

(19)



(11)

**EP 2 612 936 B9**

(12)

**CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:

**Corrected version no 1 (W1 B1)**  
**Corrections, see**  
**Description Paragraph(s) 27**

(51) Int Cl.:

**C22C 19/05** (2006.01)      **F01D 5/00** (2006.01)

(48) Corrigendum issued on:

**25.01.2017 Bulletin 2017/04**

(45) Date of publication and mention of the grant of the patent:

**27.04.2016 Bulletin 2016/17**

(21) Application number: **12174283.7**

(22) Date of filing: **29.06.2012**

**(54) Rhenium-free single crystal superalloy for turbine blades and vane applications**

Rheniumfreie Einzelkristall-Superlegierung für Turbinenschaufeln und Schaufelanwendungen

Superalliage monocristallin exempt de rhénium pour aubes de turbine et des applications d'aubes

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB**  
**GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO**  
**PL PT RO RS SE SI SK SM TR**

(30) Priority: **17.11.2011 US 201113298879**

(43) Date of publication of application:

**10.07.2013 Bulletin 2013/28**

(73) Proprietor: **CANNON-MUSKEGON CORPORATION**

**Muskegon, Michigan 49441 (US)**

(72) Inventors:

- **Harris, Kenneth**  
**Spring Lake, MI Michigan 49456 (US)**
- **Wahl, Jacqueline B.**  
**Norton Shores, MI Michigan 49441 (US)**

(74) Representative: **Grünecker Patent- und Rechtsanwälte**

**PartG mbB**  
**Leopoldstraße 4**  
**80802 München (DE)**

(56) References cited:

**EP-A1- 2 305 848**

- **HARRIS K ET AL: "DEVELOPMENT OF TWO RHENIUM-CONTAINING SUPERALLOYS FOR SINGLE-CRYSTAL BLADE AND DIRECTIONALLY SOLIDIFIED VANE APPLICATIONS IN ADVANCED TURBINE ENGINES", JOURNAL OF MATERIALS ENGINEERING AND PERFORMANCE, ASM INTERNATIONAL, MATERIALS PARK, OH, US, vol. 2, no. 4, 1 August 1993 (1993-08-01), pages 481-487, XP000394071, ISSN: 1059-9495**

**EP 2 612 936 B9**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description**FIELD

5 **[0001]** Disclosed are single crystal nickel-base superalloys exhibiting excellent high temperature creep resistance, while being substantially free of rhenium, without deleteriously affecting other relevant characteristics.

BACKGROUND

10 **[0002]** Because of a worldwide growing demand for products that have customarily required substantial quantities of relatively scarce metal elements, both the demand and prices of rare metal elements have sharply increased. As a result, manufacturers are searching for new technologies that will reduce or eliminate the need for these metal elements.

**[0003]** Rhenium is an example of a truly rare metal that is important to various industries. It is recovered in very small quantities as a by-product of copper-molybdenum and copper production. In addition to its high cost, use of rhenium presents a supply chain risk of both economic and strategic consequence.

15 **[0004]** Rhenium has been widely employed in the production of nickel-base superalloys used to cast single crystal gas turbine components for jet aircraft and power generation equipment. More specifically, rhenium is used as an alloying additive in advanced single crystal superalloys for turbine blades, vanes and seal segments, because of its potent effect at slowing diffusion and thus slowing creep deformation, particularly at high temperatures (e.g., in excess of 1,000 degrees C) for sustained periods of time. High temperature creep resistance is directly related to the useful service life of gas turbine components and engine performance such as power output, fuel burn and carbon dioxide emissions.

20 **[0005]** Typical nickel-base superalloys used for single crystal castings contain from about 3% rhenium to about 7% rhenium by weight. Although rhenium has been used as only a relatively minor additive, it has been regarded as critical to single crystal nickel-base superalloys to inhibit diffusion and improve high temperature creep resistance, it adds considerable to the total cost of these alloys.

25 **[0006]** From the foregoing discussion, it is apparent that it would be extremely desirable to develop single crystal nickel-base superalloys that exhibit excellent high temperature creep resistance, while reducing or eliminating the need for rhenium additions, and while retaining other desirable properties such as good castability and phase stability.

30 **[0007]** EP-A-2305848 discloses rhenium-free nickel-base superalloys comprising preferred levels and ratios of elements so as to achieve good high temperature strength of both gamma matrix phase and gamma prime precipitates, as well as good environmental resistance.

SUMMARY

35 **[0008]** The rhenium-free single crystal nickel-base superalloys disclosed herein rely on, among other things, balancing the refractory metal elements (tantalum, tungsten and molybdenum) at a total amount of about 17% to 20% in order to achieve good creep-rupture mechanical properties along with acceptable alloy phase stability, in particular, ensuring freedom from excessive deleterious topological close-packed (TCP) phases that are rich in tungsten, molybdenum and chromium, while substantially eliminating rhenium from the alloy.

40 **[0009]** The present invention provides:

(1) A nickel-base superalloy for single crystal casting comprising:

45 5.60% to 5.85% aluminum by weight;  
9.4% to 9.9% cobalt by weight;  
5.0% to 6.0% chromium by weight;  
0.08% to 0.35% hafnium by weight;  
0.50% to 0.70% molybdenum by weight;  
8.0% to 9.0% tantalum by weight;  
50 0.60% to 0.90% titanium by weight;  
8.5% to 9.8% tungsten by weight; and  
the balance comprising nickel and minor amounts of optional elements, the total amount of optional elements being 1% or less by weight,  
wherein the optional elements are controlled to maximums of 100 ppm carbon, 0.04% silicon, 0.01 % manganese,  
55 3 ppm sulfur, 30 ppm phosphorous, 30 ppm boron, 0.1 % niobium, 150 ppm zirconium, 0.15% rhenium, 0.01% copper, 0.15% iron, 0.1% vanadium, 0.1 % ruthenium, 0.15% platinum, 0.15 % palladium, 200 ppm magnesium, 5 ppm nitrogen, 5 ppm oxygen, 2 ppm silver, 0.2 ppm bismuth, 10 ppm gallium, 25 ppm calcium, 1 ppm lead, 0.5 ppm selenium, 0.2 ppm tellurium, 0.2 ppm thallium, 10 ppm tin, 2 ppm antimony, 2 ppm arsenic, 5 ppm zinc,

## EP 2 612 936 B9

2 ppm mercury, 2 ppm cadmium, 2 ppm germanium, 2 ppm gold, 2 ppm indium, 20 ppm sodium, 10 ppm potassium, 10 ppm barium, 2 ppm uranium, lanthanum and yttrium in a total amount of 5 to 80 ppm, and 2 ppm thorium.

- 5 (2) A nickel-base superalloy for single crystal casting according to item (1), said nickel-base superalloy containing a maximum amount of sulfur of 0.5 ppm, and further comprising an amount of lanthanum and yttrium that is targeted to achieve a total lanthanum and yttrium content that is from 5 ppm to 80 ppm in a single crystal casting.
- (3) A nickel-base superalloy for single crystal casting according to item (1), having a density of about 8.8 gms/cc (kg/dm<sup>3</sup>).
- 10 (4) A single crystal component cast from an alloy according to any one of items (1) to (3).
- (5) A single crystal component according to item (4) that is a gas turbine component.
- (6) A single crystal component according to item (4) that is a blade, a vane, or a seal segment for a gas turbine.

15 **[0010]** In accordance with certain embodiments in which enhanced oxidation resistance and/or coating and thermal barrier coating (TBC) life are desired, sulfur is present at a maximum amount of 0.5 ppm, and lanthanum and yttrium are added to target an amount of total lanthanum and yttrium of from 5 ppm to 80 ppm in single crystal components cast from the alloy.

20 **[0011]** In addition to achieving excellent high temperature creep resistance in a substantially rhenium-free composition, certain embodiments of the disclosed single crystal nickel-base superalloys have a desirably not excessive density that is about 8.8 gms/cc or less, such as 8.79 gms/cc (kg/dm<sup>3</sup>).

### BRIEF DESCRIPTION OF THE DRAWINGS

#### **[0012]**

25 Figs. 1A, 1B and 1C are optical micrographs showing the fully heat treated microstructure of castings of a disclosed embodiment (LA-11753, CMSX-7, test bar #C912, fully heat treated, primary age 2050°F/4 hours).

Figs. 2A, 2B and 2C are scanning electron micrographs of the microstructure of fully heat treated castings from embodiments disclosed herein (LA-11753, CMSX-7, test bar #C912, fully heat treated, primary age 2050°F/4 hours).

30 Figs. 3, 4 and 5 are Larson-Miller stress-rupture graphs showing the surprisingly good creep strength and/or stress-rupture life properties of single crystal test bars and turbine blade castings made from the disclosed alloys.

Figs. 6A, 6B and 6C are optical micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #D912, 2050°F/15 ksi/141.6 hours, gage area).

35 Figs. 7A, 7B and 7C are scanning electron micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #D912, 2050°F/15 ksi/141.6 hours, gage area).

Figs. 8A, 8B and 8C are optical micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11807, CMSX-7, mini-flat #53701Y-F, 2000°F/12 ksi/880.0 hours, gage area).

40 Figs. 9A, 9B and 9C are scanning electron micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11807, CMSX-7, mini-flat #53701Y-F, 2000°F/12 ksi/880.0 hours, gage area).

Figs. 10A, 10B and 10C are optical micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #B913, 1800°F/36 ksi/151.1 hours, gage area).

45 Figs. 11A, 11B and 11C are scanning electron micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #B913, 1800°F/36 ksi/151.1 hours, gage area).

Figs. 12A, 12B and 12C are optical micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #A912, 1562°F/94.4 ksi/100.9 hours, gage area).

50 Figs. 13A, 13B and 13C are scanning electron micrographs showing the post-test phase stability of the disclosed alloys, which exhibit excellent phase stability and no TCP phases (LA-11772, CMSX-7, test bar #A912, 1562°F/94.4 ksi/100.9 hours, gage area).

55 Figs. 14A, 14B and 14C are optical micrographs showing the fully heat treated microstructures of CMSX-7 MOD B single crystal test bars.

Figs. 15A, 15B and 15C are scanning electron micrographs showing the fully heat treated microstructures of CMSX-

## EP 2 612 936 B9

7 MOD B single crystal test bars.

Fig. 16 is a drawing in cross section of a single crystal solid turbine blade cast from an alloy as disclosed herein which has the facility to machine both mini-bar and mini-flat specimens for machined-from-blade (MFB) stress-rupture testing.

Figs. 17 and 18 show the tensile properties of the alloys versus test temperature.

Figs. 19A, 19B and 19C are optical micrographs showing post test microstructures from a long term, high temperature stress-rupture test of an alloy as disclosed herein (LA-11891, CMSX-7 MOD. B, test bar #M923, 2000°F/12 ksi/1176.5 hours).

Figs. 20A, 20B and 20C are scanning electron micrographs showing post test microstructures from a long term, high temperature stress-rupture test of an alloy as disclosed herein (LA-11891, CMSX-7 MOD. B, test bar #M923, 2000°F/12 ksi/1176.5 hours).

### DETAILED DESCRIPTION

**[0013]** The alloys disclosed herein will be referred to as "CMSX®-7" alloys. This is the designation that will be used commercially, the expression "CMSX" being a registered trademark of the Cannon-Muskegon Corporation used in connection with the sale of a family or series of nickel-base single crystal (SX) superalloys.

**[0014]** The alloys disclosed herein are alternatively described as being rhenium-free, or substantially free of rhenium. As used herein, these terms means that the alloys do not contain any added rhenium and/or that the amount of rhenium present in the alloy is a maximum of 0.15% by weight.

**[0015]** Unless otherwise indicated, all percentages are by weight, and all amounts in parts per million (ppm) refer to parts per million by weight based on the total weight of the alloy composition.

**[0016]** Single crystal superalloys and castings have been developed to exhibit an array of outstanding properties including high temperature creep resistance, long fatigue life, oxidation and corrosion resistance, solid solution strengthening, with desired casting properties and low rejection rates, and phase stability, among others. While it is possible to optimize a single additive alloying elements for a particular property, the effects on other properties are often extremely unpredictable. Generally, the relationships among the various properties and various elemental components are extremely complex and unpredictable such that it is surprising when a substantial change can be made to the composition without deleteriously affecting at least certain essential properties.

**[0017]** With the embodiments disclosed herein, refractory metal elements (tantalum, tungsten and molybdenum) were maintained at a total amount of from about 17% to about 20% by weight, while balancing the amounts of the refractory elements to achieve good creep-rupture mechanical properties along with acceptable alloy phase stability (freedom from excessive deleterious topological close-packed (TCP) phase - normally tungsten, molybdenum and chromium rich in this type of alloy). Chromium and cobalt were also adjusted to ensure the required phase stability. The high amount of tantalum (approximately 8%) was selected to provide excellent single crystal castability, such as freedom from "freckling" defects. The amount of titanium (approximately 0.8%) and tantalum (approximately 0.8%) were adjusted to provide low negative  $\gamma/\gamma'$  mismatch for high temperature creep strength and acceptable room temperature density (e.g., about 8.8 gms/cc, such as 8.79 gms/cc). Aluminum, titanium and tantalum were adjusted to attain a suitable  $\gamma'$  volume fraction (Vf), while the combination of aluminum, molybdenum, tantalum and titanium were selected to provide good high temperature oxidation resistance properties. The amount of hafnium addition was selected for coating life attainment at high temperatures.

**[0018]** Typical chemistry for the alloys disclosed and claimed herein are listed in Table 1. However, there are certain minor variations. In order to achieve enhanced oxidation resistance and/or enhanced thermal barrier coating life, it is desirable to add lanthanum and/or yttrium in amounts such that the total of lanthanum and yttrium is targeted to provide from about 5 to 80 ppm in the single crystal castings made from the alloys.

**[0019]** The invention will be described with respect to certain illustrative, non-limiting embodiments that will facilitate a better understanding.

**[0020]** A 400 lb 100% virgin initial heat of CMSX®-7 alloy was melted in January 2011 in the CM V-5 Consarc VIM furnace using air chemistry to CM KH 01/03/11 (CM CRMP #81-1700 Issue 1). The heat (5V0424) chemistry is shown in Table 2.

**[0021]** Two molds (#s 912 and 913) of SX NNS DL-10 test bars were cast to CMSX-4® casting parameters by Rolls-Royce Corporation (SCFO). DL-10 test bar yield at 23 fully acceptable out of a total 24 cast was excellent. A mold (#53701) of solid HP2 turbine blades were also SX cast by SCFO using CMSX-4® casting parameters with typical casting yields for this production component.

**[0022]** These DL-10 test bars and turbine blades were solutioned/homogenized + double aged heat treated at CM as follows - based on solutioning/homogenization studies on CMSX®-7 test bars.

Solution + Homogenization

- 2 hrs / 2340°F (1282°C) + 2 hrs / 2360°F (1293°C)  
 + 4 hrs / 2380°F (1304°C) + 4 hrs / 2390°F (1310°C)  
 + 12 hrs / 2400°F (1316°C) AC - ramping up at 1°F / min. between steps
- Double Age  
 4 hrs / 2050°F (1121°C) AC + 20 hrs / 1600°F (871°C) AC

**[0023]** Acceptable microstructure attainment is evident in Figs 1-2 - complete  $\gamma'$  solutioning, some remnant  $\gamma/\gamma'$  eutectic, no incipient melting and approximately 0.5  $\mu\text{m}$  average cubic, aligned  $\gamma'$ , indicating appropriate  $\gamma/\gamma'$  mis-match and  $\gamma/\gamma'$  inter-facial chemistry, following the 4 hr / 2050°F (1121 °C) high temperature age.

**[0024]** Creep - and stress-rupture specimens were low stress ground and tested by Joliet Metallurgical Labs, with the results to date shown in Table 3 and Table 4. Larson-Miller stress-rupture graphs (Figs. 3, 4 & 5) show CMSX®-7 has superior and surprisingly good creep strength / stress-rupture life properties, including machined-from-blade (MFB) 0.070"  $\varnothing$  mini-bar results, compared to CMSX-2/3® alloy (zero Re) up to approximately 1900°F (1038°C), with similar properties at 2050°F (1121°C). All these properties are surprisingly similar to Rene' N-5 (3% Re) and Rene' N-515 (1.5% Re) alloys (Published GE data) [JOM 62 No 1, pgs 55-57 Jan 2010]. MFB stress-rupture testing was performed on single crystal solid turbine blades 10 (Fig. 16) cast from alloys as disclosed herein which have facility to machine mini-bars 15 and mini-flat specimens 20.

**[0025]** Phase stability is surprisingly good with absolutely no TCP phases apparent in the post-test creep/stress rupture bars examined to date (Figs. 6-13 inclusive).

**[0026]** Burner rig dynamic, cyclic oxidation and hot corrosion (sulfidation) testing is currently scheduled at a major turbine engine company. The MFB 0.020" thick gage mini-flat results at 12 ksi/2000°F (Table 4, Fig. 5) indicate good bare high temperature oxidation resistance for this alloy.

CMSX-7 Tensile Properties

**[0027]** The alloy shows very high tensile strength (up to 200 ksi (1379 MPa) UTS at 1400°F (760°C)) and 0.2% proof stress (up 191 ksi (1318 MPa) at the same temperature and good ductility (Table 5, Figs 17 & 18). The exceptionally high UTS and 0.2% PS at 1400°F (760°C) indicates strain hardening at this temperature, possibly due to further secondary or tertiary  $\gamma'$  precipitation in the  $\gamma$  channels at this temperature impeding dislocation movement - the ductility at this maximum strength level is in the range of 13% elongation (4D) and 17% reduction in area (RA).

Table 1  
CHEMISTRY (WT% / ppm) SPECIFICATIONS CMSX®-7 ALLOY

• Aero engine Applications

C	100 ppm	Ti	.60-.90
Si	.04% Max	W	8.5 - 9.8
Mn	.01% Max	Zr	150 ppm Max
S	3 ppm Max	Re	.15% Max
Al	5.60 - 5.85	Cu	.01% Max
B	30 ppm Max	Fe	.15% Max
Cb (Nb)	.10% Max	V	.10% Max
Co	9.4 - 9.9	Ru	.10% Max
Cr	5.0-6.0	Pt	.15% Max
Hf	.08 - .35	Pd	.15% Max
Mo	.50 - .70	Mg	200 ppm Max
Ni	Balance	[N]	5 ppm Max
Ta	8.0-9.0	[O]	5 ppm Max

• Enhanced oxidation resistance/coating and thermal barrier coating (TBC) life

S	0.5 ppm max
La + Y	5 - 80 ppm (In the SX castings).

**EP 2 612 936 B9**

(continued)

TRACE ELEMENT CONTROLS - ALL APPLICATIONS

5	Ag	2 ppm Max	Hg	2 ppm Max
	Bi	.2 ppm Max	Cd	2 ppm Max
	Ga	10 ppm Max	Ge	2 ppm Max
	Ca	25 ppm Max	Au	2 ppm Max
	Pb	1 ppm Max	In	2 ppm Max
10	Se	.5 ppm Max	Na	20 ppm Max
	Te	.2 ppm Max	K	10 ppm Max
	Tl	.2 ppm Max	Ba	10 ppm Max
	Sn	10 ppm Max	P	30 ppm Max
	Sb	2 ppm Max	U	2 ppm Max
15	As	2 ppm Max	Th	2 ppm Max
	Zn	5 ppm Max		

Density: 8.79 gms/cc.

20

Table 2

**HEAT #5V0424 CMSX®-7 - 100% VIRGIN CHEMISTRY (WT ppm / %)**

	C	17 ppm	Re	< .05
	Si	< .02	Cu	< .001
25	Mn	< .001	Fe	.012
	S	1 ppm	V	< .005
	Al	5.80	Ru	< .01
	B	< 20 ppm	Pt	< .001
	Cb (Nb)	<.05	Pd	< .001
30	Co	9.7	Mg	< 100 ppm
	Cr	5.8	[N]	3 ppm
	Hf	.29	[O]	2 ppm
	Mo	.60	Y	< .001
35	Ni	Balance	La	< .001
	Ta	8.6	Ce	< .002
	Ti	.82		
	W	9.0		
40	Zr	< 25 ppm		

40

	Ag	< .4 ppm
	Bi	< .2 ppm
	Ga	< 10 ppm
45	Ca	< 25 ppm
	Pb	< .5 ppm
	Se	< .5 ppm
	Te	< .2 ppm
	Tl	< .2 ppm
50	Sn	< 2 ppm
	Sb	< 1 ppm
	As	< 1 ppm
	Zn	< 1 ppm
55	Hg	< 2 ppm
	Cd	< .2 ppm
	Ge	< 1 ppm
	Au	< .5 ppm

55

EP 2 612 936 B9

(continued)

**HEAT #5V0424 CMSX®-7 - 100% VIRGIN CHEMISTRY (WT ppm / %)**

5	In	< .2 ppm
	Na	< 10 ppm
	K	< 5 ppm
	Ba	< 10 ppm
	P	6 ppm
10	U	< .5 ppm
	Th	< 1 ppm

Table 3

**CMSX-7 Heat 5V0424**

Molds 912/913 (DL-10s) - RR SCFO [Indy] - LA 11753 (Joliet 8935/CM-354)

K912/L912 - LA 11773 (Joliet 8979/CM-356)

Fully Heat Treated - Solution + double age - 2050°F primary age

**Creep-Rupture**

Test Condition	ID	Rupture Life, hrs	% Elong	% RA	Time to 1% Creep	Time to 2% Creep
1562°F/94.4 ksi	A912	100.9	22.4	28.8	5.9	19.8
[850°C/651 MPa]	A913	100.8	18.4	27.3	7.0	22.3
1800°F/36.0 ksi	B912	147.2	41.8	14.7	58.4	71.1
[982°C/248 MPa]	B913	151.1	44.6	49.6	58.4	70.4
1922°F/27.6 ksi	C912	53.9	43.6	46.9	19.3	24.4
[1050°C/190 MPa]	C913	46.0	37.1	49.7	15.8	20.6
1950°F/18.0 ksi	L912	224.9	37.0	62.3	92.4	112.3
[1066°C/124 MPa]						
2000°F/12.0 ksi	K912	860.3	22.1	54.5	538.1	607.2
[1093°C/83 MPa]						

**Stress-Rupture**

Test Condition	ID	Rupture Life, hrs	% Elong	% RA
2050°F/15.0 ksi	D912	141.6	32.4	52.6
[1121°C/103 MPa]	E912	130.2	31.4	55.0

Machining and Testing Source: Joliet Metallurgical Laboratory

Table 4

**CMSX®-7 Heat 5V0424**

Mold 53701 - HP2 Solid Turbine Blades RR SCFO [Indy] - LA 11773 (Joliet 8980/CM- 357)

Fully Heat Treated - Solution + double age - 2050°F primary age

**MFB (LLE)**

**Stress-Rupture**

Mini Bars [0.070" Ø Gage, shown in Fig. 16]

Test Condition	ID	Rupture Life, hrs	% Elong	% RA
1562°F/72.5 ksi [850°C/500 MPa]	53701U-B	783.4	33.3	28.9
1600°F/65.0 ksi [871°C/448 MPa]	53701V-B	437.9	32.8	33.7
1800°F/40.0 ksi [982°C/276 MPa]	53701S-B	84.1	39.5	47.8
1850°F/38.0 ksi [1010°C/262 MPa]	53701T-B	43.2	38.5	37.8
1900°F/25.0 ksi [1038°C/172 MPa]	53701Y-B	105.8	36.1	28.5
1904°F/21.0 ksi [1040°C/145 MPa]	53701Z-B	238.4	59.3	44.5

**EP 2 612 936 B9**

(continued)

**MFB (LTE)**

**Mini Flats [0.020" Thick Gage, shown in Fig. 16]**

Test Condition	ID	Rupture Life, hrs	% Elong
1800°F/30.0 ksi [982°C/207 MPa]	53701S-F	387.3	42.7
	53701T-F	344.4	35.0
1904°F/21.0 ksi [1040°C/145 MPa]	53701U-F	219.8	38.1
	53701V-F	189.5	33.3
2000°F/12.0 ksi [1093°C/83 MPa]	53701Y-F	880.0	32.4
	53701Z-F	578.8	13.9

Machining and Testing Source: Joliet Metallurgical Laboratory

Table 5

**CMSX-7 - Heat 5V0424**

Molds 063/064 - RR SCFO [Indy] - LA 11753 (Joliet 8935/CM-354)

Fully Heat Treated - Solution + Double Age - 2050°F Primary Age

**TENSILE TEST RESULTS**

Test Temperature	ID	0.2% PS (ksi)	UTS (ksi)	% Elong (4D)	% RA
70°F (21°C)	A063	135.1	154.6	11.4	13.1
	A064	129.1	168.1	11.3	15.3
800°F(430°C)	B063	154.2	163.8	9.1	9.5
	B064	151.6	162.2	9.0	9.8
1000°F(538°C)	K063	149.7	163.3	8.0	10.0
	K064	148.6	163.2	8.0	13.9
1100°F(593°C)	L063	149.6	172.0	7.7	10.7
	L064	151.9	177.1	6.5	9.3
1200°F(649°C)	M063	153.8	175.5	7.8	19.2
	M064	149.0	172.0	5.4	20.4
1400°F(760°C)	N063	190.4	198.9	14.9	16.8
	N064	191.7	199.7	12.0	17.9
1600°F(871°C)	P063	131.3	148.4	31.9	33.2
	P064	133.9	145.3	29.8	36.1
1700°F(927°C)	R063	112.8	136.9	27.5	27.7
	R064	115.0	126.4	27.0	31.7
1800°F(982°C)	Y063	112.4	123.3	19.5	23.0
	W064	106.9	120.3	23.6	23.8
1900°F(1038°C)	Z063	88.3	94.6	32.5	52.2
	X064	78.9	90.2	36.6	51.4

[100 ksi = 690 Mpa]

Machining & Testing Source: Joliet Metallurgical Laboratory

Table 6

**HEAT #5V0459 CMSX®-7 Mod B -100% VIRGIN CHEMISTRY (WT ppm/%)**

C	9 ppm	Re	< .05
Si	<.02	Cu	< .001
Mn	< .001	Fe	.015
S	1 ppm	V	< .005

EP 2 612 936 B9

(continued)

**HEAT #5V0459 CMSX®-7 Mod B -100% VIRGIN CHEMISTRY (WT ppm/%)**

5	Al	5.780	Ru	< .01
	B	< 25 ppm	Pt	< .001
	Cb (Nb)	<.05	Pd	< .001
	Co	9.7	Mg	< 100 ppm
	Cr	5.6	[N]	1 ppm
10	Hf	.30	[O]	1 ppm
	Mo	.59	Y	< .001
	Ni	Balance	La	< .001
	Ta	8.4	Ce	< .002
	Ti	.70		
15	W	9.3		
	Zr	< 25 ppm		
			Ag	< .4 ppm
20			Bi	< .2 ppm
			Ga	< 10 ppm
			Ca	< 25 ppm
			Pb	< .5 ppm
25			Se	< .5 ppm
			Te	< .2 ppm
			Tl	< .2 ppm
			Sn	< 2 ppm
			Sb	< 1 ppm
30			As	< 1 ppm
			Zn	< 1 ppm
			Hg	< 2 ppm
			Cd	< .2 ppm
35			Ge	< 1 ppm
			Au	< .5 ppm
			In	< .2 ppm
			Na	< 10 ppm
			K	< 5 ppm
40			P	8 ppm
			U	< .5 ppm
			Th	< 1 ppm

Table 7

**CMSX-7 MOD B - Heat 5V0459**

Molds 923/924 - (DL- 10s) - RR SCFO [Indy] - LA11834 (Joliet 9156/CM-368) [DL-10s]

Fully Heat Treated - Solution + double age

<b>Creep-Rupture</b>						
<b>Test Condition</b>	<b>ID</b>	<b>Rupture Life, hrs</b>	<b>% Elong</b>	<b>% RA</b>	<b>1% Creep</b>	<b>2% Creep</b>
1562°F/72.5 ksi	A923	972.7	19.6	25.2	298.3	463.7
[850°C/500 MPa]	H923	861.8	20.6	27.6	275.7	411.2
1600°F/65.0 ksi	B923	667.4	21.8	26.5	224.6	323.0
[871°C/448 MPa]	R924	670.4	19.8	31.3	262.8	363.8
1800°F/36.0 ksi	C923	139.2	37.9	45.6	56.2	68.0
[982°C/248 MPa]	N924	151.5	31.6	38.0	64.6	77.2
1800°F/40.0 ksi	D923	97.4	34.8	41.5	39.4	48.0

**EP 2 612 936 B9**

(continued)

<b>Creep-Rupture</b>							
	<b>Test Condition</b>	<b>ID</b>	<b>Rupture Life, hrs</b>	<b>% Elong</b>	<b>% RA</b>	<b>1% Creep</b>	<b>2% Creep</b>
5	[982°C/276 MPa]	M24	106.3	28.8	33.7	45.3	55.2
	1850°F/38.0 ksi	E923	51.7	34.3	35.2	21.1	25.6
	[1010°C/262 MPa]	L924	54.1	36.5	36.6	21.2	26.0
	1900°F/25.0 ksi	J923	103.0	25.1	43.5	39.5	49.3
10	[1038°C/172 MPa]	H924	111.2	27.6	40.2	38.6	51.1
	1904°F/21.0 ksi	K923	240.2	31.0	47.1	90.6	112.9
	[1040°C/145 MPa]	E924	245.7	43.4	46.7	86.5	109.1
	1950°F/18.0 ksi	L923	260.5	27.4	37.5	86.0	112.4
	[1066°C/124 MPa]	D924	219.1	38.4	41.7	79.8	101.5
<b>Stress-Rupture</b>							
	<b>Test Condition</b>	<b>ID</b>	<b>Rupture Life, hrs</b>	<b>% Elong</b>	<b>% RA</b>		
15	2000°F/12.0 ksi	M923	1176.5	34.4	42.4		
	[1093°C/83 MPa]	B924	960.4	37.4	42.9		
20	2050°F/15.0 ksi	N923	143.7	20.7	36.5		
	[1121 °C/103 MPa]	A924	135.8	26.3	38.2		
Machining and Testing Source: Joliet Metallurgical Laboratory							

25 **[0028]** A further heat (5V0459) of 100% Virgin (470 lbs) designated CMSX®-7 Mod B was melted in May 2011 in the CM V-5 Consarc VIM furnace using aim chemistry to CM KH 04/13/11 (CM CRMP #81-1703 Issue 1). The heat (5V0459) chemistry is shown in Table 6.

30 **[0029]** Two molds (#s 923 & 924) of SX NNS DL-10 test bars were cast to CMSX-4® casting parameters by Rolls-Royce Corporation (SCFO). DL-10 test bar yield at 22 fully acceptable out of a total 24 cast was excellent.

**[0030]** These DL-10 test bars were solutioned/homogenized + double aged heat treated at Cannon-Muskegon Corporation as follows - based on solutioning/ homogenization studies on CMSX®-7 Mod B test bars.

Solutioning and Homogenization

35 **[0031]**

- 2 hrs / 2360°F (1293°C) + 2 hrs /2370°F (1299°C)  
+ 2 hrs / 2380°F (1304°C) + 12 hrs / 2390°F (1310°C) AC - ramping up at 1°F/min.
- Double Age Heat Treatment  
4 hrs / 2050°F (112 °C) AC  
+ 20 hrs / 1600°F (871 °C) AC

45 **[0032]** Acceptable microstructure attainment is evident Figs. 14 & 15, almost complete  $\gamma'$  solutioning, remnant  $\gamma/\gamma'$  eutectic, no incipient melting and approximately 0.45  $\mu\text{m}$  average cubic aligned  $\gamma'$ , indicating appropriate  $\gamma/\gamma'$  mismatch and  $\gamma/\gamma'$  inter-facial chemistry, following the 4 hr / 2050°F (1121 °C) high temperature age.

**[0033]** The creep-rupture properties of CMSX®-7 Mod B are very similar to that of CMSX®-7, with no apparent advantage (Table 7).

50 **[0034]** Post-test microstructures from a longer term, high temperature stress-rupture test [2000°F/12 ksi (1093°C/83 MPa)/1176.5 hours] are shown (Figs. 19A-19C) to exhibit good phase stability, with negligible TCP phase ("needles") apparent, combined with good stress-rupture life and rupture ductility (34% elongation (4D)) and 42% RA (Figs. 19A-20C).

**Claims**

55 1. A nickel-base superalloy for single crystal casting comprising:

- 5.60% to 5.85% aluminum by weight;
- 9.4% to 9.9% cobalt by weight;

5.0% to 6.0% chromium by weight;  
 0.08% to 0.35% hafnium by weight;  
 0.50% to 0.70% molybdenum by weight;  
 8.0% to 9.0% tantalum by weight;  
 5 0.60% to 0.90% titanium by weight;  
 8.5% to 9.8% tungsten by weight; and  
 the balance comprising nickel and minor amounts of optional elements, the total amount of optional elements  
 being 1% or less by weight,  
 wherein the optional elements are controlled to maximums of 100 ppm carbon, 0.04% silicon, 0.01% manganese,  
 10 3 ppm sulfur, 30 ppm phosphorous, 30 ppm boron, 0.1% niobium, 150 ppm zirconium, 0.15% rhenium, 0.01%  
 copper, 0.15% iron, 0.1 % vanadium, 0.1 % ruthenium, 0.15% platinum, 0.15 % palladium, 200 ppm magnesium,  
 5 ppm nitrogen, 5 ppm oxygen, 2 ppm silver, 0.2 ppm bismuth, 10 ppm gallium, 25 ppm calcium, 1 ppm lead,  
 0.5 ppm selenium, 0.2 ppm tellurium, 0.2 ppm thallium, 10 ppm tin, 2 ppm antimony, 2 ppm arsenic, 5 ppm zinc,  
 15 2 ppm mercury, 2 ppm cadmium, 2 ppm germanium, 2 ppm gold, 2 ppm indium, 20 ppm sodium, 10 ppm  
 potassium, 10 ppm barium, 2 ppm uranium, lanthanum and yttrium in a total amount of 5 to 80 ppm, and 2 ppm  
 thorium.

2. A nickel-base superalloy for single crystal casting according to claim 1, said nickel-base superalloy containing a  
 20 maximum amount of sulfur of 0.5 ppm, and further comprising an amount of lanthanum and yttrium that is targeted  
 to achieve a total lanthanum and yttrium content that is from 5 ppm to 80 ppm in a single crystal casting.
3. A nickel-base superalloy for single crystal casting according to claim 1, having a density of about 8.8 gms/cc (kg/dm<sup>3</sup>).
4. A single crystal component cast from an alloy according to any one of claims 1 to 3.
- 25 5. A single crystal component according to claim 4 that is a gas turbine component.
6. A single crystal component according to claim 4 that is a blade, a vane, or a seal segment for a gas turbine.

### 30 Patentansprüche

1. Nickelbasis-Superlegierung zum Einkristall-Gießen, umfassend:

35 5,60 % bis 5,85 % Aluminium, bezogen auf das Gewicht;  
 9,4 % bis 9,9 % Cobalt, bezogen auf das Gewicht;  
 5,0 % bis 6,0 % Chrom, bezogen auf das Gewicht;  
 0,08 % bis 0,35 % Hafnium, bezogen auf das Gewicht;  
 0,50 % bis 0,70 % Molybdän, bezogen auf das Gewicht;  
 40 8,0 % bis 9,0 % Tantal, bezogen auf das Gewicht;  
 0,60 % bis 0,90 % Titan, bezogen auf das Gewicht;  
 8,5 % bis 9,8 % Wolfram, bezogen auf das Gewicht; und  
 wobei der Rest Nickel und kleinere Mengen von optionalen Elementen umfasst, wobei die Gesamtmenge der  
 optionalen Elemente 1 % oder weniger, bezogen auf das Gewicht, beträgt,  
 45 wobei die optionalen Elemente auf Höchstwerte von 100 ppm Kohlenstoff, 0,04 % Silicium, 0,01 % Mangan, 3  
 ppm Schwefel, 30 ppm Phosphor, 30 ppm Bor, 0,1 % Niob, 150 ppm Zirconium, 0,15 % Rhenium, 0,01 %  
 Kupfer, 0,15 % Eisen, 0,1 % Vanadium, 0,1 % Ruthenium, 0,15% Platin, 0,15% Palladium, 200 ppm Magnesium,  
 5 ppm Stickstoff, 5 ppm Sauerstoff, 2 ppm Silber, 0,2 ppm Bismut, 10 ppm Gallium, 25 ppm Calcium, 1 ppm  
 Blei, 0,5 ppm Selen, 0,2 ppm Tellur, 0,2 ppm Thallium, 10 ppm Zinn, 2 ppm Antimon, 2 ppm Arsen, 5 ppm Zink,  
 50 2 ppm Quecksilber, 2 ppm Cadmium, 2 ppm Germanium, 2 ppm Gold, 2 ppm Indium, 20 ppm Natrium, 10 ppm  
 Kalium, 10 ppm Barium, 2 ppm Uran, Lanthan und Yttrium in einer Gesamtmenge von 5 bis 80 ppm, und 2 ppm  
 Thorium kontrolliert werden.

2. Nickelbasis-Superlegierung zum Einkristall-Gießen gemäß Anspruch 1, wobei die Nickelbasis-Superlegierung eine  
 55 Höchstmenge von Schwefel von 0,5 ppm enthält und außerdem eine Menge von Lanthan und Yttrium umfasst, die  
 darauf abzielt, einen Gesamt-Lanthan- und Yttrium-Gehalt, der 5 ppm bis 80 ppm beträgt, in einem Einkristall-  
 Gießen zu erreichen .

3. Nickelbasis-Superlegierung zum Einkristall-Gießen gemäß Anspruch 1, mit einer Dichte von ungefähr 8,8 g/cm<sup>3</sup> (kg/dm<sup>3</sup>).
4. Einkristall-Komponente, gegossen aus einer Legierung gemäß einem der Ansprüche 1 bis 3.
5. Einkristall-Komponente gemäß Anspruch 4, welche eine Gasturbinenkomponente ist.
6. Einkristall-Komponente gemäß Anspruch 4, welche eine Turbinenschaufel, eine Leitschaufel oder ein Dichtungssegment für eine Gasturbine ist.

## Revendications

1. Superalliage à base de nickel pour moulage monocristallin comprenant :

de 5,60 % à 5,85 % d'aluminium en poids ;  
de 9,4 % à 9,9 % de cobalt en poids ;  
de 5,0 % à 6,0 % de chrome en poids ;  
de 0,08 % à 0,35 % d'hafnium en poids ;  
de 0,50 % à 0,70 % de molybdène en poids ;  
de 8,0 % à 9,0 % de tantale en poids ;  
de 0,60 % à 0,90 % de titane en poids ;  
de 8,5 % à 9,8 % de tungstène en poids ; et

le reste étant constitué de nickel et de quantités mineures d'éléments facultatifs, la quantité totale d'éléments facultatifs étant inférieure ou égale à 1 % en poids,

les éléments facultatifs étant contrôlés pour respecter les maxima suivants : 100 ppm de carbone, 0,04 % de silicium, 0,01 % de manganèse, 3 ppm de soufre, 30 ppm de phosphore, 30 ppm de bore, 0,1 % de niobium, 150 ppm de zirconium, 0,15 % de rhénium, 0,01 % de cuivre, 0,15 % de fer, 0,1 % de vanadium, 0,1 % de ruthénium, 0,15 % de platine, 0,15 % de palladium, 200 ppm de magnésium, 5 ppm d'azote, 5 ppm d'oxygène, 2 ppm d'argent, 0,2 ppm de bismuth, 10 ppm de gallium, 25 ppm de calcium, 1 ppm de plomb, 0,5 ppm de sélénium, 0,2 ppm de tellurium, 0,2 ppm de thallium, 10 ppm d'étain, 2 ppm d'antimoine, 2 ppm d'arsenic, 5 ppm de zinc, 2 ppm de mercure, 2 ppm de cadmium, 2 ppm de germanium, 2 ppm d'or, 2 ppm d'indium, 20 ppm de sodium, 10 ppm de potassium, 10 ppm de baryum, 2 ppm d'uranium, du lanthane et de l'yttrium dans une quantité totale de 5 à 80 ppm et 2 ppm de thorium.

2. Superalliage à base de nickel pour moulage monocristallin selon la revendication 1, ledit superalliage à base de nickel contenant une quantité maximale de soufre de 0,5 ppm, et comprenant en outre une quantité de lanthane et d'yttrium ciblée pour atteindre une teneur totale de lanthane et d'yttrium allant de 5 ppm à 80 ppm dans une coulée de monocristal.
3. Superalliage à base de nickel pour moulage monocristallin selon la revendication 1, ayant une masse volumique d'environ 8,8 g/cc (kg/dm<sup>3</sup>).
4. Composant monocristallin moulé à partir d'un alliage selon l'une quelconque des revendications 1 à 3.
5. Composant monocristallin selon la revendication 4 qui est un composant de turbine à gaz.
6. Composant monocristallin selon la revendication 4 qui est une aube, une ailette ou un segment pour une turbine à gaz.

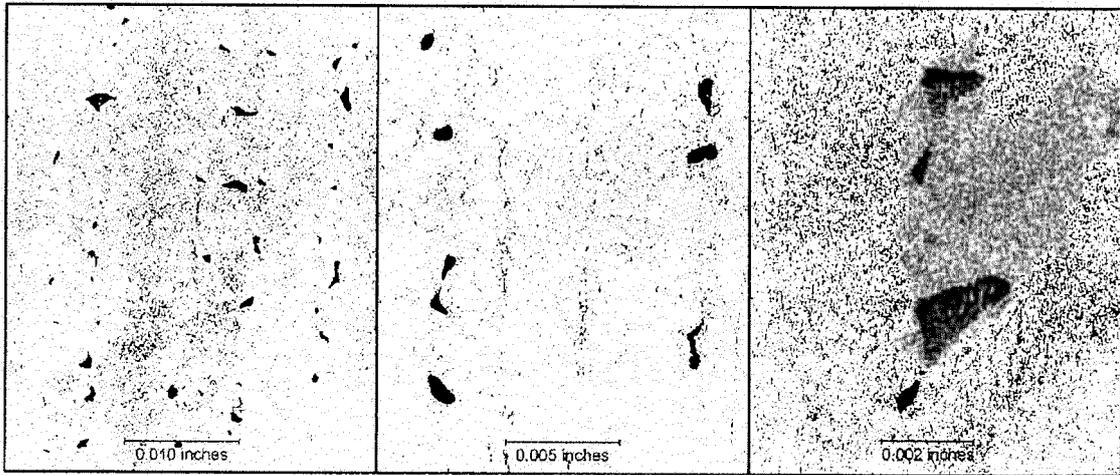


FIG. 1A

FIG. 1B

FIG. 1C

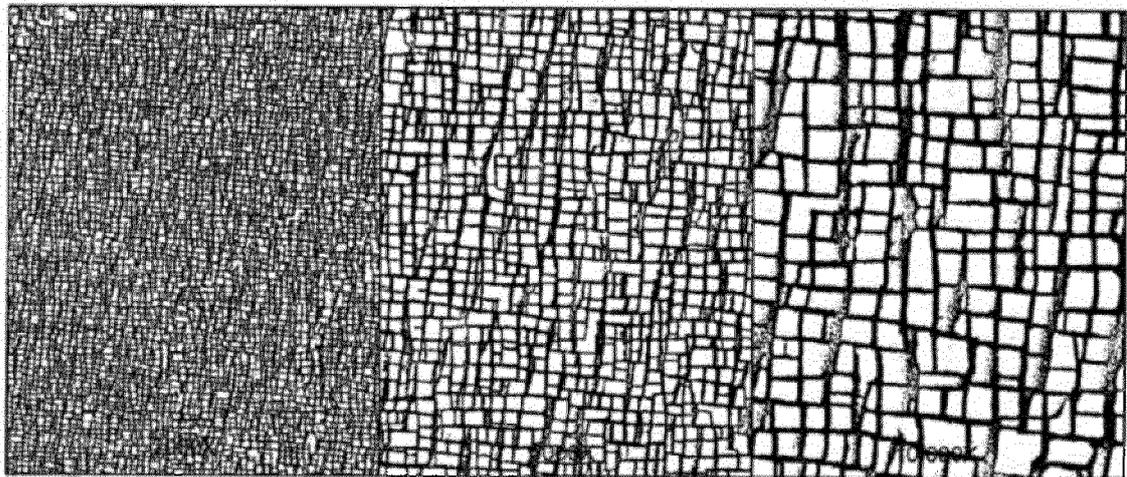


FIG. 2A

FIG. 2B

FIG. 2C

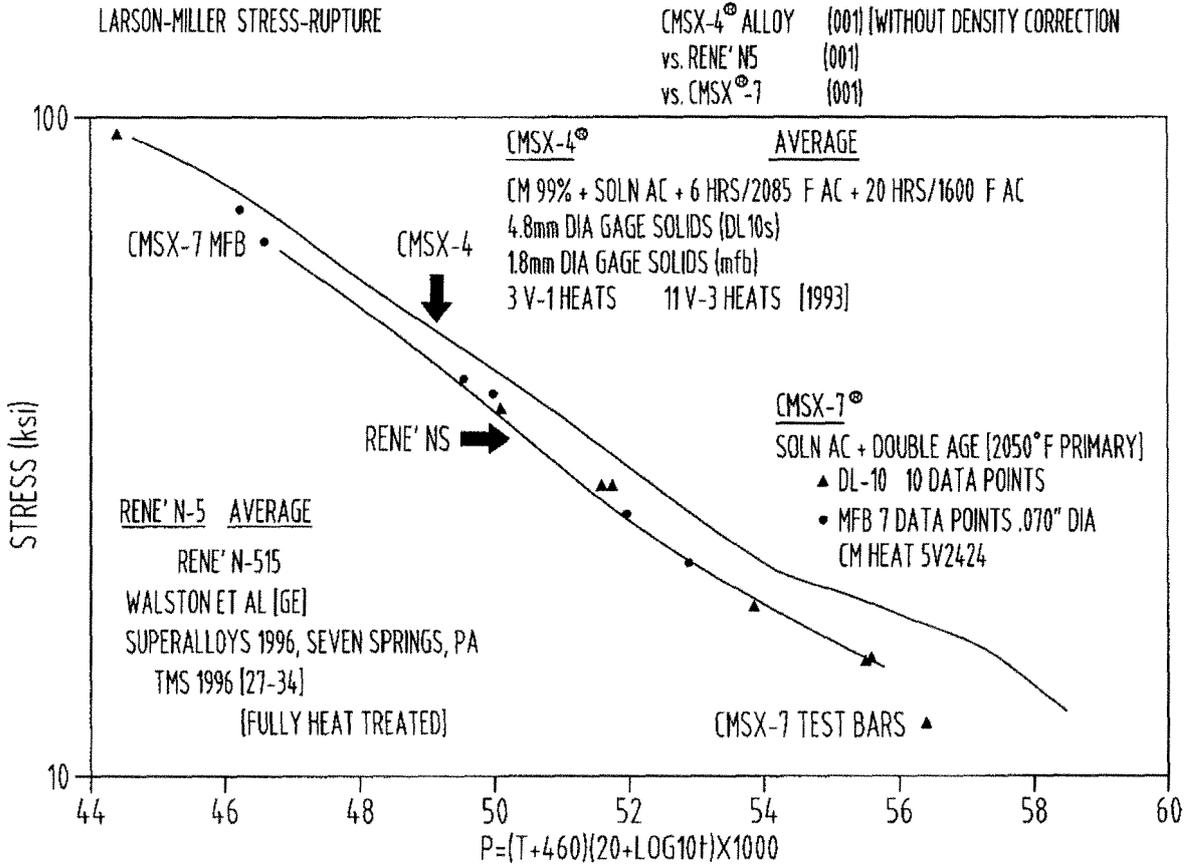


FIG. 3

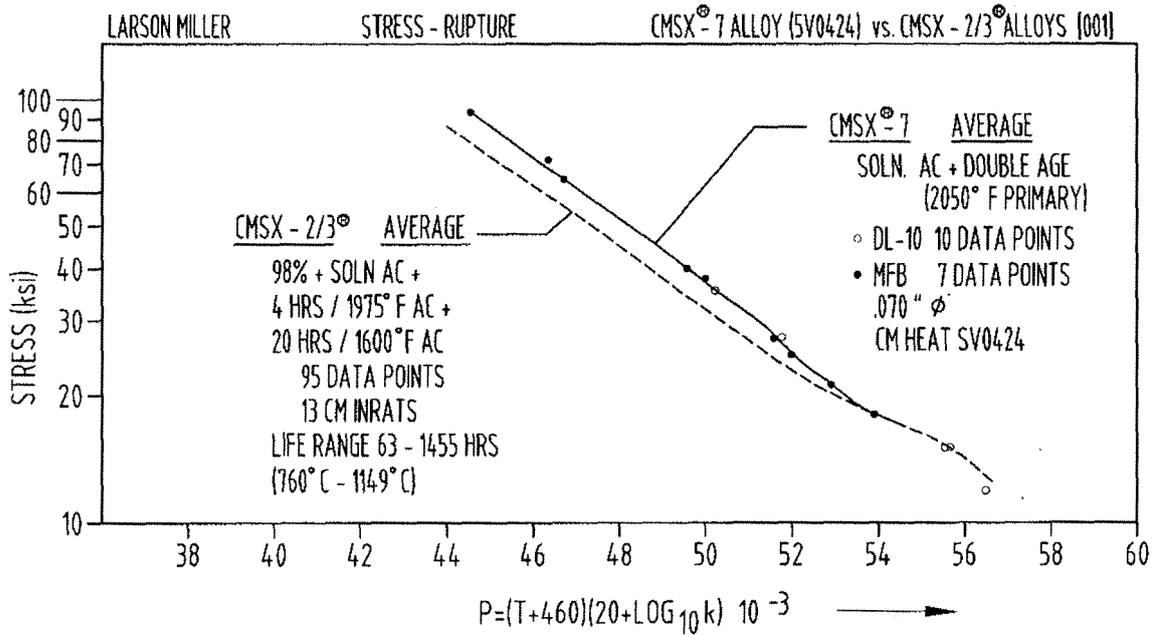


FIG. 4

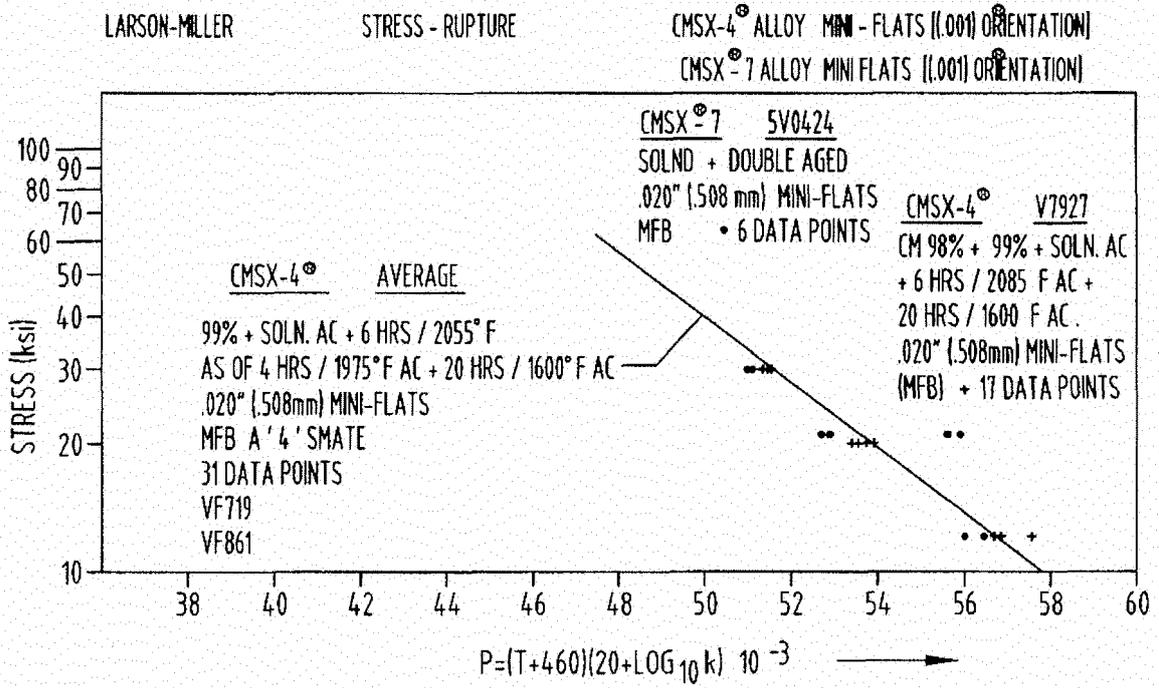


FIG. 5

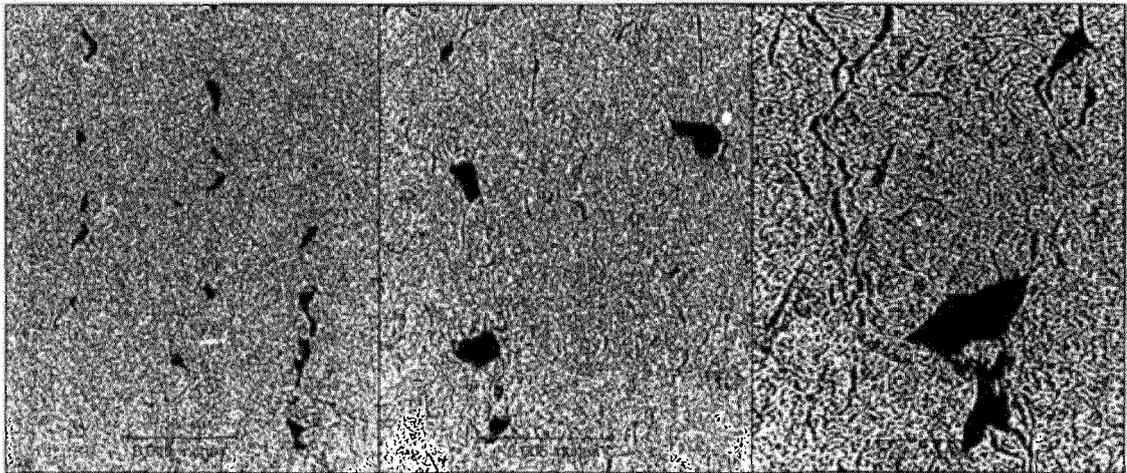


FIG. 6A

FIG. 6B

FIG. 6C

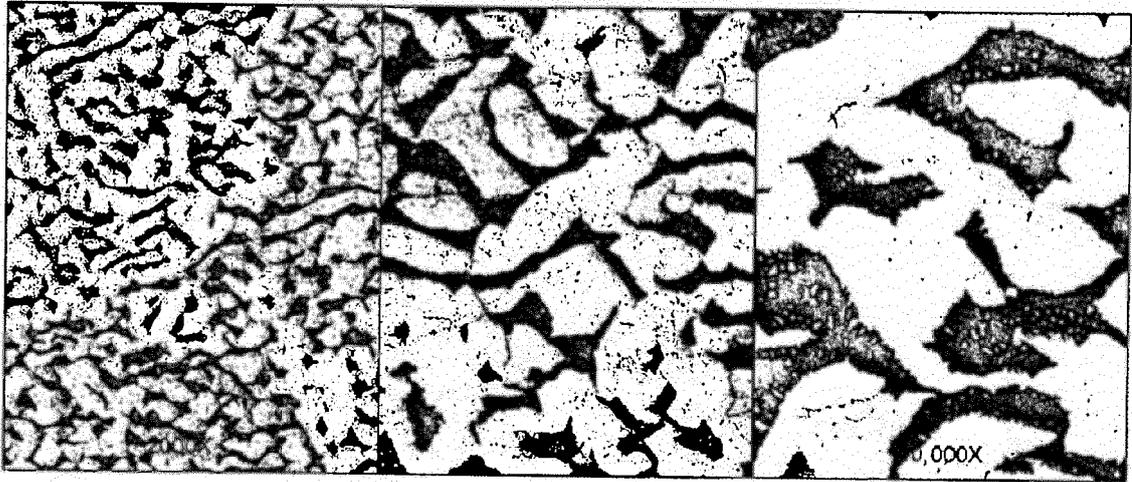


FIG. 7A

FIG. 7B

FIG. 7C

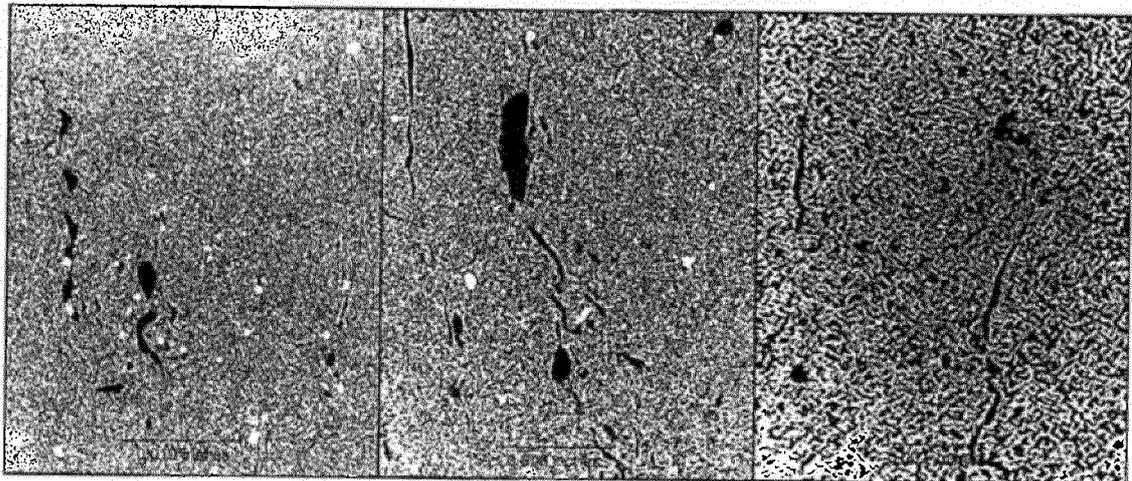


FIG. 8A

FIG. 8B

FIG. 8C

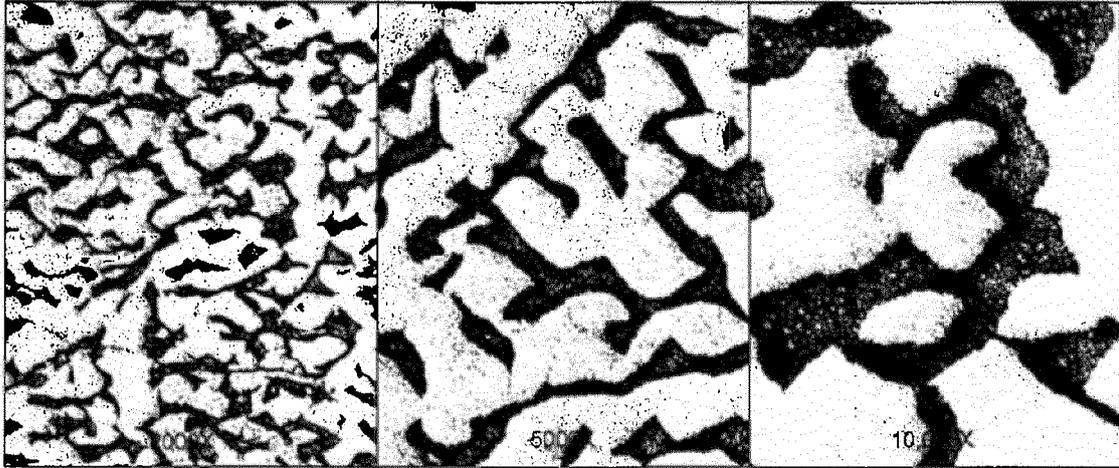


FIG. 9A

FIG. 9B

FIG. 9C

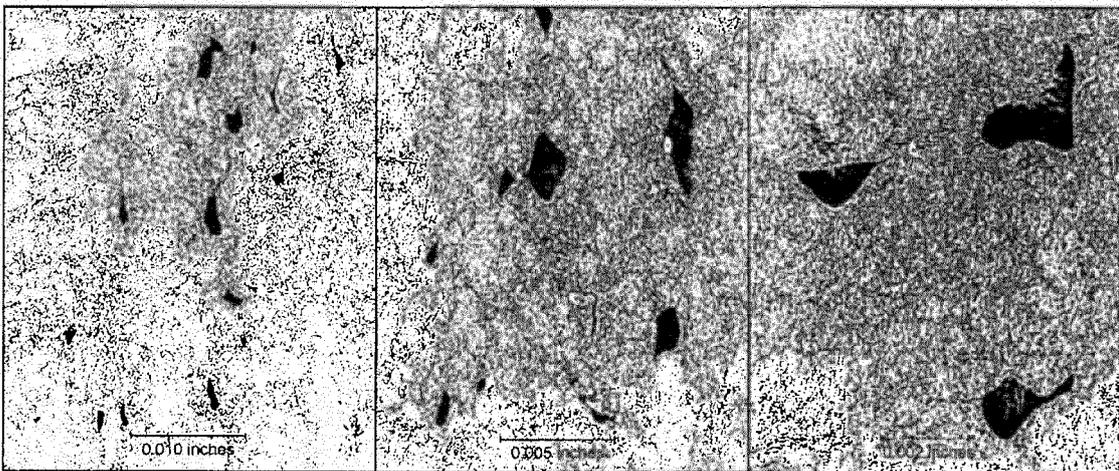


FIG. 10A

FIG. 10B

FIG. 10C

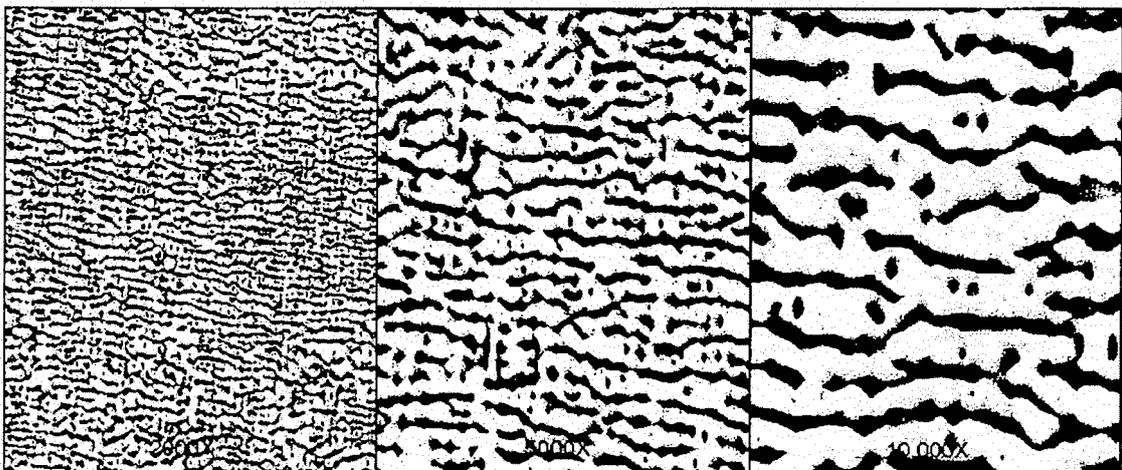


FIG. 11A

FIG. 11B

FIG. 11C

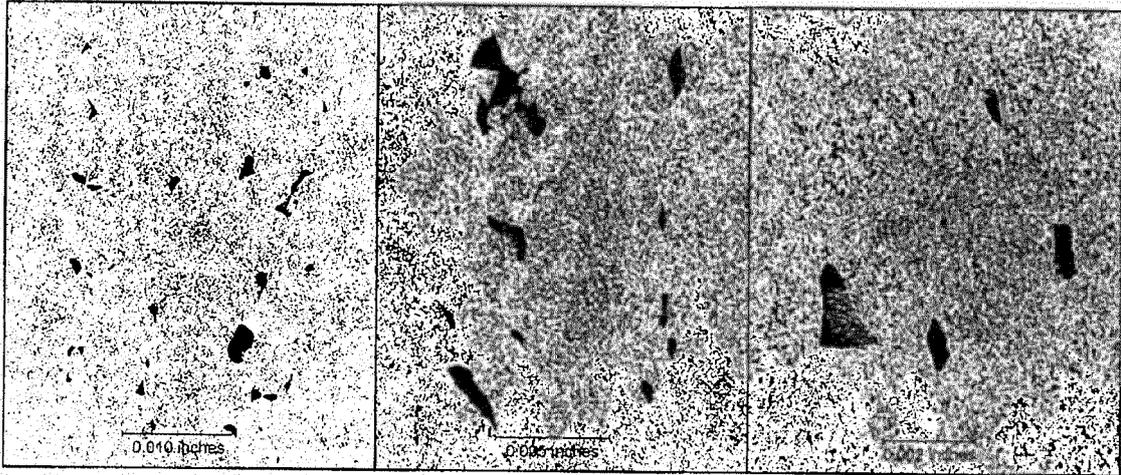


FIG. 12A

FIG. 12B

FIG. 12C

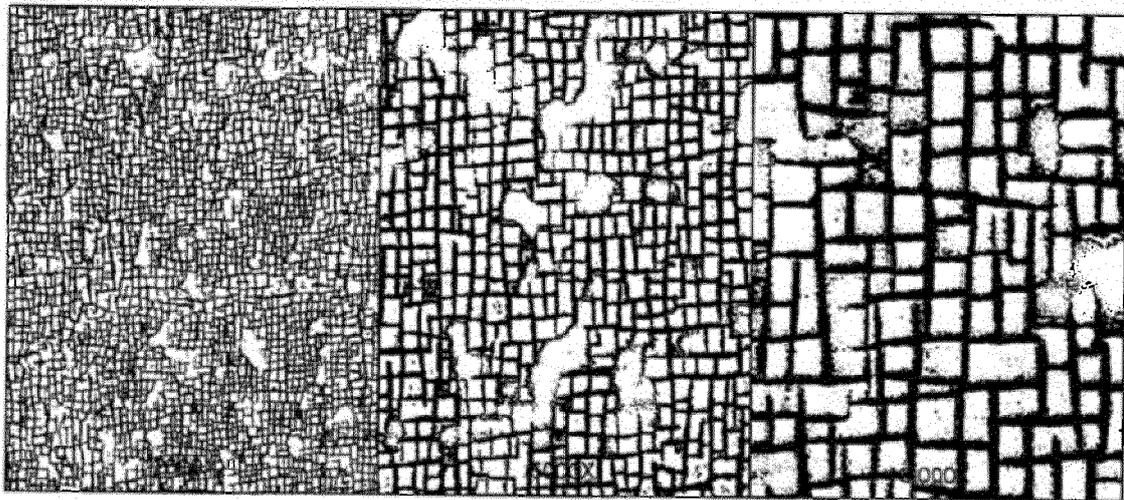


FIG. 13A

FIG. 13B

FIG. 13C

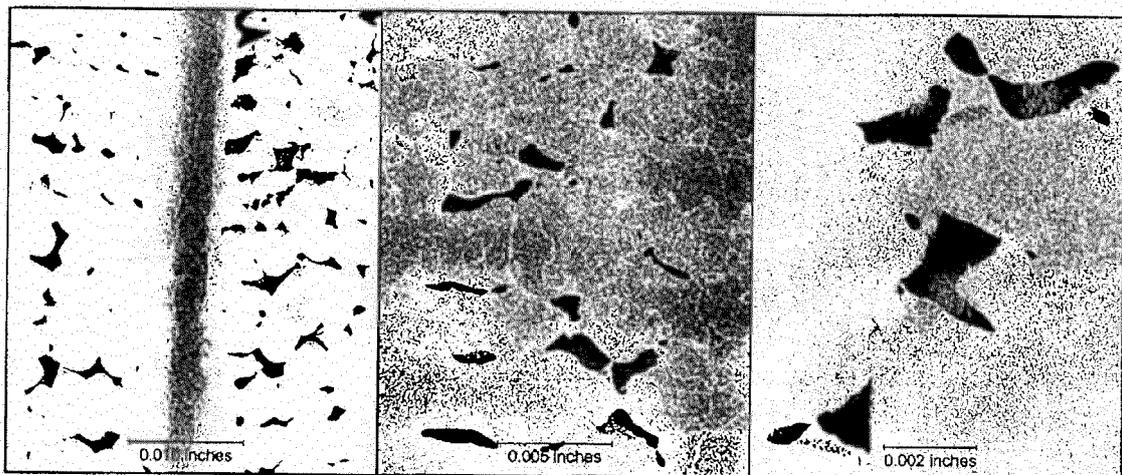


FIG. 14A

FIG. 14B

FIG. 14C

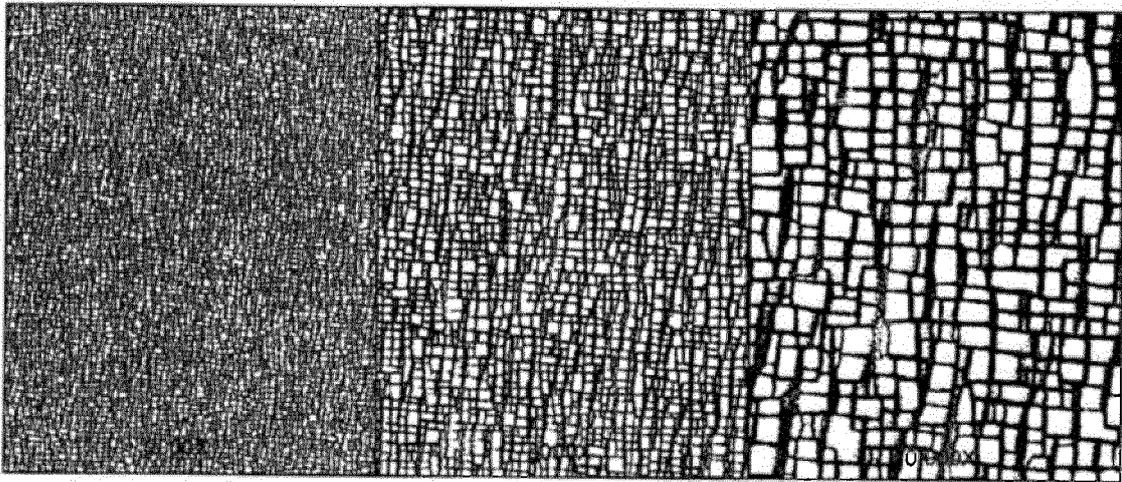


FIG. 15A

FIG. 15B

FIG. 15C

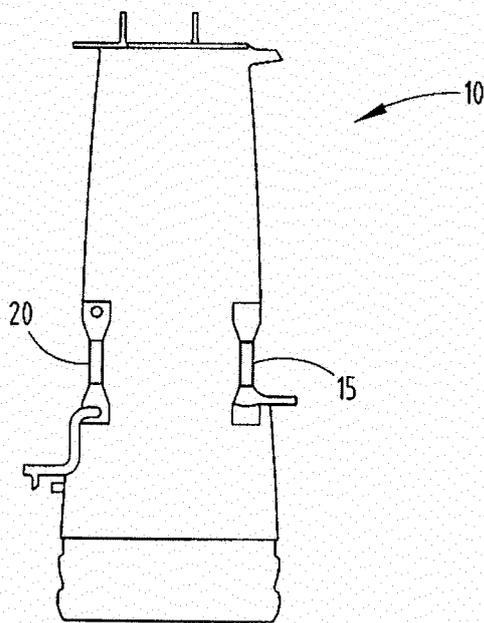


FIG. 16

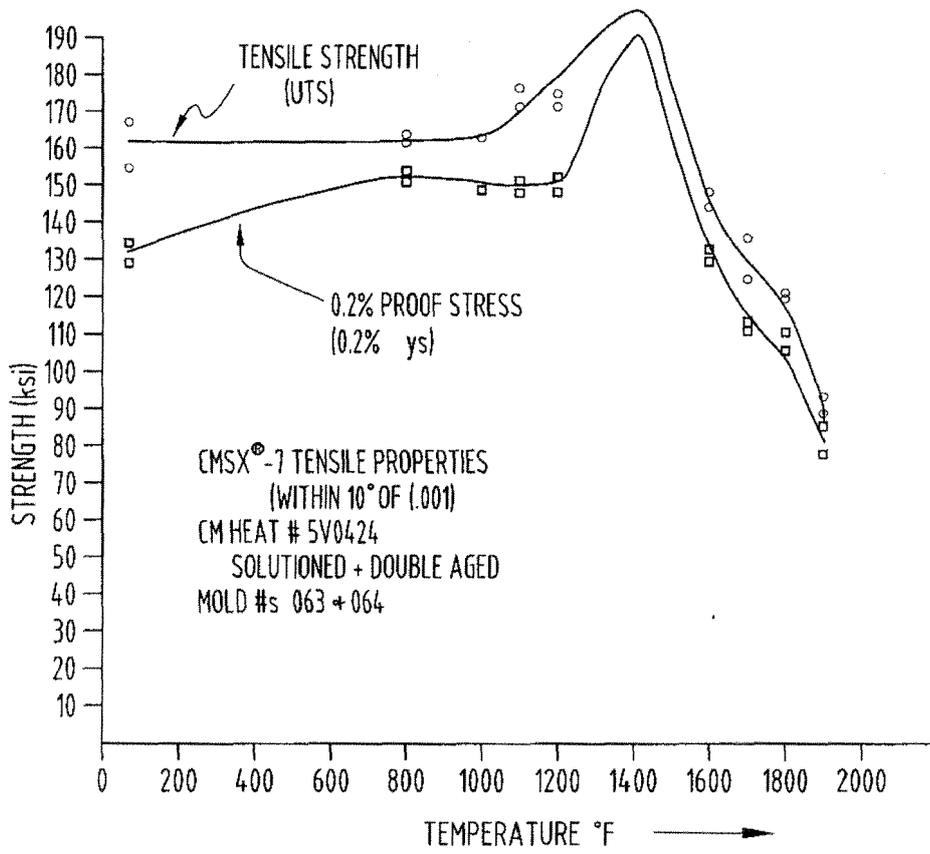


FIG. 17

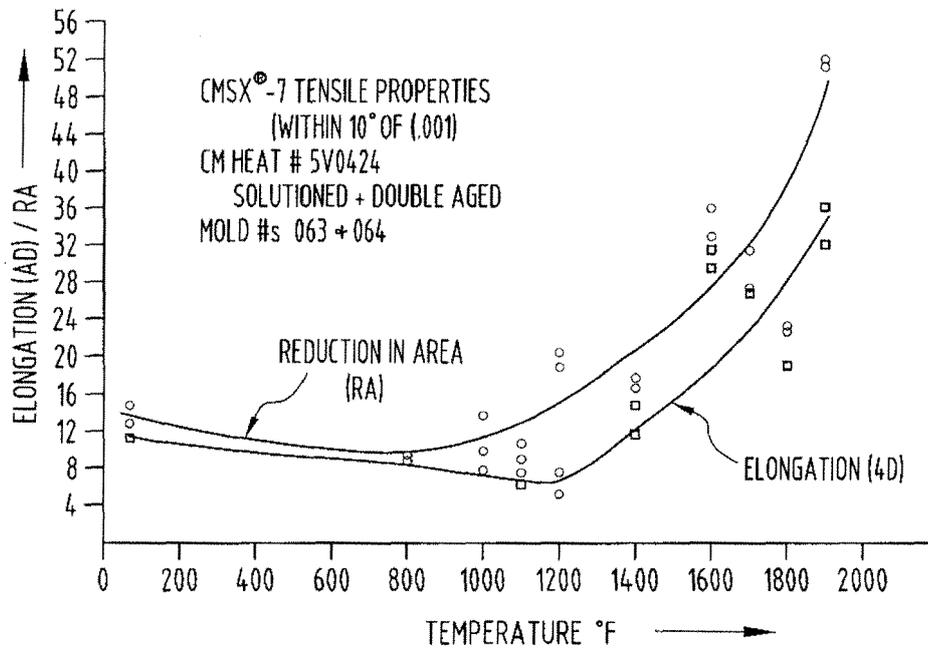


FIG. 18

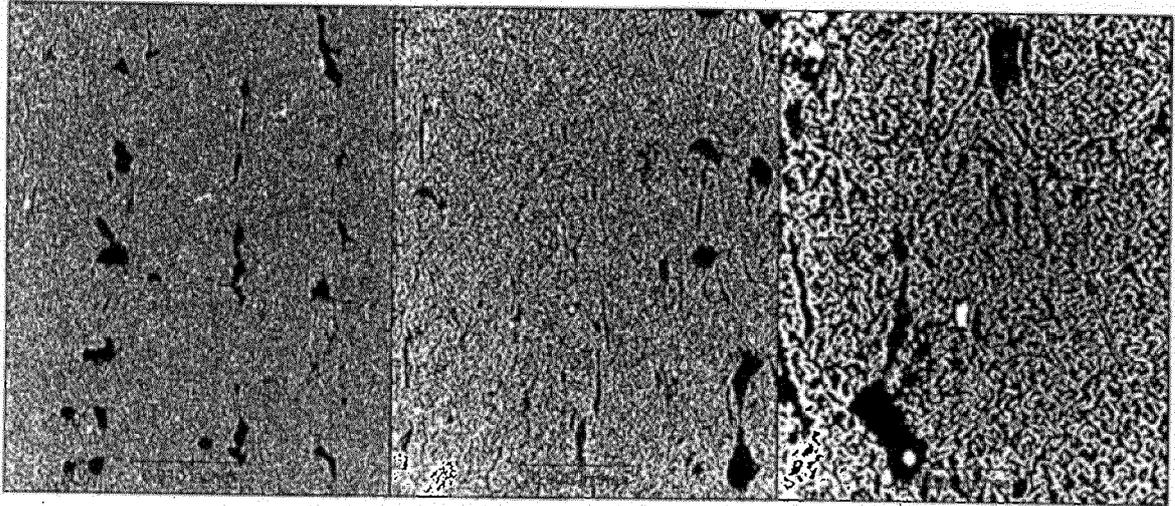


FIG. 19A

FIG. 19B

FIG. 19C

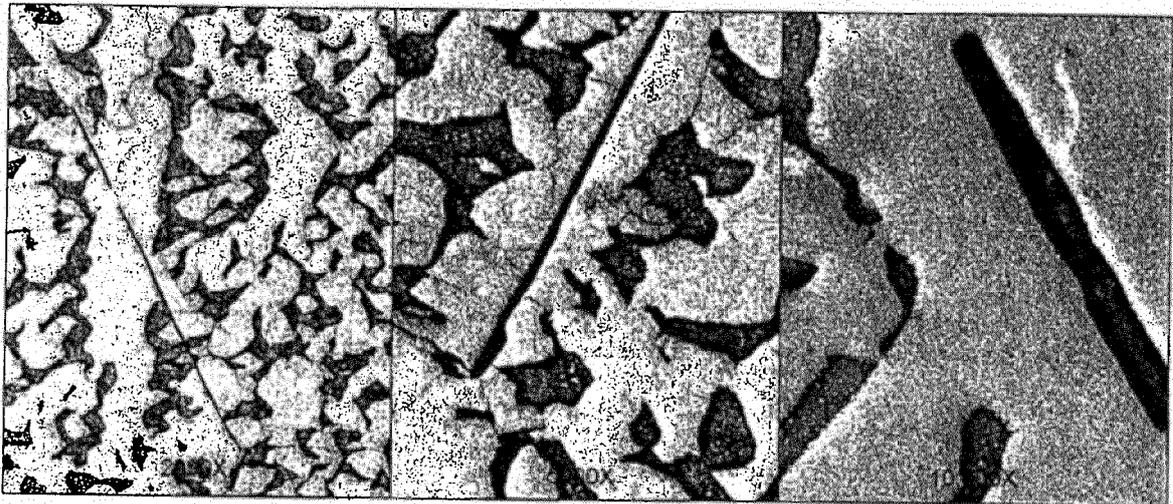


FIG. 20A

FIG. 20B

FIG. 20C

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- EP 2305848 A [0007]