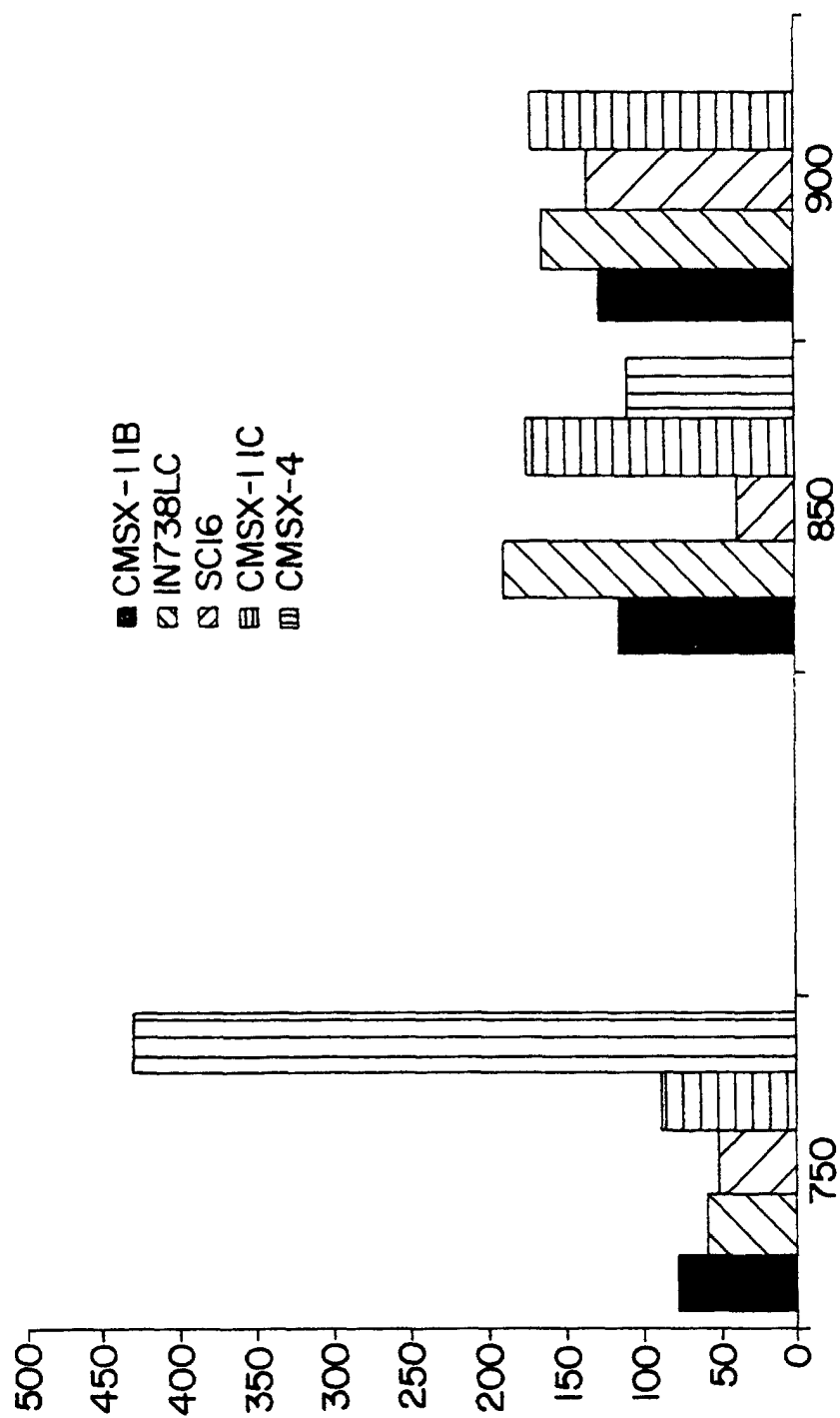


FIG. 1

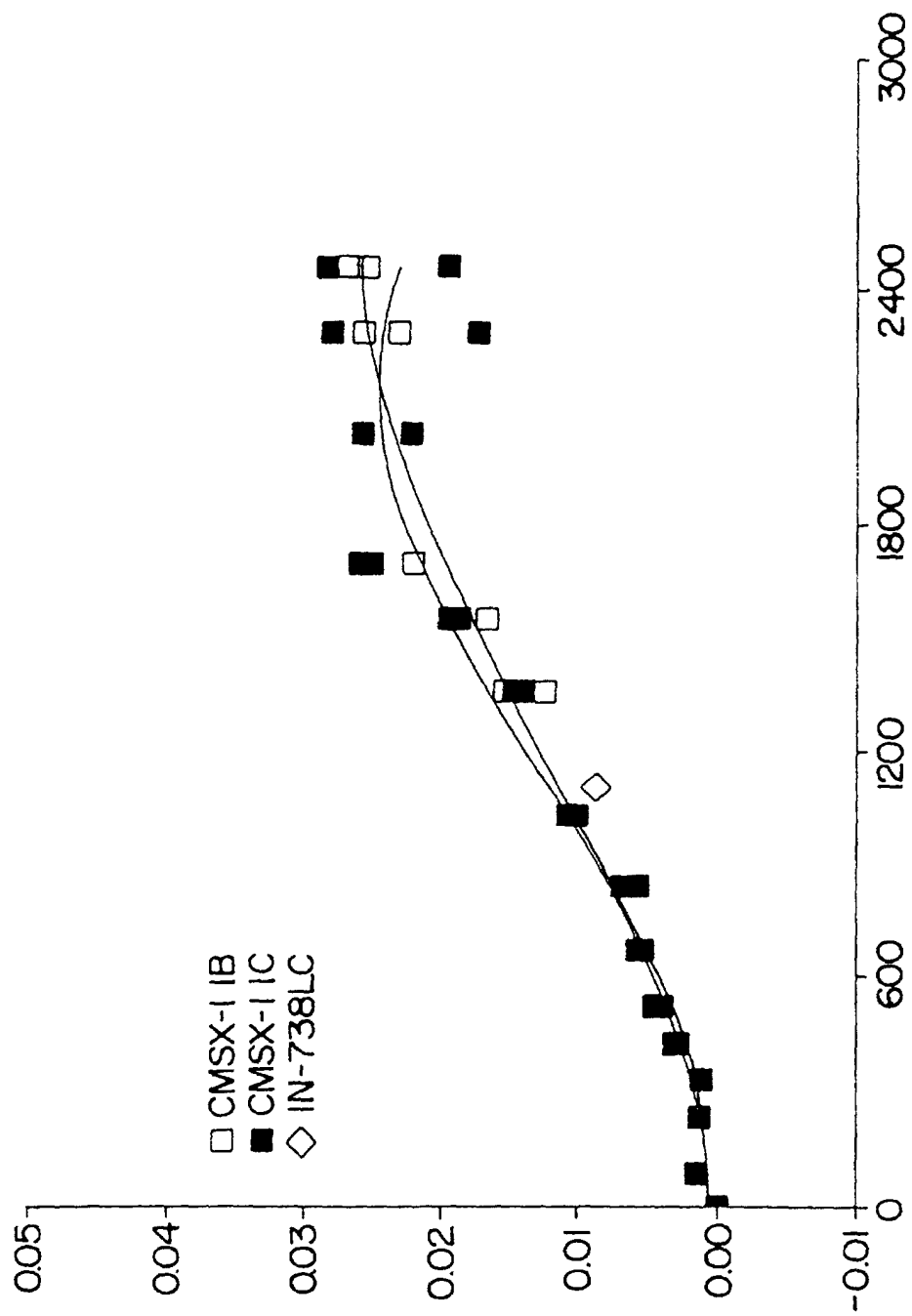


FIG. 2

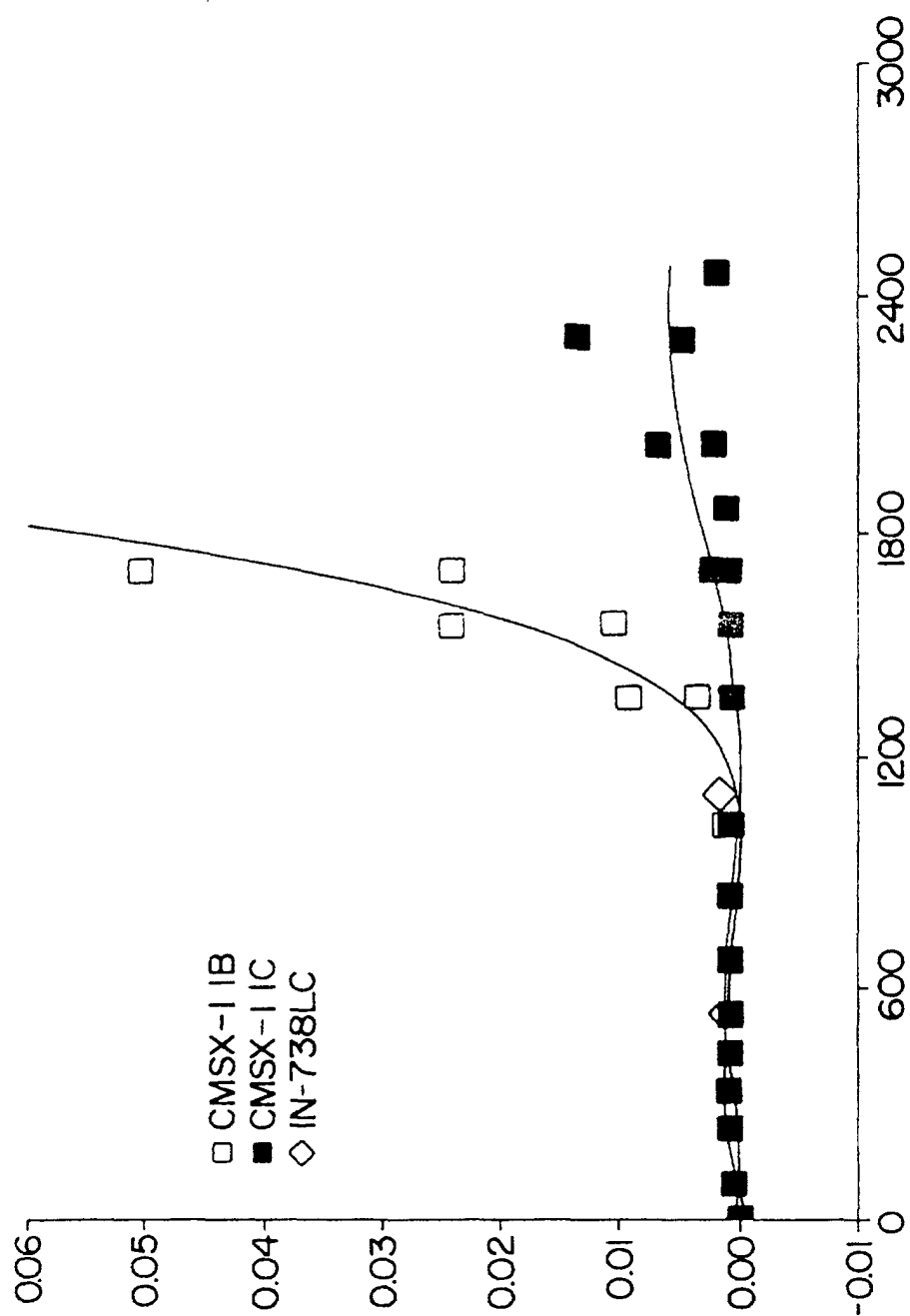


FIG. 3

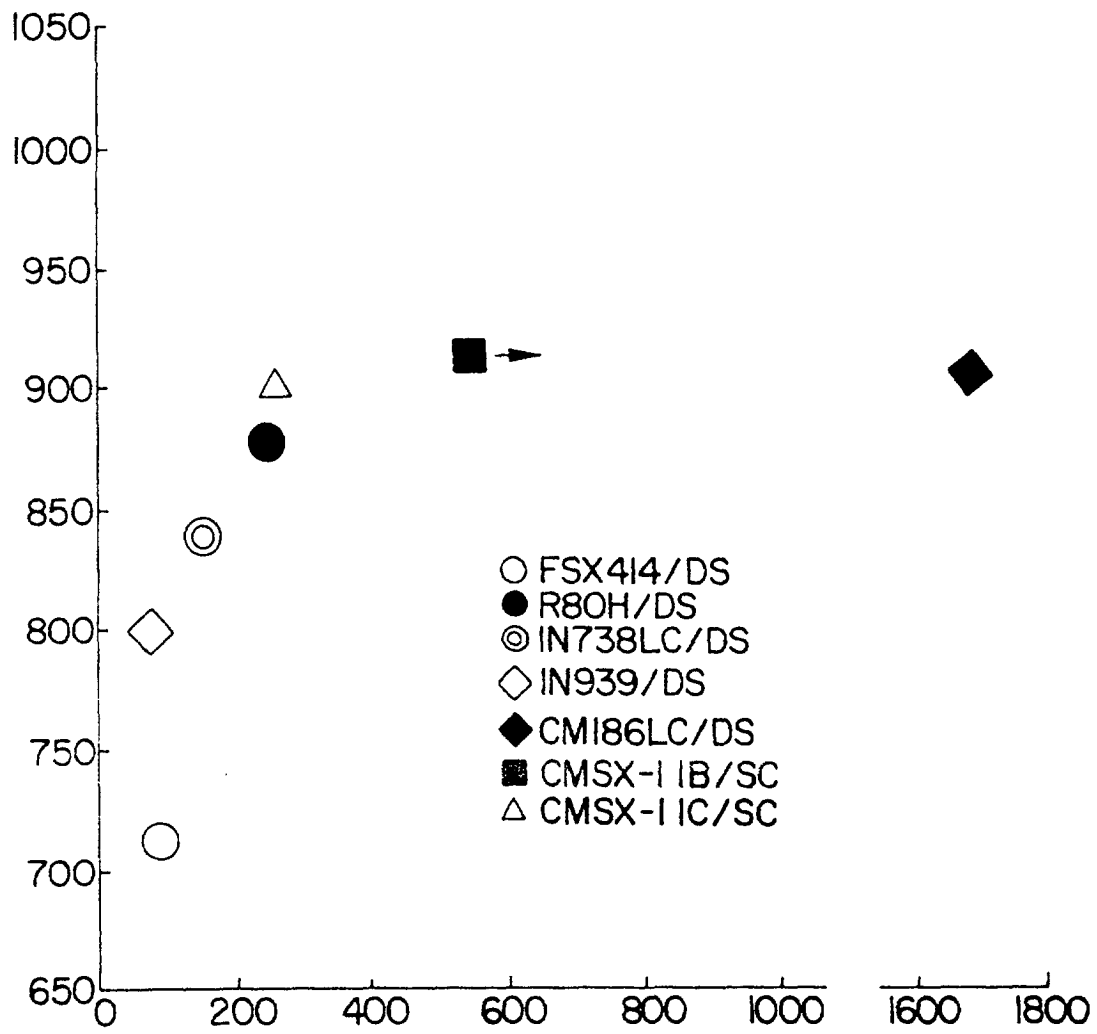


FIG. 4

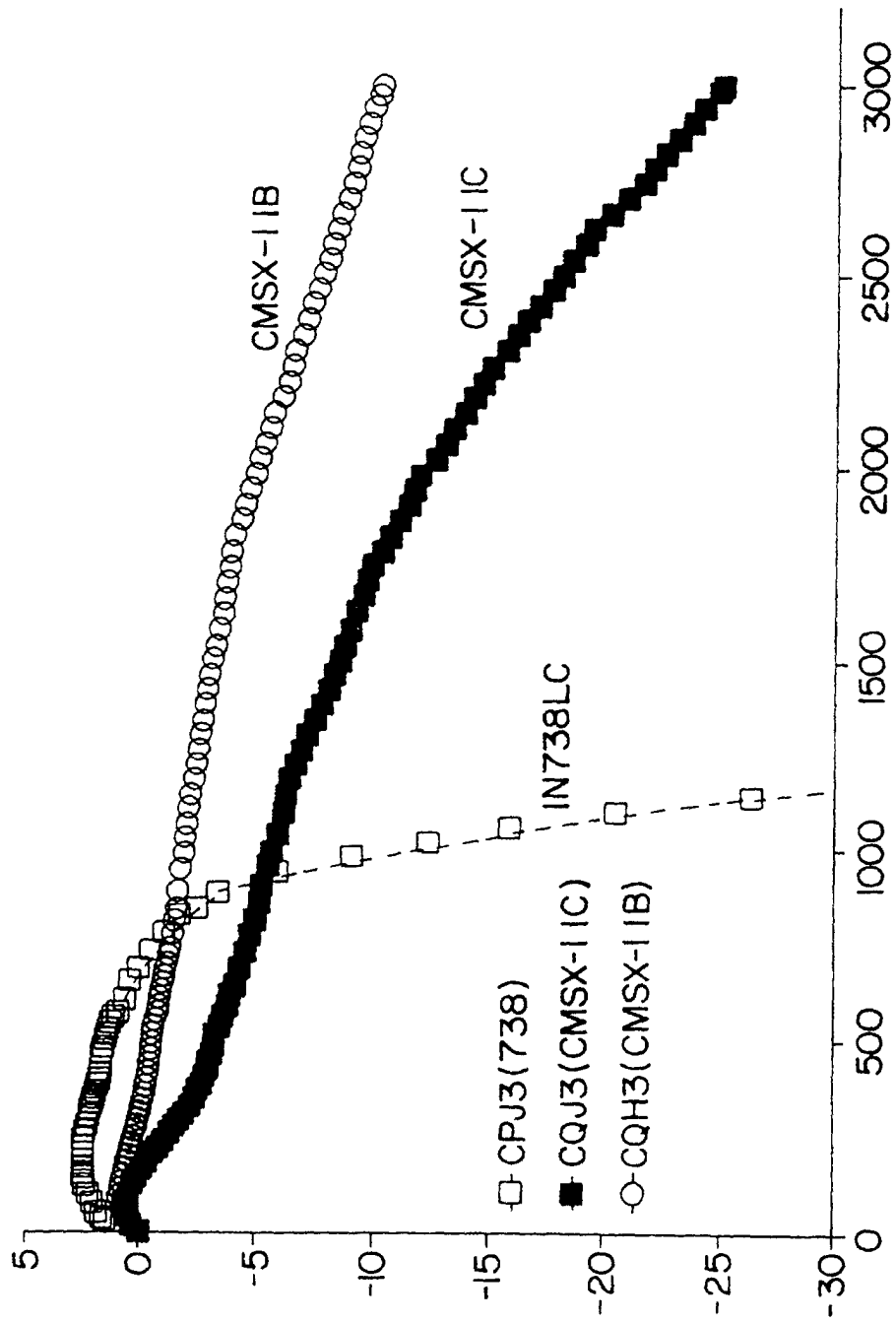


FIG. 5

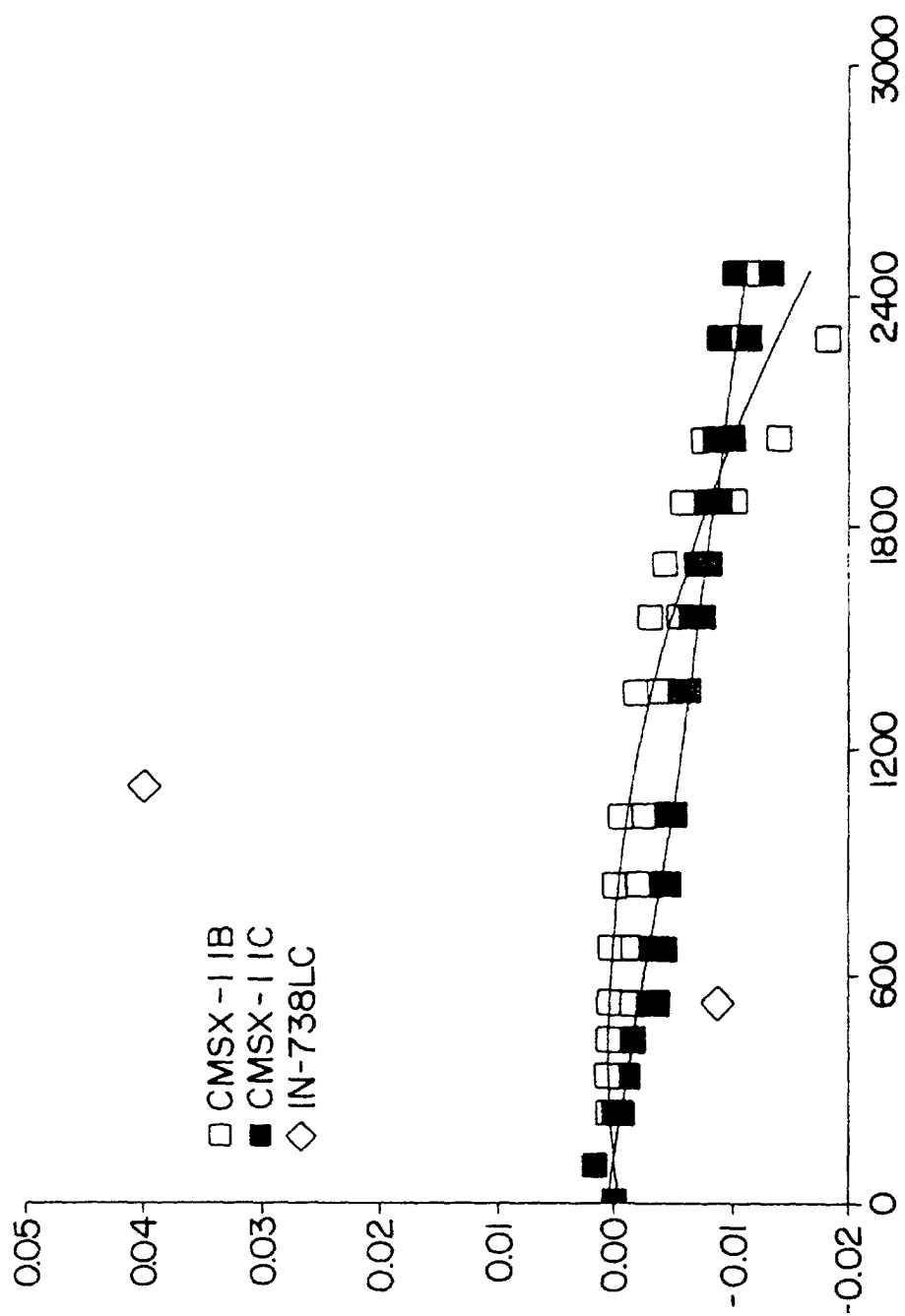


FIG. 6

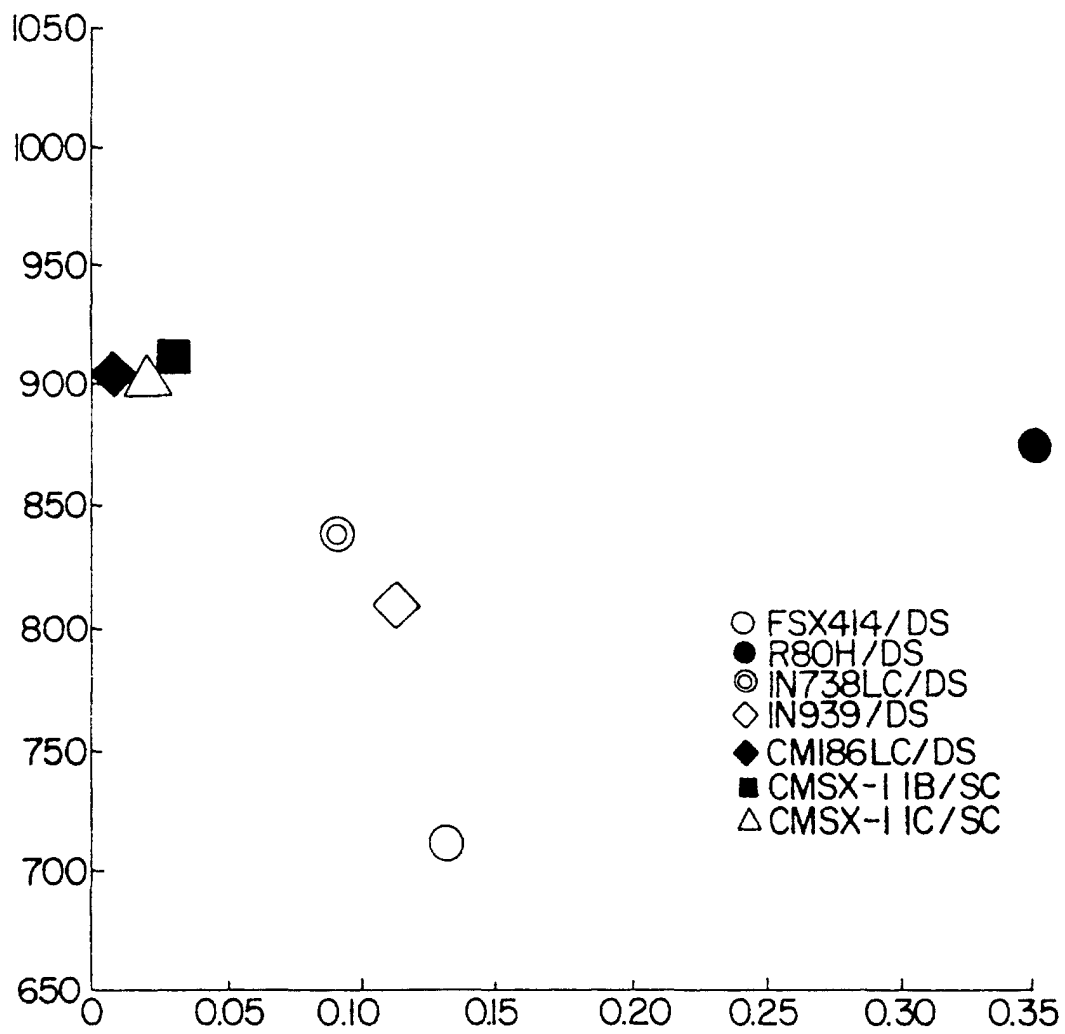


FIG. 7