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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C22C 19/05, 19/07, 30/00

A1

(11) International Publication Number: WO 96/00310

(43) International Publication Date: 4 January 1996 (04.01.96)

(21) International Application Number: PCT/US95/07594

(22) International Filing Date: 22 June 1995 (22.06.95)

(30) Priority Data:
08/264,944 24 June 1994 (24.06.94) US

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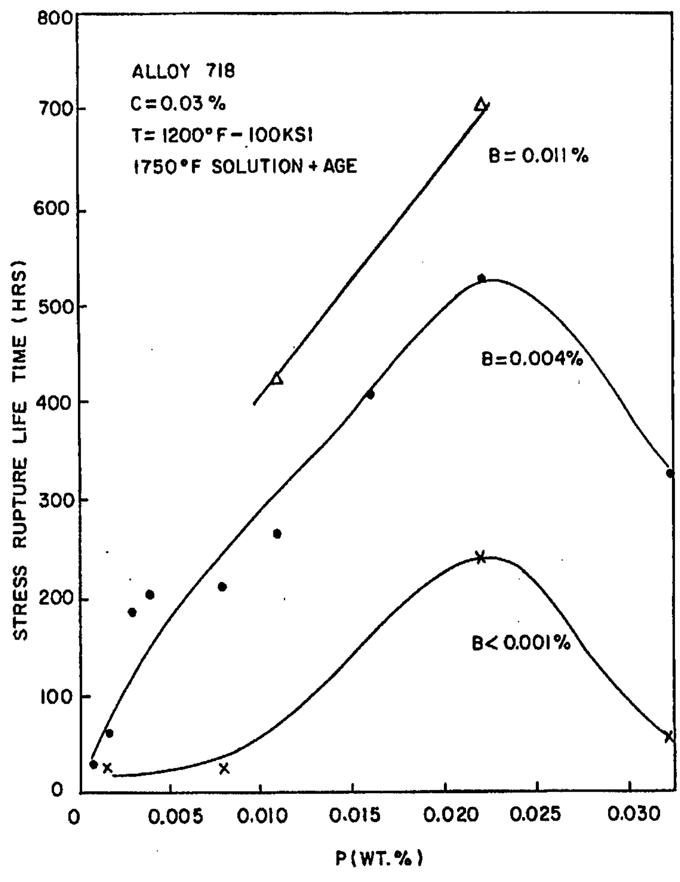
(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.

(54) Title: NICKEL-BASED ALLOY AND METHOD

(57) Abstract

A method of increasing the creep resistance, fatigue resistance, and stress rupture life of superalloys, and the alloys formed thereby, the method comprising adjusting the content of the alloy to a content of (in wt.%) 0.012-0.05 % P, up to 0.1 % C, and up to 0.03 % B.



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TITLE: NICKEL-BASED ALLOY AND METHOD

FIELD OF THE INVENTION

The present invention relates in general to improvements in nickel-based superalloys and more particularly to compositions and methods for improving the creep resistance of such alloys at specific preselected temperatures.

BACKGROUND OF THE INVENTION

Exemplary of nickel-based superalloys is alloy 718 which has a composition specification, according to the Society of Automative Engineering and Aerospace Material Specification AMS5662E of 50-55 wt% Ni, 17-21 wt% Cr, 4.75-5.50 wt.% Nb + Ta, 2.8-3.3 wt% Mo, 0.65-1.15 wt% Ti, 0.2-0.8 wt% Al, 0.35 wt% Mn (max.), 0.08 wt% C (max), 0.015 wt% S (max), 0.015 wt% phosphorus (max), 0.015 wt% Si (max), 1.00 wt% Co (max), 0.006 wt% boron (max), 0.30 wt% Cu (max), with the balance FE.

The nominal composition of the alloy is 53 wt% Ni, 18.0 wt% Cr, 18.5 wt% FE, 5.2 wt% Nb (and Ta), 3.0 wt% Mo, 1.00 wt% Ti, 0.50 wt% Al, 0.04 wt% carbon, and 0.004 wt% boron with phosphorus in the range of 0.005-0.009 wt% or 50-90 ppm. This alloy is a precipitation hardened nickel-base alloy with excellent strength, ductility and toughness throughout the temperature range -423°F to +1300°F. The alloy is normally provided in both cast and wrought forms and typical end use parts, such as, blades, discs, cases and fasteners are characterized by high resistance to creep deformation at temperatures up to 1300°F (705°C) and by oxidation resistance up to 1800°F (908°C). In particular, parts which are formed or welded and then precipitation hardened develop the desired properties. These properties, along with oxidation resistance, good weldability and formability, account for its wide use in aerospace, nuclear and commercial applications.

It is well known, as in U.S. Patent No. 3,660,177, that the fatigue resistant properties of the alloy can be substantially improved by adjusting the processing practice in ways that promote the formation of ultra fine grain size. Unfortunately, the formation of ultra fine grain size and its beneficial effect on fatigue properties is accompanied by an unwanted reduction in stress rupture properties or creep resistance at preselected test temperatures. It is therefore desirable to provide an improved and novel alloy which exhibits better stress rupture and creep resistance while maintaining a constant ultra-fine grain size and therefore fatigue resistance comparable to conventional 718 alloy.

OBJECTS OF THE INVENTION

It is therefore an objective of the present invention to provide a composition of matter and method whereby the creep resistance of nickel based alloys is substantially improved while maintaining a constant ultra-fine grain size and other desired properties, such as, fatigue resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graphical representation of the effect on stress rupture life time of changes in the phosphorus content of alloy 718 of nominal alloy composition with standard-heat treatment, tested at a temperature of 1200°C and a loading of 100 KSI, with the nominal phosphorus composition range shown cross-hatched.

Fig. 2 is a series of line graphs showing the effect on stress rupture life of various percentages by weight of boron at various percentages by weight of phosphorus at a single percentage by weight of carbon, tested at a temperature 1200°.

Fig. 3 is a series of line graphs showing the effect on stress rupture life of various percentages by weight of phosphorus at various percentages by weight of boron at a single percentage by wt. of carbon and tested at a temperature of 1200°F and a loading of 100 ksi.

Fig. 4 is a three axis graphical representation of the effect on stress rupture life of varying amounts of phosphorus and boron in nickel-based alloy 718 having a predetermined carbon content, tested at 1200°F and a load of 100 KSI.

Fig. 5 is a graph showing the effect on stress rupture life of varying amounts of boron in alloy 718 at fixed concentrations of phosphorus and carbon at the test conditions indicated.

Fig. 6 is a graph showing fatigue resistance data for conventional 718 alloy and alloys according to this invention.

SUMMARY OF THE INVENTION

The stress rupture life of nickel-based alloys and particularly fine grained, nickel based alloys is improved at preselected temperatures and stresses by the synergistic effect of predetermined amounts of phosphorus (P) and boron (B) in the alloy composition and more particularly in such alloys containing a pre-selected, preferably low carbon (C) content.

DETAILED DESCRIPTION OF THE INVENTION

The element boron by itself, or in combination with zirconium has in the past been purposely added to nickel-based alloys for the purpose of improving stress rupture and creep properties. Phosphorus, on the other hand, is considered a "tramp" element - that is, it is not purposely added, but carried in as a contaminant with various raw materials used to produce nickel-based alloys and has generally been considered as detrimental to properties if the content is allowed to exceed very low limits. Most commercial specifications for nickel-based alloys place a low maximum limit on phosphorus content. Specification AMS 5662E, for example, restricts phosphorus to .015% maximum.

It has been discovered however, that purposeful additions of phosphorus, even in excess of the nominal commercial specification limits, can surprisingly improve the stress rupture properties of certain nickel-base superalloys by as much as an order of magnitude (10X) or 1000%.

It has further been discovered that specific amounts of phosphorus, boron, and carbon in nickel-base alloys work together in a synergistic manner and that when all three elements are present in specific, controlled amounts, that even greater improvements in stress rupture properties can be obtained. These results are obtained with values that are more than additive of the results expected of each element individually. This synergistic effect is achieved while maintaining other desired properties such as tensile strength and fatigue resistance.

The desired effect of phosphorus and boron on stress rupture or creep deformation of superalloys according to the invention described herein, can best be understood from the following discussion.

The controlling mechanism of creep deformation in most applications in nickel-based superalloys, particularly the alloys described herein, is dislocation creep which can occur at grain boundaries and the interior of the grains. Phosphorus and boron in nickel-based alloys have a strong tendency to segregate to grain boundaries and also remain inside the grains as solute atoms or as compounds (phosphides or borides), particularly when the grain boundaries are heavily occupied by phosphorus or boron. Usually phosphorus and boron will compete with each other for available grain boundary sites and phosphorus in this side competition has a stronger tendency to grain boundary segregation. At lower test temperatures, as described herein, transgranular dislocation creep dominates. Phosphorus and boron which remain in the interior of grains can retard creep deformation by their interaction with dislocations through several possible mechanisms, and a strong synergistic effect of phosphorus and boron on dislocation creep was observed, as more fully described hereinafter. However, phosphorus and boron which segregate to grain boundaries will not play any important role in retarding the transgranular dislocation creep. This may explain the lack of any observed effect of boron at low levels in alloys with ultra low phosphorus. That is, boron preferentially segregates to the grain boundaries, due to lack of site competition from phosphorus.

The synergistic effect described and the roles of varying amounts of phosphorus, boron and carbon in nickel-based alloys in improving stress rupture properties without detrimentally affecting fatigue life was characterized in the results of a systematic series of comparison tests described hereinafter.

A number of test alloys were prepared by the usual manufacturing method. Fifty pound heats were vacuum induction plus vacuum die melted. Following a homogenization treatment, all ingots were rolled to 0.625" diameter bar and heat treated with a standard solution + aging treatment of 1750°F/1 HR/AC + 1325°F/8 HRS/FC. Phosphorus, boron and carbon contents were varied in different heats but all of their chemistry and processing conditions were held constant.

PHOSPHORUS EFFECT

The effects of varying only phosphorus over a very wide range, e.g. much greater than defined in most specifications, on the mechanical properties of a nominal 718 alloy are presented in Table 1 and Figure 1. The tests demonstrated that increasing phosphorus up to a level much higher than the maximum allowed in most specifications, and certainly much higher than current commercial practice, significantly improved the stress rupture properties of alloy 718. When compared to the alloy with phosphorus content typical of normal commercial 718, an increase of more than 2.5X was achieved at a phosphorus content of 0.022% over the entire range of phosphorus levels studied, an increase in rupture life of more than 10X was observed. The desirable high levels of phosphorus had no significant effect on stress rupture ductility compared to standard 718. Tensile strengths at both room temperature and 1200°F were not effected by phosphorus content while tensile ductilities were unchanged or slightly improved (at 1200°F).

The stress rupture life improvements noted were grain size dependent and showed up most significantly in fine grained structures. It is well known that fine grained 718 has excellent fatigue properties but relatively inferior creep and stress rupture resistance. This study showed that the drawback of fine grained 718 could be overcome by increasing the phosphorus level, leading to a new type of nickel-based alloy which has both excellent fatigue resistance and outstanding creep/stress rupture properties.

Increased phosphorus levels enhanced the resistance to intergranular cracking of alloy 718, as shown by the transition of fracture mode from intergranular to transgranular separation in stress rupture tests at lower stresses. This effect is probably related to increased phosphorus segregation to grain boundaries.

PHOSPHORUS-BORON INTERACTION

The interactive effects of phosphorus and boron on stress rupture properties are shown in Table 1 and Figure 2. Figure 2 illustrates that rupture life increases as the boron content is raised. Surprisingly, however, these data also show that boron has no effect on rupture life if the phosphorus content is at a very low level (0.016%). This suggests a very strong interaction effect between phosphorus and boron which has not been recognized previously. To a slightly lesser degree the reverse effect is also true. As shown in Figure 3, at very low levels of boron, phosphorus has a smaller effect on rupture life than at higher boron levels.

The synergistic interaction between

phosphorus and boron on rupture life can best be seen when examined as a three dimensional plot shown in Figure 4. This plot clearly shows that the longest stress rupture lives are achieved when both phosphorus and boron are present in certain critical amounts. It is also evident from figures 2 to 4 that the maximum rupture life hours are greater than the sum expected from each of these elements acting independently, an unexpected synergistic effect.

CARBON EFFECT

It has also been discovered that still further improvements in rupture life can be obtained by reducing carbon content in conjunction with critical phosphorus and boron contents. This effect is illustrated in Table 1 and Figure 5.

The invention described clearly demonstrates that phosphorus up to a certain amount substantially improved the stress rupture properties of alloy 718 without degrading the tensile properties and hot workability. The upper limit of phosphorus which could be employed in fine grained alloys was typically much higher than that presently employed or dictated by the 718 specifications. As more fully described herein, the phosphorus-boron interaction provided an ability to selectively achieve desired properties and particularly enhanced stress rupture properties by manipulation of phosphorus and boron levels in nickel-based alloys. It was also observed that a low carbon level was generally beneficial to stress rupture properties in the presence of beneficial amounts of phosphorus and boron.

STRESS RUPTURE PROPERTIES OF TEST ALLOYS
TABLE 1

Heat No. of Test Alloy	Level of Variable Elements (wt%)			S/R Properties (1200°F-100ksi)		
	P	B	C	Life Time (HRS)	Elong-ation (%)	Reduction in Area (%)
G577-1	0.0007	0.003	0.032	25.2	42.9	68.0
G453-1	0.0016	0.004	0.031	42.6	34.7	-
G455-1	0.0016	0.004	0.032	41.8	26.5	60.0
G454-1	0.0016	<0.001	0.030	28.9	32.7	-
G670-1	0.0016	<0.001	0.004	26.1	29.6	-
G499-1	0.0016	0.007	0.034	58.2	30.2	-
G498-1	0.003	0.004	0.035	184.6	27.2	45.0
G497-1	0.004	0.004	0.033	204.0	25.8	46.0
G500-1	0.008	0.004	0.035	208.0	31.7	65.0
G671-1	0.008	<0.001	0.028	24.8	36.6	-
G672-1	0.009	0.005	0.013	277.5	30.3	-
G670-2	0.009	<0.001	0.005	13.2	37.4	-
G729-1	0.010	0.003	0.032	217.0	30.5	68.0
G720	0.010	0.006	0.033	300.7	22.6	-
G499-2	0.010	0.007	0.037	355.0	29.3	-
G729-2	0.010	0.009	0.032	425.8	30.6	-
G721	0.013	0.005	0.005	277.5	25-7	-
G672-2	0.015	0.005	0.035	406.7	30.3	68.0
G671-2	0.023	0.004	0.028	522.8	32.0	78.0
G726-1	0.026	<0.001	0.030	241.8	25.6	-
G726-2	0.024	0.007	0.032	537.1	17.0	-
G727-2	0.025	0.011	0.033	704.3	22.9	-
G723	0.020	<0.001	0.005	385.5	22.0	-
G724	0.022	0.003	0.005	660.9	20.2	-
G730	0.026	0.006	0.011	672.0	22.9	-
G727-1	0.025	0.011	0.009	749.1	22.7	-
G728-2	0.033	0.004	0.033	329.8	24.3	75.0
G728-1	0.032	<0.001	0.006	57.3	24.0	-

The contemplated ranges of phosphorus and boron which will achieve the benefit of the invention described herein are 0.012% to 0.050% by weight phosphorus, up to 0.030% by weight boron and where the carbon content is equal to or less than about 0.01% by weight.

It is therefore contemplated that other alloys could advantageously benefit from both phosphorus addition and the phosphorus boron interaction observed.

The following composition embraces the alloys in which it is believed, the described phosphorus boron interaction described herein will be synergistically effective.

TABLE 2

40-55	Ni
14.5-21	Cr
2.5-5.5	Nb + Ta
up to 3.3	Mo
0.65-2.00	Ti
0.10-0.80	Al
up to .35	Mn
up to 0.07	C
up to 0.015	S
0.016 to 0.33	P
up to 0.006	B
Balance	Fe
up to 0.35	Si

The invention has been described in terms of specific alloys and effects, however, it will be appreciated that the beneficial effects described can be obtained in alloy compositions significantly different than those described. Therefore, the scope of the invention should be limited to only the scope of the appended claims interpreted in view of the applicable prior art.

CLAIMS

1. A method of increasing creep resistance in nickel-based superalloys containing less than about 0.10% by weight carbon, comprising the steps of adjusting the phosphorus content of the alloy to an amount of from about 0.012% by weight to about 0.050% by weight of the alloy and adjusting the boron content of the alloy up to about 0.030% by weight of the alloy, whereby the stress rupture life of the alloy measured at a temperature of up to at least 1200°F is significantly improved.

2. The method of claim 1 wherein the carbon content is less than about 0.01% by weight, the phosphorus content is an amount from about 0.016 to about 0.030% by weight and the boron content is about 0.004 to about 0.012% by weight.

3. A method of retaining fatigue resistance characteristic of fine grained nickel-based alloys while increasing stress rupture life at temperatures up to 1200°F comprising the steps of providing the alloy containing less than about 0.10% by weight carbon, with phosphorus in an amount by weight of the alloy of from between 0.012% to about 0.050%, and providing the alloy with boron in an amount by weight of the alloy of up to about 0.030% whereby the stress rupture life of the alloy is substantially increased without substantial reduction in fatigue properties.

4. A method for improving the stress rupture life of an alloy comprising 40-55 wt % Ni, 14.5-21% wt% Cr, 2.5-5.50 wt.% Nb + Ta, up to 3.3 wt% Mo, 0.65-2.00 wt% Ti, 0.10-0.8 wt% Al, up to 0.35 Mn, up to 0.10 wt% C, up to 0.35 wt% Si, up to 0.010 wt% each Mg + Ca with the balance FE,

including the steps of:

a) providing the alloy with phosphorus in an amount by weight of the alloy of from about 0.012% to about 0.050%; and

b) providing the alloy with boron in an amount by weight of the alloy of up to about 0.03% by weight.

5. A nickel-based alloy consisting essentially of 40-55 wt% Ni, 14.5-21 wt% Cr, 2.5-5.50 wt% Nb + Ta, up to 3.3 wt% Mo, 0.65-2.00 wt% Ti, 0.10-0.8 wt% Al, up to 0.35 wt% Mn, up to 0.10 wt% C, up to 0.015 wt% S, 0.012-0.50 wt% P, up to 0.030 wt% B, with the balance FE and incidental impurities.

6. A nickel-based alloy exhibiting substantially improved stress rupture life comprising by weight the alloy of about 53 wt% Ni, 18.0 wt% Cr, up to 0.010% each Mg + Ca, 5.2% Nb and Ta, 3.0% Mo, 1.00% Ti, 0.50% Al, less than 0.012, between 0.004 to .020 B and between about 0.015% to 0.033% phosphorus, whereby the stress rupture life of the alloy tested at 1200°F and 100 ksi, after solution treating at 1750°F plus aging exceeds the stress rupture lifetime of nominal 718 alloy identified by AMS 5662 specification.

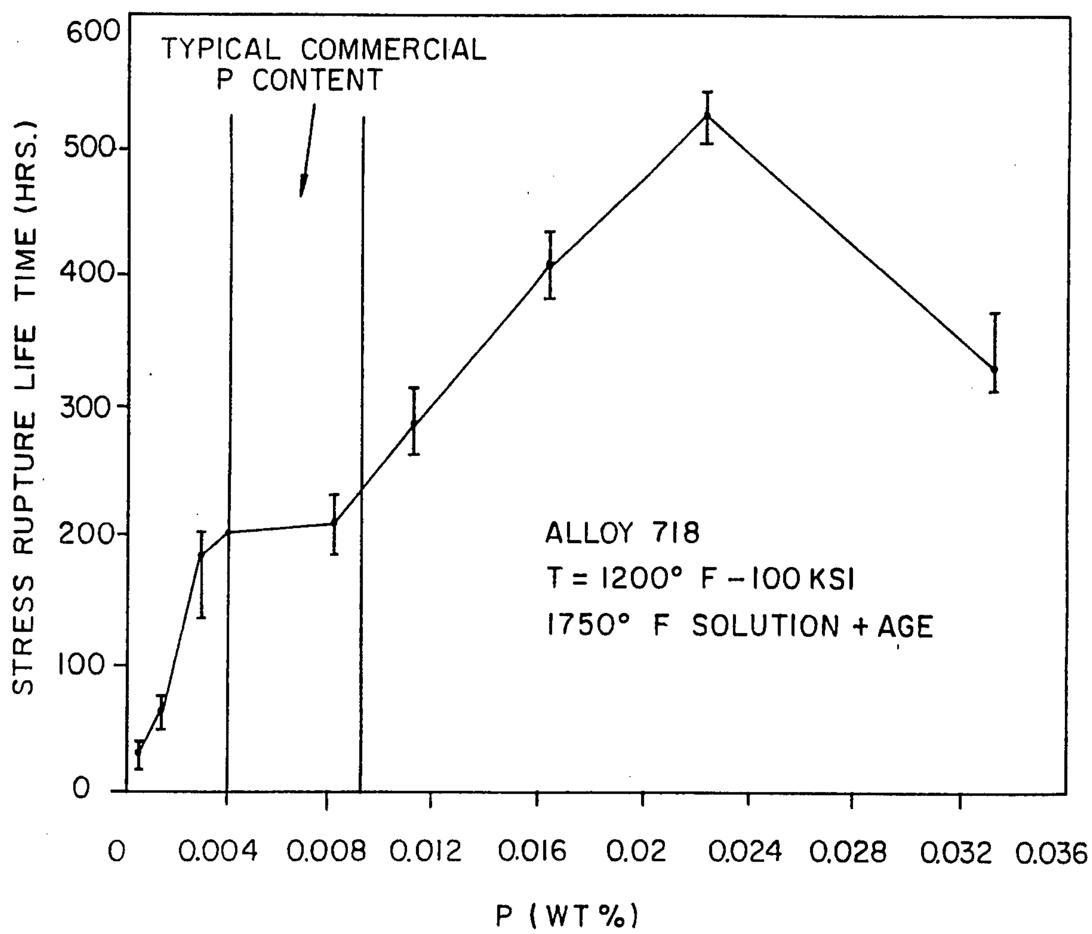
TYPICAL COMMERCIAL
P CONTENT
STRESS RUPTURE LIFE TIME (HRS.)
600
500
400
300
200
100
0
0
0.004
0.008
0.012
0.016
0.02
0.024
0.028
0.032
0.036
P (WT %)
ALLOY 718
T = 1200° F – 100 KSI
1750° F SOLUTION + AGE

FIG. 1

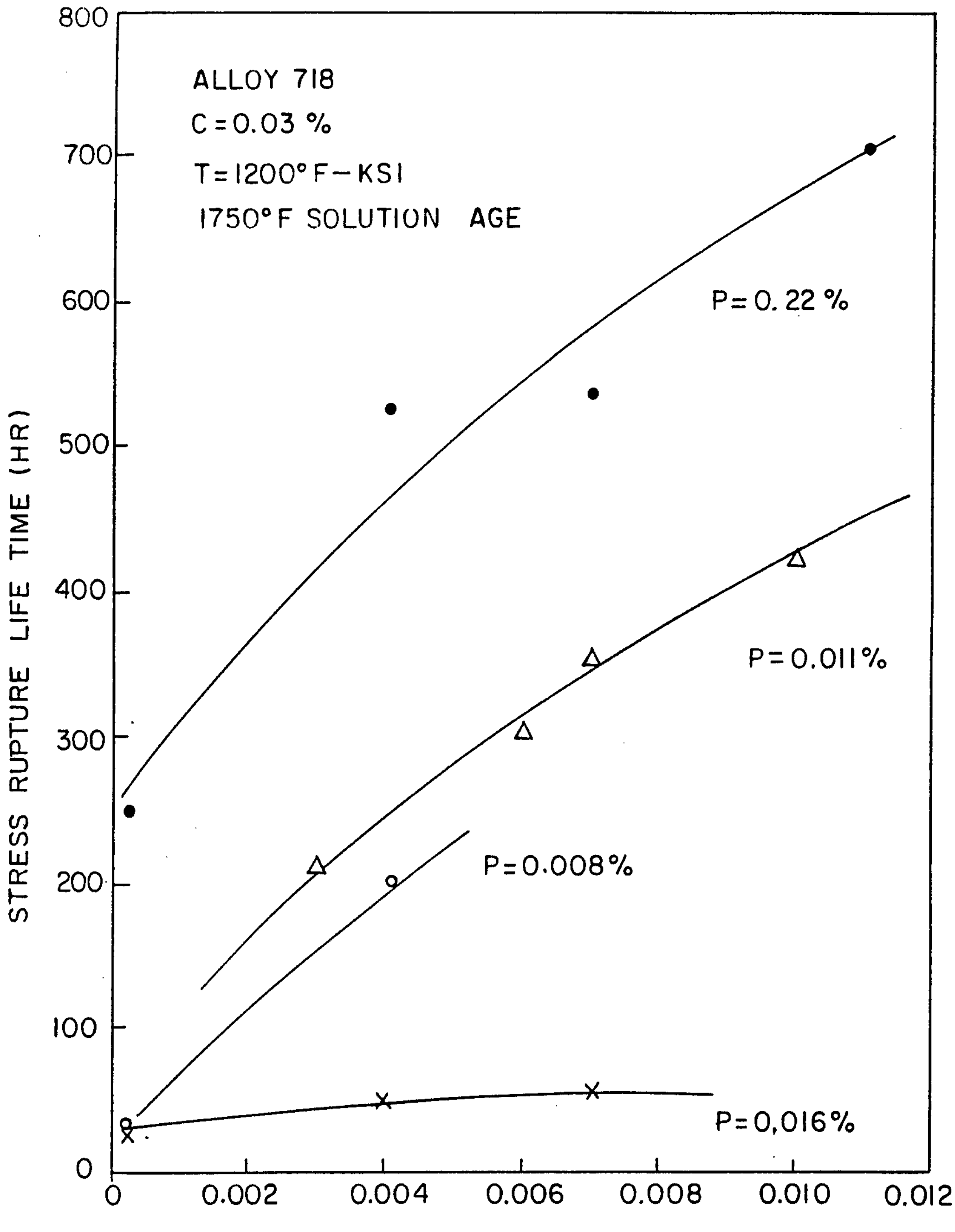
ALLOY 718
C=0.03 %
T=1200°F−KSI
1750°F SOLUTION AGE
P=0.22 %
P=0.011%
P=0.008%
P=0.016%
STRESS RUPTURE LIFE TIME (HR)
B (WT. %)
0
100
200
300
400
500
600
700
800
0.002
0.004
0.006
0.008
0.010
0.012

FIG. 2

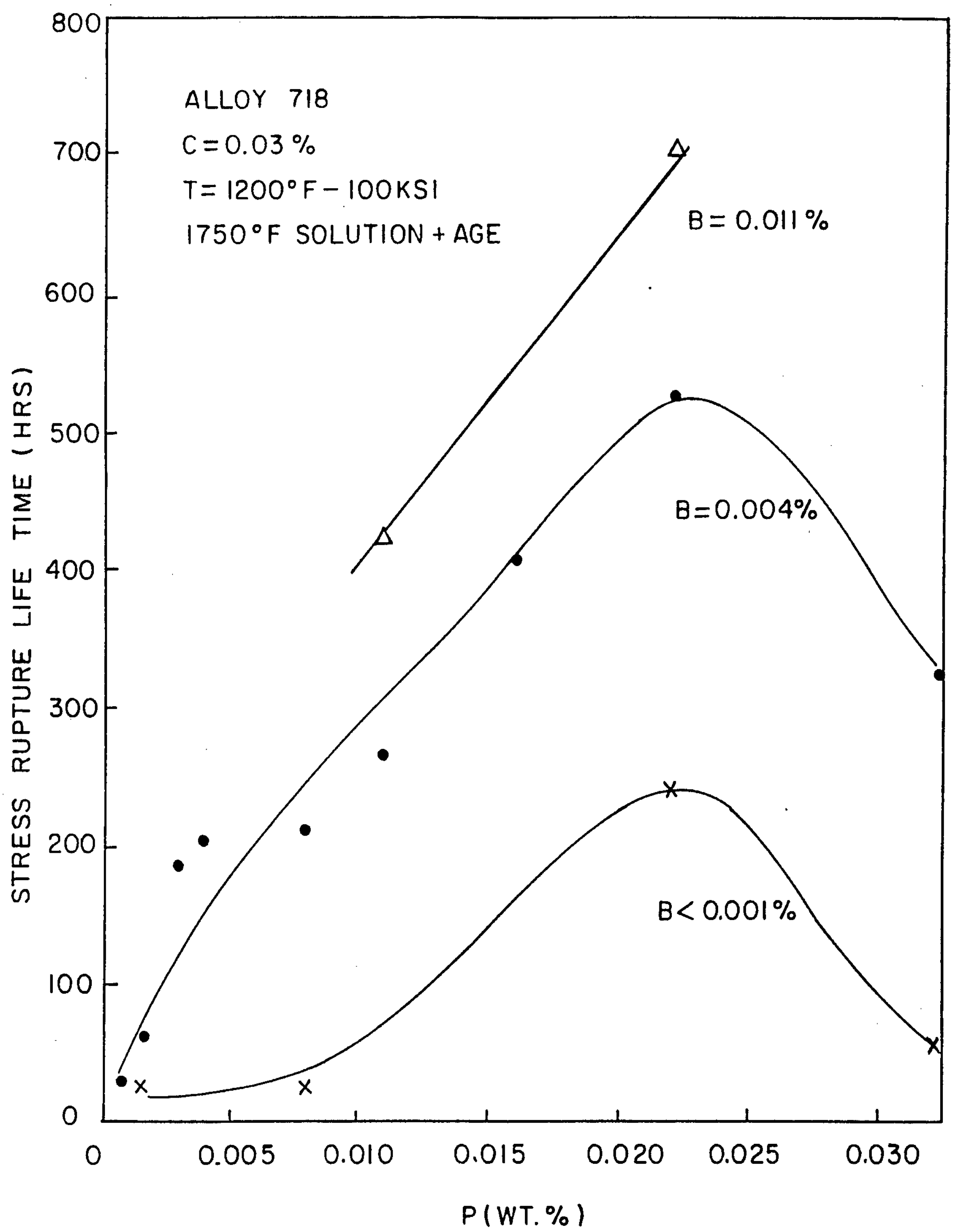
ALLOY 718
C=0.03%
T= 1200°F - 100KSI
1750°F SOLUTION + AGE
B= 0.011%
B=0.004%
B< 0.001%
STRESS RUPTURE LIFE TIME (HRS)
800
700
600
500
400
300
200
100
0
0
0.005
0.010
0.015
0.020
0.025
0.030
P (WT. %)

FIG. 3

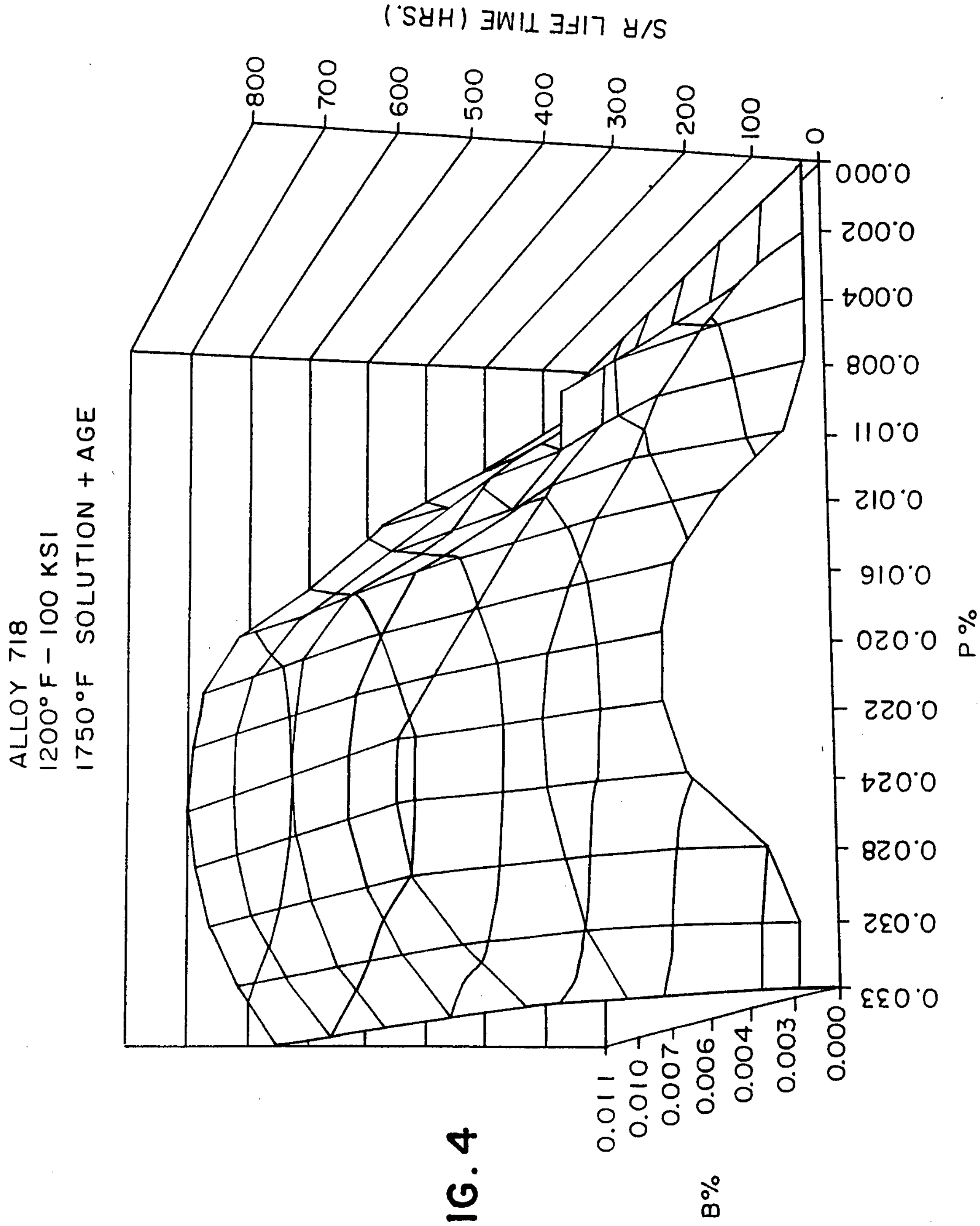
ALLOY 718
1200° F – 100 KSI
1750°F SOLUTION + AGE
S/R LIFE TIME (HRS.)
0
100
200
300
400
500
600
700
800
0.000
0.002
0.004
0.008
0.011
0.012
0.016
0.020
0.022
0.024
0.028
0.032
0.033
P %
0.000
0.003
0.004
0.006
0.007
0.010
0.011
B%

FIG. 4

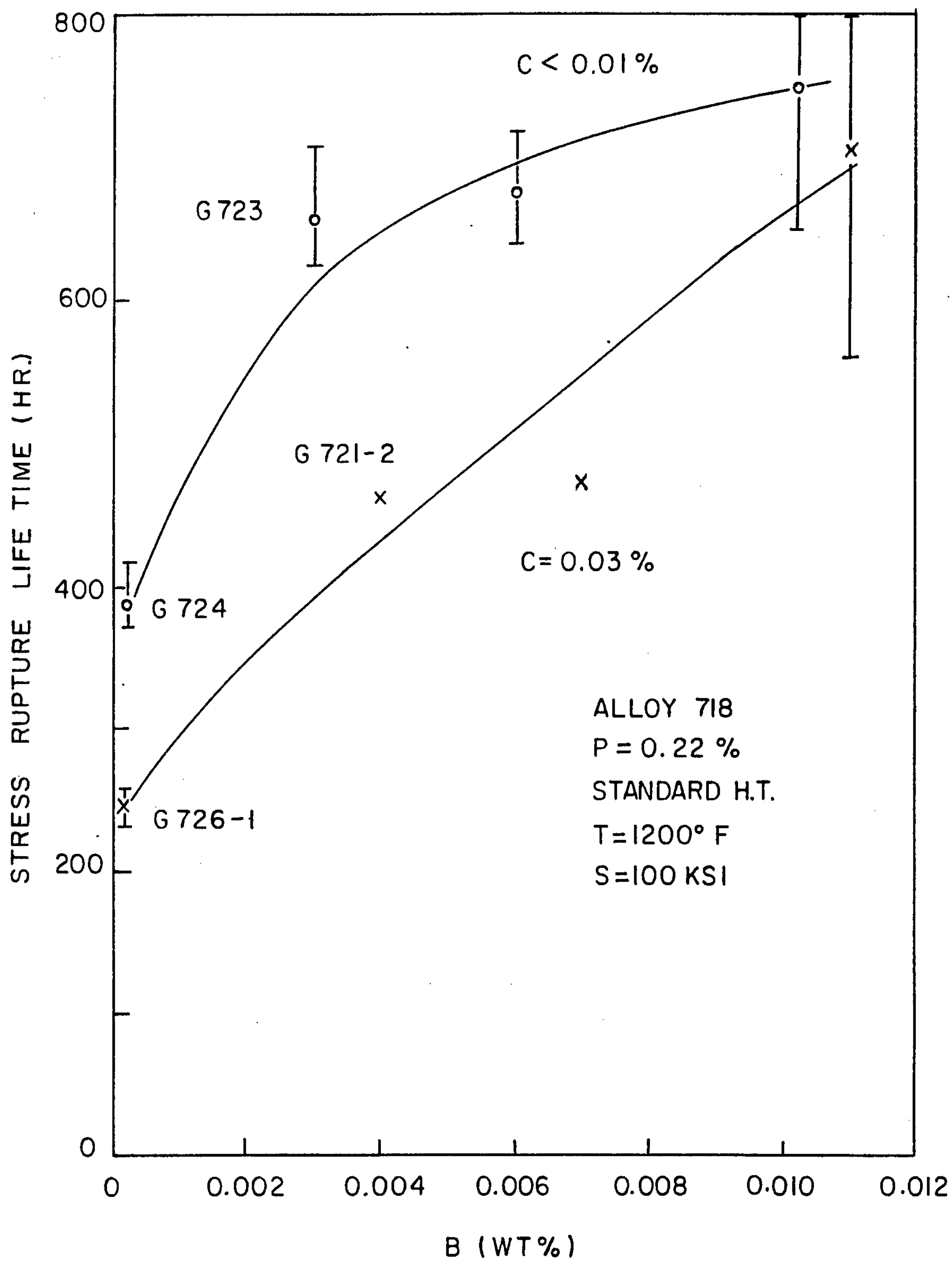
800
600
400
200
0
STRESS RUPTURE LIFE TIME (HR.)
C < 0.01 %
G 723
G 721-2
C= 0.03 %
G 724
G 726-1
ALLOY 718
P = 0. 22 %
STANDARD H.T.
T=1200° F
S=100 KSI
0
0.002
0.004
0.006
0.008
0.010
0.012
B (WT%)

FIG. 5

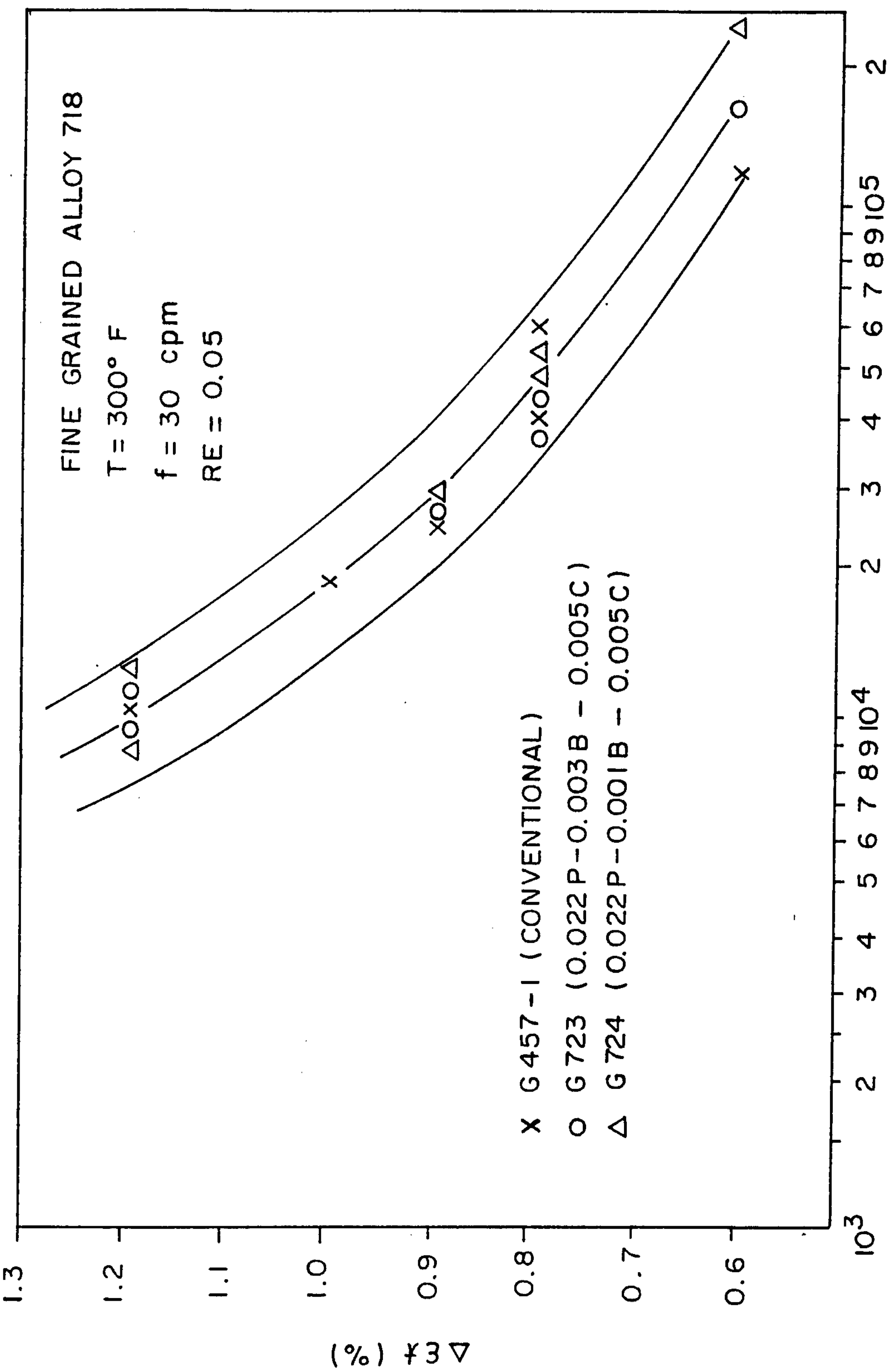
FINE GRAINED ALLOY 718
T = 300° F
f = 30 cpm
RE = 0.05
X G 457-I (CONVENTIONAL)
O G 723 (0.022 P-0.003 B - 0.005 C)
Δ G 724 (0.022 P-0.001 B - 0.005 C)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
Δε_t (%)
10^3
2
3
4
5
6
7
8
9
10^4
2
3
4
5
6
7
8
9
10^5
2

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/07594

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C22C 19/05, 19/07, 30/00
US CL :420/443,447,448,584.1; 148/410,419,428,442
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/443,447,448,584.1,586,586.1; 148/409,410,419,426,428,442

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

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

CAS ONLINE, REGISTRY FILE
search terms:(40< =ni< =55 and 14.5< =cr< =21 and .65< =ti< =2 and .1< =al< =.8 and 8< =fe< =42.5 and p)/mac

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 3,046,108, (EISELSTEIN) 24 July 1962, col. 2, lines 1-13; col. 10, lines 8-14.	1-6
Y	US,A, 4,888,253 (SNYDER ET AL) 19 December 1989, col. 1, lines 56-59.	1-6
Y	US,A, 4,400,211 (KUDO ET AL), 23 August 1983, abstract, col. 7, lines 57-59.	1-6
A	US,A, 4,476,091 (KLARSTROM) 09 October 1984.	
A	US,A, 4,844,864 (FRANK) 04 July 1989.	
A	US,A, 5,000,914 (IGARASHI ET AL) 19 March 1991.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 AUGUST 1995	05 OCT 1995

Name and mailing address of the ISA/US	Authorized officer
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