(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 186 797
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 85115301.5

(22) Date of filing: 03.12.85

(51) Int. Cl.⁴: C 22 C 19/07

(30) Priority: 04.12.84 US 678118

(43) Date of publication of application: 09.07.86 Bulletin 86/28

(84) Designated Contracting States: DE FR GB IT NL

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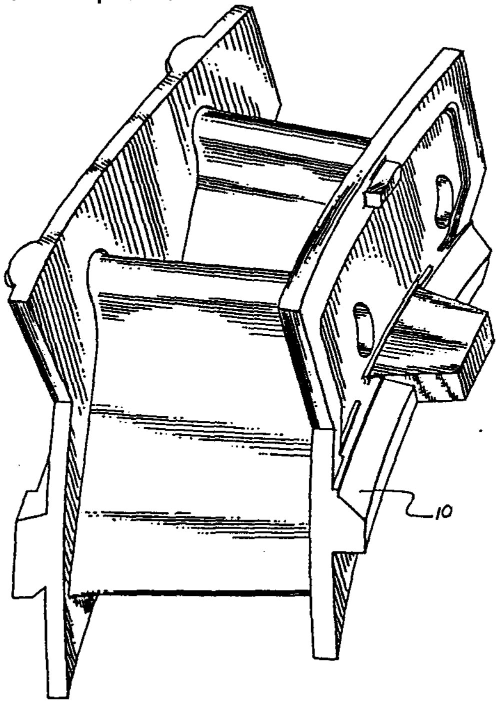
(54) **Novel cobalt-base superalloy and cast and welded industrial gas turbine components thereof.**

(57) Cobalt-base superalloys having special utility in the production of industrial gas turbine hot gas path components because of their unique combination of properties including excellent hot corrosion resistance, creep rupture strength at high temperature, metallurgical stability, tensile ductility and weldability, consist essentially of 0.3 to 0.6% carbon, 27–35% chromium, 9–16% nickel, 6–9% tungsten, 0.45 to 2.0% tantalum, up to 3.0% hafnium, up to 0.1% columbium, up to 0.7% zirconium, not more than 2.0% iron, 1.5% manganese and silicon and 0.05% boron, balance cobalt, the carbide formers being selected to satisfy the following equation:

$$\frac{\text{Atomic Percent }(Ta+Hf+Ti+Cb+Zr)}{\text{Atomic Percent C}} = 0.4 \text{ to } 0.8$$



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Field of the Invention

This invention relates generally to the superalloy branch of the metallurgical art, and is more specifically concerned with new cobalt-base superalloys having an unique combination of properties and consequent special utility in the production of both cast articles and welded structures, and with novel industrial gas turbine hot gas path components of those new alloys.

Background

Cobalt-base superalloys disclosed and claimed in U.S. Patent No. 3,383,205 have superior oxidation and hot corrosion resistance and as a consequence have long been used extensively in commercial production of industrial gas turbine nozzles. In fact, one of those superalloys is the current first stage nozzle alloy of the Gas Turbine Division of General Electric Company, the assignee hereof. The creep rupture and fatigue strength of that alloy, however, are marginal for new industrial gas turbine nozzle applications and in recognition of that fact, a program was launched to improve those properties without significantly diminishing the resistance of the superalloy either to oxidation or to hot corrosion. While the resulting superalloys met those objectives as a consequence of their relatively high carbon contents (0.40 to 0.50%), they were still not the answer to the problem because of their inferior weldability and low tensile ductility.

Summary of the Invention

Through our discoveries and new concepts detailed below, we have created new cobalt-base superalloys having a previously unobtainable combination of desirable properties. Thus we have found the way to avoid having to make the trade-offs of desirable properties exemplified by the problem mentioned above. This invention in providing the answers to that problem embodies those discoveries and new concepts of ours and they are epitomized in the appended claims directed both to alloy compositions and to articles of manufacture of those compositions.

One of our concepts upon which this invention is based is that weldability and tensile ductility of cobalt-base superalloys need not be significantly compromised in order to increase creep strength and fatigue strength very substantially. In particular, beneficial effects of increased carbon content can be obtained without the normally attending detrimental effects thereof by addition of one or more of the following strong monocarbide MC-formers: hafnium, tantalum, columbium, zirconium and titanium.

We have discovered that these additive elements are effective for this purpose in relatively small amounts and that within certain limits they can be used singly or together in any desired combination to secure consistently the new results and advantages of this invention.

Still further, we have found that while the more reactive elements such as titanium and zirconium, and to some extent hafnium, are suitable for vacuum melting operations, it is preferable to substitute columbium for them in melting operations carried out in air. In addition, it is important that the amount of columbium not exceed about one percent because of its detrimental effect on superalloy hot corrosion resistance. For the same reason columbium is preferably not used in vacuum melting practice involving the new superalloys of this invention.

In making this invention, we have established that the beneficial effects of carbon on creep strength and fatigue strength are not forfeited to any appreciable degree as a result of isolating the carbon in the form of monocarbide throughout the grains and in the grain boundaries of the superalloy. Further, we have established that such segregation and isolation of carbon results in good weldability, metallurgical stability and tensile ductility, all of which are normally adversely affected by carbon in proportions preferred in accordance with this invention.

We have further discovered that the new results and advantages of this invention can consistently be obtained only through the use of at least 0.45% tantalum, and that while selection of other elements of the monocarbide MC-carbide former group is a matter of choice for the operator as to kind, the total amounts used are critically important. Thus the balance between the carbon content of the alloy and the total of those elements expressed as the ratio of the sum of the atomic percent of those elements to the atomic percent of carbon must be within the range of 0.4 to 0.8. In the superalloy of our present preference that ratio is 0.62.

Briefly described in its composition of matter aspect, the present invention is a cobalt-base superalloy having an unique combination of properties at high temperature and consequent special utility in the production of industrial gas turbine hot gas path components, which alloy consists essentially of 0.3-0.6% carbon, 27-35% chromium, 9-16% nickel, 6-9% tungsten, up to 3% hafnium, .45-2.0% tantalum, up to .7% zirconium, up to .5% titanium, up to 1% columbium, manganese and silicon, up to .05% boron, up to 2.0% iron, remainder essentially cobalt. An additional important requirement is that the carbide-forming elements be so selected as to satisfy the relationship stated above and represented by the following equation:

$$\frac{\text{Atomic Percent (Ta+Hf+Ti+Cb+Zr)}}{\text{Atomic Percent C}} = 0.4 \text{ to } 0.8$$

Similarly described in its article-of-manufacture aspect, the present invention is a cast cobalt-base superalloy industrial gas turbine nozzle consisting of the new alloy set forth immediately above. Also, in this aspect the invention takes the form of transition pieces and shrouds, and of a fabricated cobalt-base superalloy gas turbine combustion chamber comprising a plurality of sheets of the said new alloy rolled and formed in predetermined shape and assembled and welded together.

Brief Description of the Drawings

In the drawings accompanying and forming a part of this specification,

Fig. 1 is a view in perspective of an industrial gas turbine nozzle of this invention;

Fig. 2 is a Larson-Miller plot of the stress-rupture properties of an alloy of U.S. Patent 3,383,205 and one of this invention;

Fig. 3 is a chart bearing curves illustrating varestraint welding test results of tests on five alloys of this invention and two prior art alloys including that of U.S. Patent 3,383,205 treated in Fig. 2, total crack length in mils being plotted against percent augmented strain; and,

Fig. 4 is a view in perspective of an industrial gas turbine transition piece of this invention.

Detailed Description of the Preferred Embodiments

While our present preference is to prepare these new alloys by the vacuum melting and vacuum casting procedure, we alternatively contemplate using the air melting, air casting approach. Additions of hafnium, titanium, zirconium and tantalum are made in the former while columbium and tantalum and optionally hafnium are employed in the air melting case. In any event the amounts of these additives used in producing the alloys of this invention are carefully controlled to insure that the cast or fabricated products of these alloys have all the desirable characteristics described above. Likewise, the best practice along each of of these two lines involves controlling the amounts of the elements other than these several monocarbide MC-carbide formers as to both the ranges of the major constituents and the maximum amounts of the minor or impurity elements such as iron, manganese, silicon and boron.

As stated above and shown below, the consequence of failure to exert such control is the loss of one or more of the important advantages of this invention. The excellent weldability of these new alloys are forfeited, for example, when the amounts of monocarbide MC-carbide formers used are not in balance with the alloy carbon content as described above and set forth in the appended claims. Likewise, while we prefer to use columbium in air melting, air casting practice because it is not as reactive and so doesn't tend to oxidize as readily as titanium, zirconium or even hafnium, care is taken not to use an amount greater than about one percent because columbium detrimentally affects hot corrosion resistance. Further in this regard the chromium content of these alloys is preferably targeted at 28-30% in recognition that departures in each direction can penalize alloy properties, specifically amounts less than about 27% result in loss of oxidation and hot corrosion resistance and amounts greater than about 35% result in loss of ductility without offsetting gain in either oxidation resistance or hot corrosion resistance.

The cast and fabricated bodies of this invention being components of industrial gas turbines are quite different from aircraft jet engine components especially in respect to size and mass. Because of this, they represent problems unlike those of the relatively lighter weight counterparts such as marked cracking tendency associated with welding operations.

This has significant implication for cast as well as fabricated industrial gas turbine components as it would obviously be highly desirable to be able to weld repair industrial gas turbine nozzles to avoid the time and expense of replacement. Gaining this advantage without forfeiting any other constitutes an important advance in the art. Likewise, the opportunity to build industrial gas turbine combustion chamber structures by welding preformed sheets or plates together which is enabled as a result of this invention, its alloys having excellent weldability, is an important new advance in the production of industrial gas turbines. In our practice of such welding operations as these we prefer to use the gas tungsten arc technique and equipment in general use in industry in the fabrication of both ferrous and nonferrous metal structures, including those of cobalt-base superalloys.

The first stage nozzle 10 of an industrial gas turbine shown in Fig. 1 is a casting of our preferred alloy composition produced by the injection molding and investment casting technique in general use in the art. Also, the shape and size and the design details of nozzle 10 essentially duplicate those features of the present standard first stage nozzle. Transition piece 20 similarly resembles that which has long been in general use in industrial gas turbines differing importantly, however, in that it is constructed of parts of an alloy of this invention welded together to provide a strong crack-free assembly of integrally bonded elements. Thus, bracket 22 is fitted in place on body 23 and welded securely and fluid tightly thereto.

Those skilled in the art will gain a further and better understanding of this invention and its important new advantages and results from the following illustrative, but not limiting, examples.

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Example I

Investment castings for test purposes were made of a commercial cobalt-base alloy of the following analysis:

carbon	0.25
chromium	29.0
nickel	10.0
tungsten	7.0
manganese	0.7
silicon	0.7
phosphorus	0.02
sulphur	0.02
iron	1.0
boron	0.015
cobalt	remainder

This superalloy is disclosed and claimed in U.S. Patent 3,383,205 assigned to the assignee hereof and has long been in general use in the production of industrial gas turbine hot stage components, particularly cast non-rotating parts such as first stage nozzles.

The cast test specimens were subjected to standard tensile, creep rupture and varestraint weldability tests, the tensile and creep rupture data being set out in Table I and the varestraint data illustrated in Fig. 2. Curve A of Fig. 2 illustrates the Larson-Miller data and curve AA of Fig. 3 represents the varestraint data.

Example II

A cobalt-base superalloy of this invention was tested in a duplication of the test conditions and procedures of Example I the superalloy having the following analyses:

carbon	0.357
chromium	28.56
nickel	10.88
tungsten	7.33
tantalum	0.53
hafnium	1.00
zirconium	0.496

titanium	0.184
iron	0.270
silicon	0.024
sulphur	0.004
phosphorus	<0.005
manganese	<0.005
cobalt	remainder

The resulting test data are set forth in Tables 1 and 2 ~~and 3~~ for a ready comparison with those of Example I and those detailed below. Curve B of Fig. 2 illustrates the Larson-Miller data and curve BB of Fig. 3 represents the varestraint data. Further, this superalloy was found on the performance of standard tests to have the superior oxidation and hot corrosion resistance of the cobalt-base alloy of Example I.

Example III

The same experimental tests were carried out on four additional superalloys of this invention of the following compositions:

	Alloy A 481	Alloy B 482	Alloy C 483	Alloy D 485
Carbon	0.25	0.25	0.35	0.35
Manganese	0.70	0.70	0.70	0.70
Silicon	0.75	0.75	0.75	0.75
Phosphorus	<0.04	<0.04	<0.04	<0.04
Sulphur	<0.04	<0.04	<0.04	<0.04
Chromium	28.0	28.0	29.0	29.0
Nickel	10.0	10.0	10.0	10.0
Tungsten	7.0	7.0	7.0	5.0
Iron	<0.5	<0.5	<0.5	<0.5
Zirconium				
Hafnium				
Titanium				
Columbium	0.5	1.0	1.0	1.25
Tantalum	0.5	0.5	0.5	
Boron				0.01
Cobalt	REM	REM	REM	REM

Again the test data developed in measuring the properties of these alloys as described above are stated in Tables 1 and 2 ~~and 3~~.

Example IV

Another superalloy of the prior art of the cobalt-base type was likewise tested as to the foregoing properties with the results stated in the three tables below, this particular alloy (Alloy E) being of the following compositions:

carbon	0.35
manganese	0.70
silicon	0.75
phosphorus	<0.04
sulphur	<0.04
chromium	29.0
nickel	10.0
tungsten	7.0
iron	<0.5
zirconium	0.20
hafnium	
titanium	0.15
columbium	0.25
tantalum	
boron	0.01
cobalt	REM

In regard to the tests carried out in the course of this experimental work to measure the properties of these various alloy compositions, as indicated above, standard test procedures were followed in every instance and the same procedures were applied for each respective alloy in the several tests so that comparisons could be made directly and conclusions could be drawn from the resulting data which were reliable. The ASTM procedures were used, therefore, in the tensile and creep rupture tests and in the case of the varestraint test the procedure followed was that described in Welding Research Council Bulletin 280 in the article entitled "The Varestraint Test", C.D. Ludlum, et al., August 1982.

Table I

SUPERALLOY	Tensile Tests: Temp (°F)	ULT Tensile Strength (Kpsi)	Elong Percent	RA Percent	Stress Rupture Tests: Temp (°F)	Stress (Kpsi)	Life (Hrs)	Elong Percent	RA Percent
EXAMPLE I	70	92.0	6.5	9.5	(See Fig. 2)				
EXAMPLE II	70	102.0-107.8	7.0-5.5	7.9-5.6	1700	11	984.4	20.9	
					1750	11	286.4		
					1800	11	161.1		
EXAMPLE III-A	70	97.0-77.9	10.0-8.0	12.3-15.3	1700	11	153.4	34.2	
					1800	7.4	233.9	22.6	
EXAMPLE III-B	70	73.6-83.1			1700	11	212.7	26.4	
EXAMPLE III-C	70	92.8-85.1	4.0-4.0	3.2-7.2	1700	11	299.2	18.4	38
					1800	8	392.4	20.8	34
EXAMPLE III-D	70	90.5-85.5	4.0-4.0	4.8-10.0	1700	11	526.9	25.8	39
EXAMPLE IV -E	70	115.1-116.2	7.0-7.0	9.3-7.8	1700	11	986.4		
					1750	11	166.0	21.0	47

Table II

VARESTRAINT TESTS

SUPERALLOY	Augmented Strain (%)	Number of Cracks	Ave. Crack Length (mils)	Total Crack Length (mils)	Longest Crack Length (mils)
EXAMPLE II	0.50	0	0	0	0
	1.04	0	0	0	0
	1.56	0	0	0	0
	2.50	1	14	14	14
EXAMPLE III-A	0.50	0	0	0	0
	1.04	3	5	11.2	56.0
	1.56	5	21.40	107.0	36.0
	2.50	8	24.38	195	64.0
EXAMPLE III-B	0.50	0	0	0	0
	1.04	1	9	9	9
	1.56	3	19.33	58	32
	2.50	6	15.17	91	24
EXAMPLE III-C	0.50	1	36	36	36
	1.04	5	15.80	79.0	36
	1.56	4	23.25	93	37
	2.50	9	20.87	188	37
EXAMPLE III-D	0.50	0	0	0	0
	1.04	3.0	14.33	43.0	23.0
	1.56	6.0	17.67	106.0	36.0
	2.50	8.0	16.75	134	32.0
EXAMPLE IV-E	0.50	0	0	0	0
	1.04	7	18.71	131	30.0
	1.56	5	27.40	137	36.0
	2.50	15	24.27	364	50.0

As evident from Table I, the superalloys of this invention (Examples II and Examples IIIA-D) have ultimate tensile strengths equal to or better than the commercial superalloy of Example I and have creep rupture strength substantially greater than that commercial superalloy. Further it is apparent from Table I that these new superalloys have good room temperature tensile elongation characteristics and as Table II shows and Fig. 3 graphically illustrates, the weldability of the superalloys of this invention is superior to commercial superalloys A and E and even spectacularly so in the case of the superalloy of Example II which as indicated above is our present preferred embodiment of the invention. It will also be noted that as indicated in parentheses on that chart, the superalloys of this invention set forth in Examples II and III have carbideformer-carbon atomic percent ratios within the above prescribed critical range of 0.4 to 0.8, while the prior art alloys of Examples I and IV do not come close to meeting that important requirement.

What is claimed is:

1. A cobalt-base superalloy having an unique combination of desirable properties at high temperature and consequent special utility in the production of industrial gas turbine hot gas path components including nozzles and combustors, said superalloy consisting essentially of, by weight:

0.3 to 0.6	percent	carbon
27 to 35	"	chromium
9 to 16	"	nickel
6 to 9	"	tungsten
0.45 to 2.0	"	tantalum
up to 0.5	"	titanium
up to 3.0	"	hafnium
up to 1.0	"	columbium
up to 0.7	"	zirconium
up to 1.0	"	manganese
up to 1.0	"	silicon
up to 0.05	"	boron
up to 2.0	"	iron

Balance cobalt, the carbon (C), tantalum (Ta), hafnium (Hf), titanium (Ti), columbium (Cb) and zirconium (Zr) being so selected as to satisfy the following equation:

$$\frac{\text{Atomic Percent (Ta+Hf+Ti+Cb+Zr)}}{\text{Atomic Percent C}} = 0.4 \text{ to } 0.8$$

2. A cobalt-base superalloy of Claim 1 in which the atomic percent ratio of carbide-forming element to carbon is about 0.65.

3. A cobalt-base superalloy of Claim 1 which contains about 0.35% carbon, about 29% chromium, about 10% nickel, about 7% tungsten, about 0.5% zirconium, about 0.2% titanium, less than 0.01% manganese, less than 0.07% silicon, about 1.0% tantalum, less than about 0.4% iron, about 0.5% hafnium, remainder essentially cobalt.

4. An industrial gas turbine nozzle of cobalt-base superalloy having excellent hot corrosion resistance, creep strength and creep rupture strength at high temperature, metallurgical stability, tensile ductility and weldability, said superalloy consisting essentially of, by weight:

0.3 to 0.6	percent	carbon
27 to 35	"	chromium
9 to 16	"	nickel
6 to 9	"	tungsten
0.45 to 2.0	"	tantalum
up to 0.5	"	titanium
up to 3.0	"	hafnium
up to 1.0	"	columbium
up to 0.7	"	zirconium
up to 1.0	"	manganese
up to 1.0	"	silicon
up to 0.05	"	boron
up to 2.0	"	iron

Balance cobalt, the carbon (C), tantalum (Ta), hafnium (Hf), titanium (Ti), columbium (Cb) and zirconium (Zr) being so selected as to satisfy the following equation:

$$\frac{\text{Atomic Percent (Ta+Hf+Ti+Cb+Zr)}}{\text{Atomic Percent C}} = 0.4 \text{ to } 0.8$$

5. A fabricated industrial gas turbine transition piece of cobalt-base superalloy comprising a plurality of sheets rolled and formed in predetermined shape and assembled and welded together to define the piece, said superalloy consisting essentially of, by weight:

0.3	to 0.6	percent	carbon
27	to 35	"	chromium
9	to 16	"	nickel
6	to 9	"	tungsten
0.45	to 2.0	"	tantalum
up	to 0.5	"	titanium
up	to 3.0	"	hafnium
up	to 1.0	"	columbium
up	to 0.7	"	zirconium
up	to 1.0	"	manganese
up	to 1.0	"	silicon
up	to 0.05	"	boron
up	to 2.0	"	iron

Balance cobalt, the carbon (C), tantalum (Ta), hafnium (Hf), titanium (Ti), columbium (Cb) and zirconium (Zr) being so selected as to satisfy the following equation:

$$\frac{\text{Atomic Percent (Ta+Hf+Ti+Cb+Zr)}}{\text{Atomic Percent C}} = 0.4 \text{ to } 0.8$$

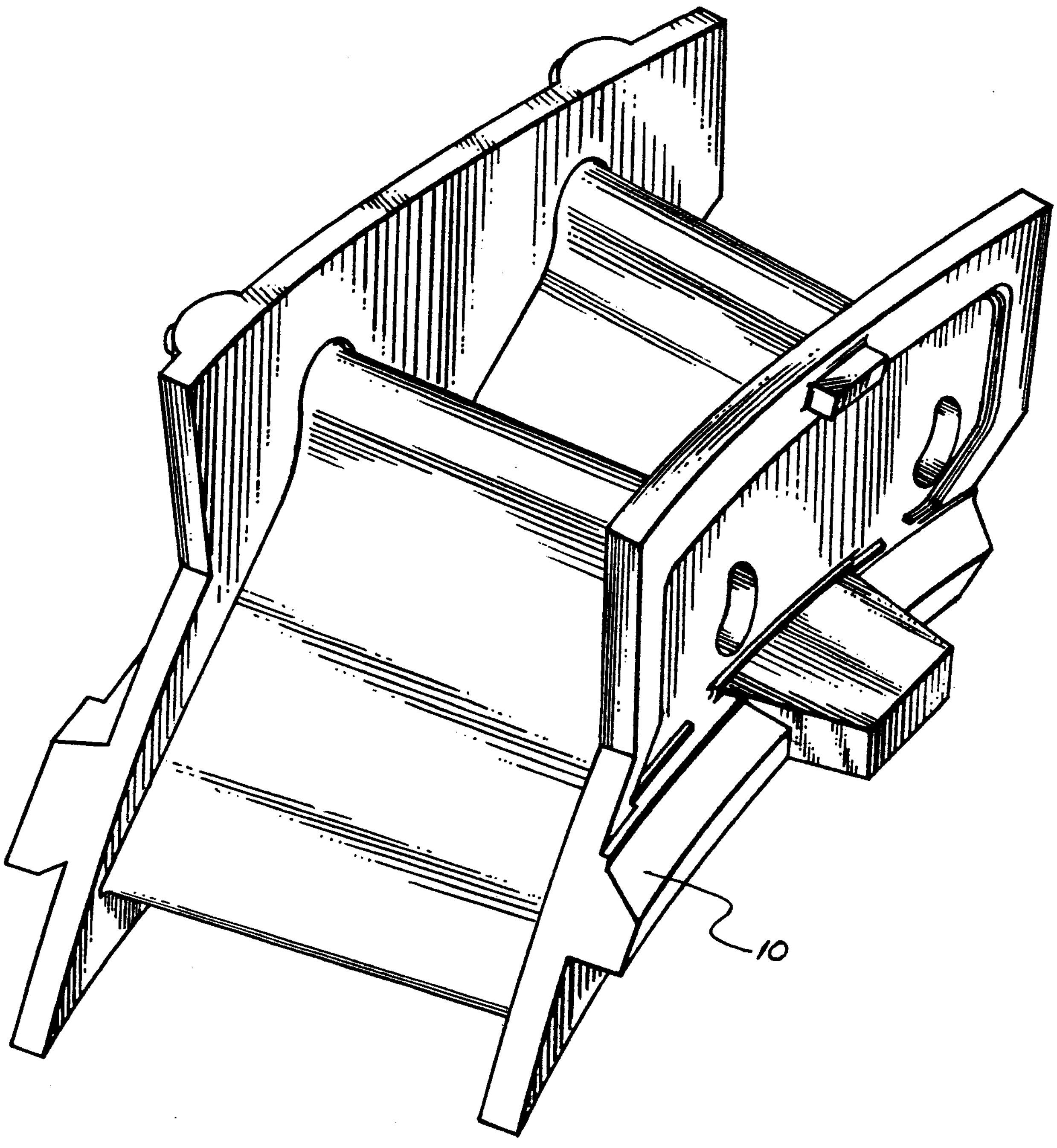
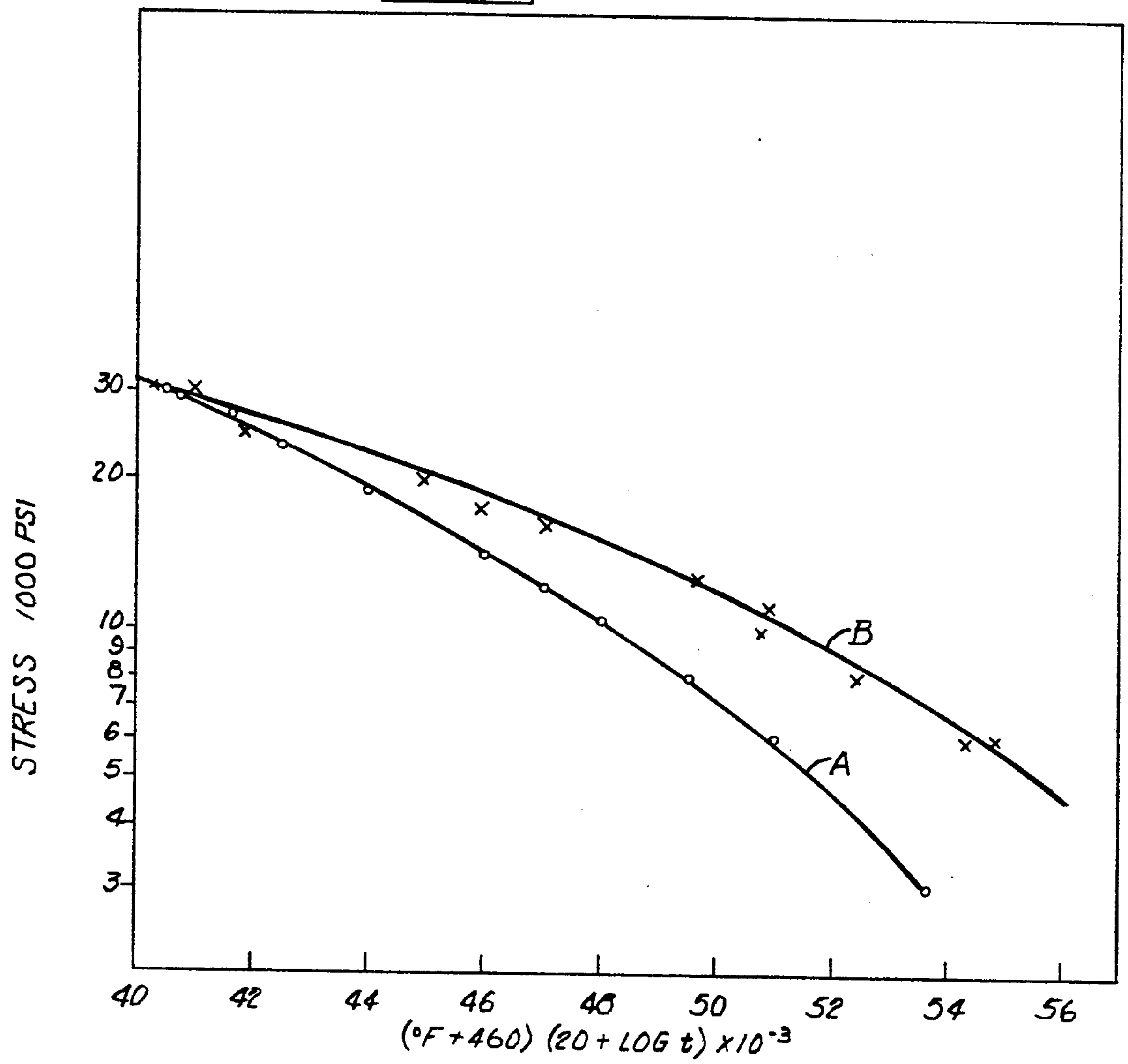


Fig 1

Fig. 2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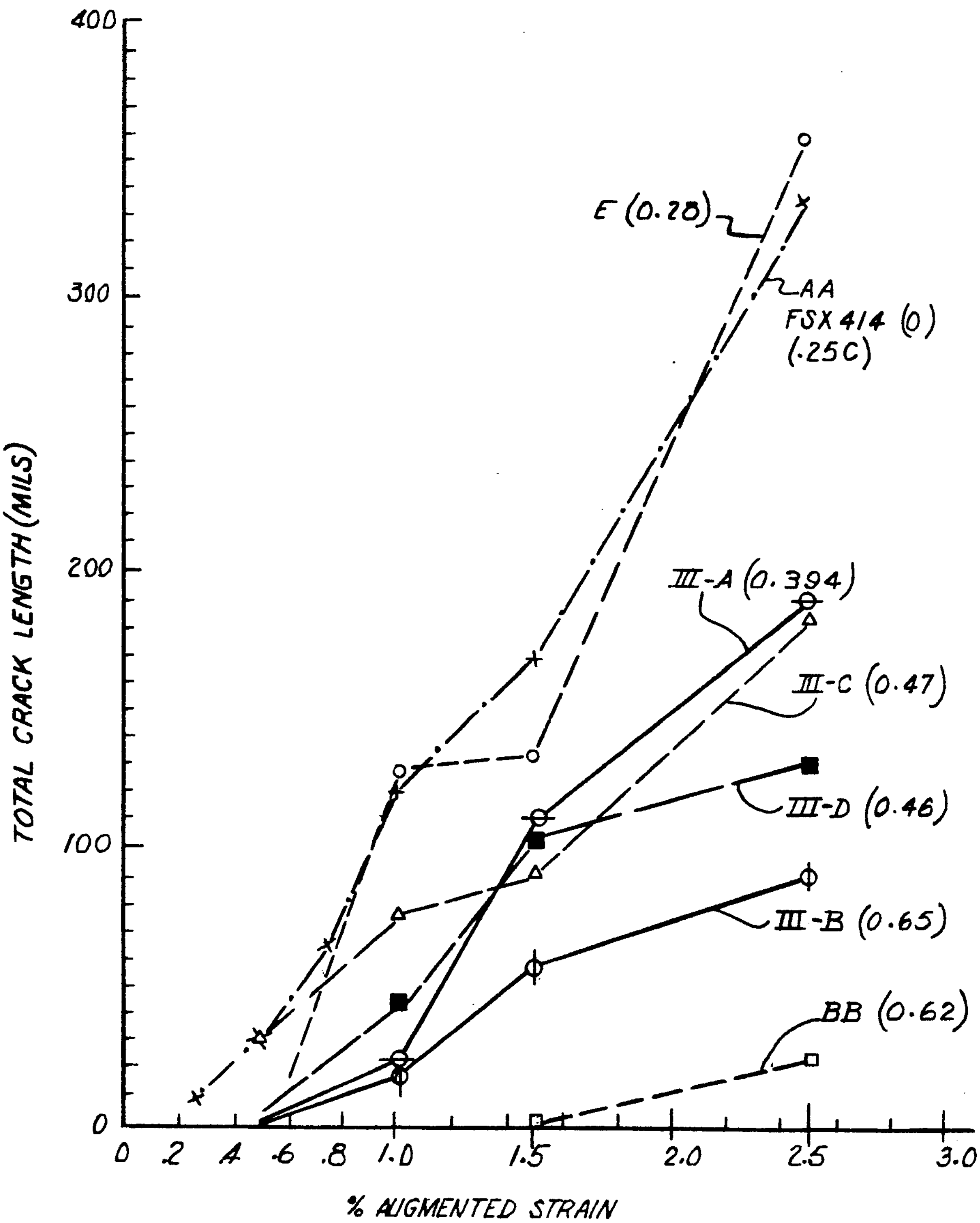
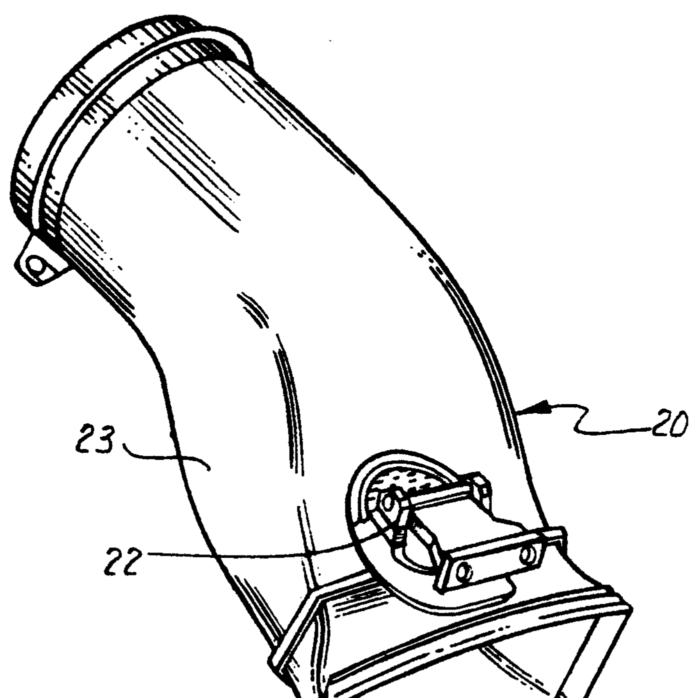

400
300
200
100
0
TOTAL CRACK LENGTH (MILS)
E (0.28)
AA
FSX 414 (0)
(.25C)
III-A (0.394)
III-C (0.47)
III-D (0.46)
III-B (0.65)
BB (0.62)
0 .2 .4 .6 .8 1.0 1.5 2.0 2.5 3.0
% AUGMENTED STRAIN

Fig. 3

Fig 4



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EUROPEAN SEARCH REPORT

Application number

EP 85 11 5301

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
			C 22 C 19/07
A	US-A-3 549 356 (SIMS et al.) * Claims 1,2 * ---	1,3	
A	FR-A-2 273 075 (OWENS-CORNING FIBERGLAS CORP.) * Claims 1-4 * & US - A - 3 933 484 ---	1,3	
A	FR-A-2 074 104 (CABOT CORP.) * Claims 1-3 * & US - A - 3 582 320 ---	1	
A,D	US-A-3 383 205 (SIMS et al.) * Claims 1-3 * ---	1	
A	GB-A- 891 550 (SIERRA METALS) * Claims 1-5 * -----	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 22 C 19/07

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04-04-1986	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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