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(54) **Precipitation hardening copper alloys.**

(57) A precipitation and dispersion hardening copper alloy which combines useful properties of high tensile and yield strength, proportional limit, modulus of elasticity, ductility and formability, corrosion resistance, high fatigue resistance and electrical conductivity comprises 2 to 9% nickel, 0.05 to 2% each of silicon, chromium and aluminum, the balance being copper and impurities.

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PRECIPITATION HARDENING COPPER ALLOYS

This invention relates to precipitation and dispersion hardening copper alloys and more particularly to precipitation hardening copper alloys that combine good mechanical and electrical properties.

There are many applications in which a strong resilient part having good electrical conductivity is desired. Due to its excellent conductivity, copper would be an ideal metal to use were it not for its relatively poor mechanical properties such as comparative softness, low modulus of elasticity and low tensile and tensile yield strengths.

Unlike many kinds of steel, most copper alloys are not susceptible to improvement in hardness and strength by heat treatment processes. One useful exception to this is the copper-beryllium alloys which are precipitation or age hardenable. These copper alloys, typically containing between 1 and 2% beryllium, are useful because of their non magnetic properties, good electrical conductivity, high tensile strength, high degree of hardness, and their ability to be cast, wrought, forged or drawn. Because of these properties they find utility in the manufacture of various types of scientific instruments, electrical contact points, coil springs, non magnetic cutting tools and the like.

While copper beryllium alloys have useful mechanical and electrical properties, their cost is comparatively high due to the scarceness of beryllium in the earth's crust. Of even greater concern, however is that it is now recognized that beryllium is an extremely toxic material and is a hazardous carcinogen. This makes it difficult to process copper beryllium alloys with conventional techniques without creating danger to the health of workers and without violating exposure standards as set by various governmental health organisations. Copper-beryllium alloys present a health hazard not only at the time of manufacturing the alloy, but also in subsequent operations which give rise to air borne metallic oxide dust particles.

Other copper base alloys also tend to be deficient in certain respects. For example, brasses, phosphor bronzes, nickel silvers and most copper alloys obtain their property increases through cold working, which decreases formability in proportion to the amount of cold work. Other dispersion hardening alloys have insufficient electrical conductivity to be useful in electrical applications.

This invention provides a beryllium-free precipitation hardenable copper alloy that has mechanical and electrical properties similar to those ordinarily only obtained with copper-beryllium alloys.

The copper alloys of the invention combine useful properties of tensile strength, yield strength, hardness, formability, corrosion resistance and resistance to fatigue, and electrical conductivity.

According to the invention, a copper-nickel alloy includes minor quantities of silicon, chromium and aluminum.

To achieve the desired mechanical properties at least 2% nickel is required and the practical upper limit from the standpoint of electrical conductivity is 9%. The silicon, chromium and aluminum are all essential, at least in small amounts, of from 0.05% to 2%. Within these limits, a large number of alloys can be made. No specific percentages can be given as ideal since, as is so often the case, an increase or decrease in a particular component is a trade off of one desirable property for another and the exact formulation selected will depend on the end use requirements. The total amount of silicon, aluminum and chromium, however, preferably does not exceed 2%. A typically useful alloy with a good average range of properties comprises 4.5% nickel, 0.5 to 0.7% aluminum and silicon and 0.25% chromium. It may also be desirable to add trace amounts (i.e. up to 0.01%) of incidental elements such as lithium, boron or phosphorous for deoxidizing or fluidity purposes.

Generally speaking, depending upon the end use application, it is desired to provide a conductivity of at least 8.1×10^6 Sm^{-1} (14% I.A.C.S. (International Association of Conductivity Standards).

The alloys of this invention have a very complex structure of the various pseudo-binary systems with copper as the base component and the other elements combined in various combinations as the other phases. The alloy has increased solubility at elevated temperatures and this alpha state can be maintained by rapidly quenching to room temperature, thereby creating an unstable, super saturated condition that only requires the proper temperature to precipitate the hardening phases.

The alloys of this invention are readily hardenable, which is a time/temperature related function. For example, maximum hardness can be obtained in less than 2 hours if the alloys are heated to about 400°C., but, this time can be reduced to only about 15 seconds at a temperature of about 750°C.

The variation of various properties of the alloys of the invention with changing constitution is illustrated in the drawings of which:-

Fig. 1 is a graph showing the effect upon ultimate tensile strength and conductivity when the nickel content of an alloy of this invention is varied as shown along the abscissa and the alloying amount of Si and Al are held constant at 0.75% and the Cr at 0.5%.

Fig. 2 is a graph showing the effect upon ultimate tensile strength and conductivity when the aluminum content of an alloy of this invention is varied as shown along the abscissa and the Ni is held constant at 5%, the Si at 0.75%. and the Cr at 0.5%.

Fig. 3 is a graph showing the effect upon ultimate tensile strength and conductivity when the silicon content of an alloy of this invention is varied as shown along the abscissa and the Ni is held constant at 5%, the Al at 0.75% and the Cr at 0.5%.

Fig. 4 is a graph showing the effect upon ultimate tensile strength and conductivity when the chromium content of an alloy of this invention is varied as shown along the abscissa and the Ni content is held constant at 5% and the Al and Si at 0.75%.

Fig. 5 is a graph showing the time required to achieve maximum hardness of typical alloys of this invention plotted against the function of temperature.

Table I shows typical property values of the alloys according to the invention.

TABLE I

		Unaged	Aged
DENSITY	gm/cm^3 at 20^oC	8.694	8.681
	lb/in^3 at 68^oF	0.3140	0.3136
SPECIFIC HEAT CAPACITY	$J/(kg.^oK)$	397	397
	$BtU/(lb^oF)$	0.0948	0.0948
THERMAL CONDUCTIVITY (0-200°C)	W/(m.k)	78.9	78.9
	$BtU\ ft^{-1}h^{-1}\,^oF^{-1}$	45.6	45.6
	$Cal\ cm^{-1}S^{-1}\,^oC^{-1}$	0.188	0.188
MODULUS OF ELASTICITY	$lbf/in^2 x\ 10^6$	17-19	17-19
	kPa x 10^6	117.2-131.0	117.2-131.0
MAGNETIC PERMEABILITY	mOe	1.001 - 1.005	1.001
	$(HM^{-1}) \times 10^{-9}$	1.257 - 1.262	1.257
ELECTRICAL CONDUCTIVITY	% IACS	12	18-20
	$Sm^{-1} \times 10^6$	7.0	10.4-11.6
VOLUME RESISTIVITY (at 20°C)	~ (circ mil/ft)	88	53-69
	~ m	146.3	88.1-114.7
MAXIMUM WORKING TEMPS	(stable for 24 hours)	375°C 707°F	375°C 707°F

The following examples illustrate the invention.

In the examples, alloys having the constitution shown in Table II were made in accordance with this invention using standard techniques. Table III shows the variation in properties obtained for the alloys of Table II. The property data listed was obtained after heat ageing at 450°C for the times shown.

TABLE II

Alloy No.	Ni%	Si%	Al%	Cr%
1	5.60	0.72	1.46	0.46
2	5.44	0.97	1.00	0.50
3	5.81	0.79	0.28	0.44
4	5.52	0.74	0.77	0.22
5	5.54	0.89	0.78	0.33
6	5.35	1.41	0.82	0.40
7	5.23	1.41	0.83	0.42
8	5.44	1.30	0.80	0.42
9	5.30	0.28	0.72	0.36
10	2.15	0.88	0.78	0.46
11	3.18	0.90	0.77	0.41
12	4.55	0.95	0.86	0.41
13	4.23	1.02	0.92	0.47
14	8.63	1.31	1.16	0.20
15	7.88	1.42	1.23	0.18
16	7.11	1.36	0.86	0.21
17	7.89	1.38	0.01	0.19
18	5.37	0.86	0.78	0.43
19	5.20	0.80	0.80	0.40
20	3.27	0.88	0.81	0.44
21	7.67	1.25	1.15	0.19
22	5.14	0.89	0.70	0.41

TABLE III

Alloy No	Optimum Ageing Time (Mins)	0.1% Proof Stress		0.2% Proof Stress		U.T.S		Elongation % (on 250 mm)	Response to Ageing		Conductivity (%I.A.C.S.)	
		psi x 10^3	Pa x 10^6	psi x 10^3	Pa x 10^6	psi x 10^3	Pa x 10^6		psi x 10^3	Pa x 10^6	%IACS	Sm^{-1} x 10^6
1	16	141	972	159	1096	176	1214	0.5	37	225	14.50	8.4
2	20	126	869	144	993	155	1069	0.25*	37	225	16.27	9.2
3	20	116	800	131	903	133	917	0.5*	28.5*	197	20.02	11.6
4	45	99	683	111	765	123	848	1.75	17.5	121	18,47	10.7
5	22	138	952	153	1055	161	1110	0.25*	33	228	16.70	9.7
6	10	132	910	156	1076	182	1255	0.1	27.5	190	13.18	7.6
7	22	129	889	140	1020	165	1138	0.25*	28	193	14.44	9.4
8	25	119	821	135	931	149	1027	0.25	36.5	252	17.47	10.1
9	60	93	641			96	662	0.25*	10	69	18.08	10.5
10	45	125	862	141	972	154	1062	0.75	35	241	20.00	11.6
11	40	106	731	121	834	137	945	1.5	31.5	217	19.65	11.4
12	30	102	703	116	800	133	917	1.0*	27.5	190	10.53	10.7
13	16	100	690	116	800	129	889	0.5*	18	124	16.28	9.4
14	20	159	1096	177	1220	188(201**)	1296(1386**)	0.1	42.5	293	15.23	8.8
15	30	136	938	154	1062	168	1158	0.5	27.5	190	15.91	9.2
16	15	119	820	139	952	159	1096	-*	30.5	210	17.33	13.0
17	5	156	1076	170	1172	179	1234	0.25*	32.5	224	19.27	11.2
13	51	124	855	139	958	143	986	-*	35.5	245	19.23	11.2
19		102	703	118	814	134	924	1.5	32	221	18.24	10.6
20	40	104	717	118	814	132	910	1.5	32	221	19.35	11.2
21	10	138	952	170	1172	175	1207	0.25*	30	207	15.11	8.8
22	22	125	862	140	965	148	1020	0.25*	40	276	17.99	10.4

* Tensile specimen fractures outside its gauge length ** Reached on subsequent Tensile Tests

CLAIMS:

1. A precipitation hardenable copper alloy comprising 2 to 9 weight percent nickel, 0.05 to 2 weight percent of aluminum, chromium and silicon, the balance being copper and impurities.

2. A precipitation hardenable copper alloy according to claim 1, wherein the total amount of silicon, aluminum and chromium does not exceed 2% by weight.

3. A precipitation hardenable copper alloy according to claim 1, comprising substantially 4.5 weight percent nickel, substantially 0.5 to 0.7 weight percent each silicon and aluminum and substantially 0.25 weight percent chromium, the balance being copper and impurities.

4. A precipitation hardenable copper alloy according to any one of claims 1 to 3 of which the conductivity after heat ageing is at least 8.1×10^6 Sm^{-1} (14% I.A.C.S.).

5. A precipitation hardenable copper alloy according to any one of claims 1 to 4 of which the ultimate tensile strength after heat ageing is in excess of 620×10^6 Pa (90,000 psi).

6. A precipitation hardenable copper alloy according to any one of claims 1 to 5 in which the impurities include trace amounts of conventional deoxidizers and fluidity improving agents.

7. A precipitation hardenable copper alloy substantially as described herein with reference to Table I.

FIG. 1

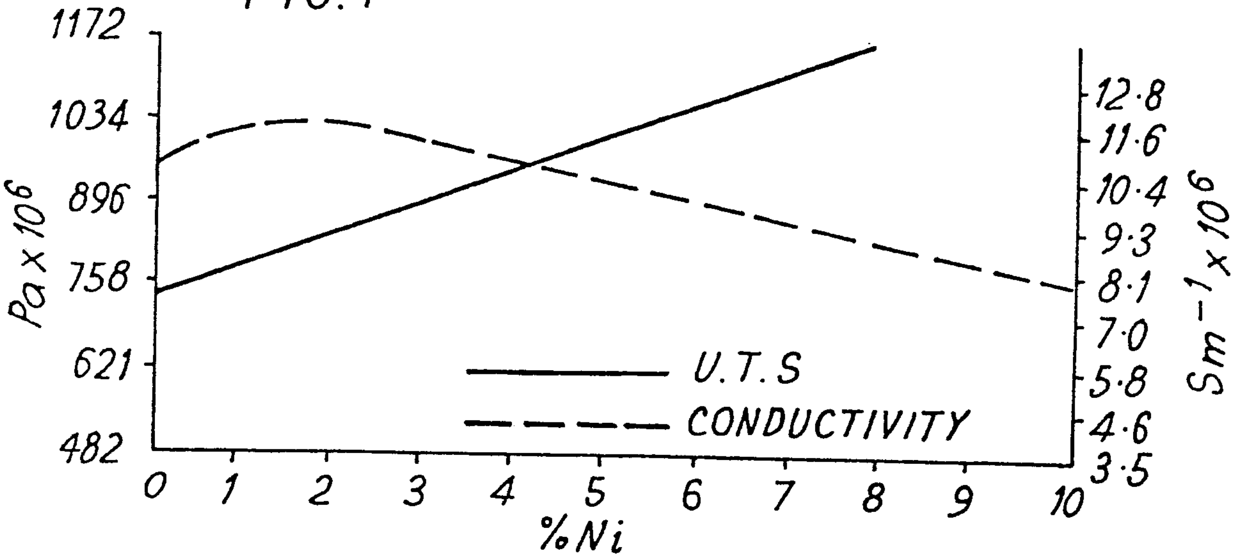


FIG. 2

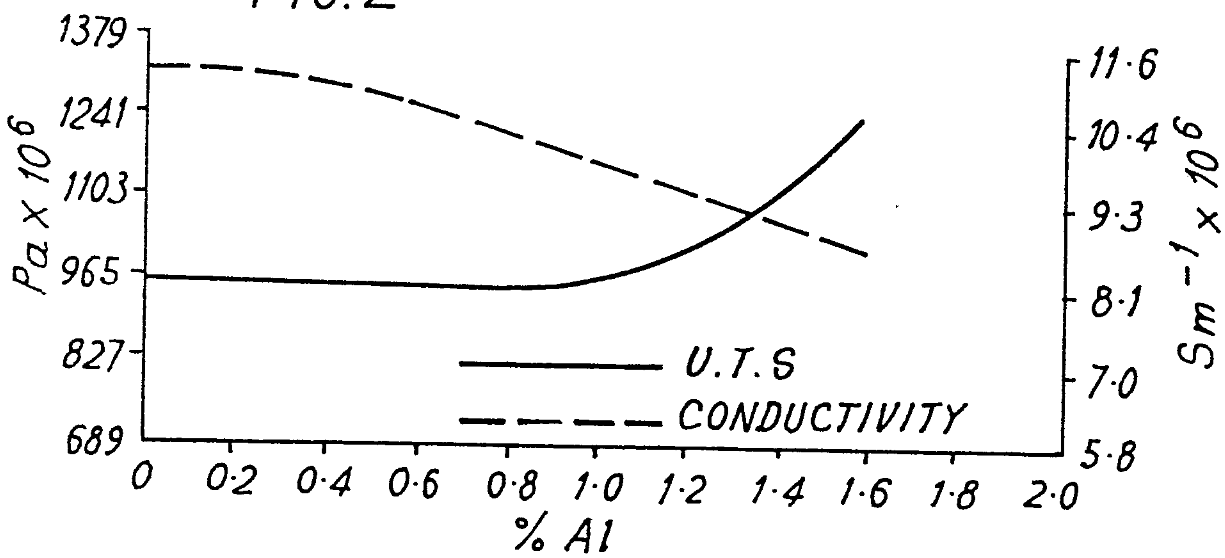


FIG. 3

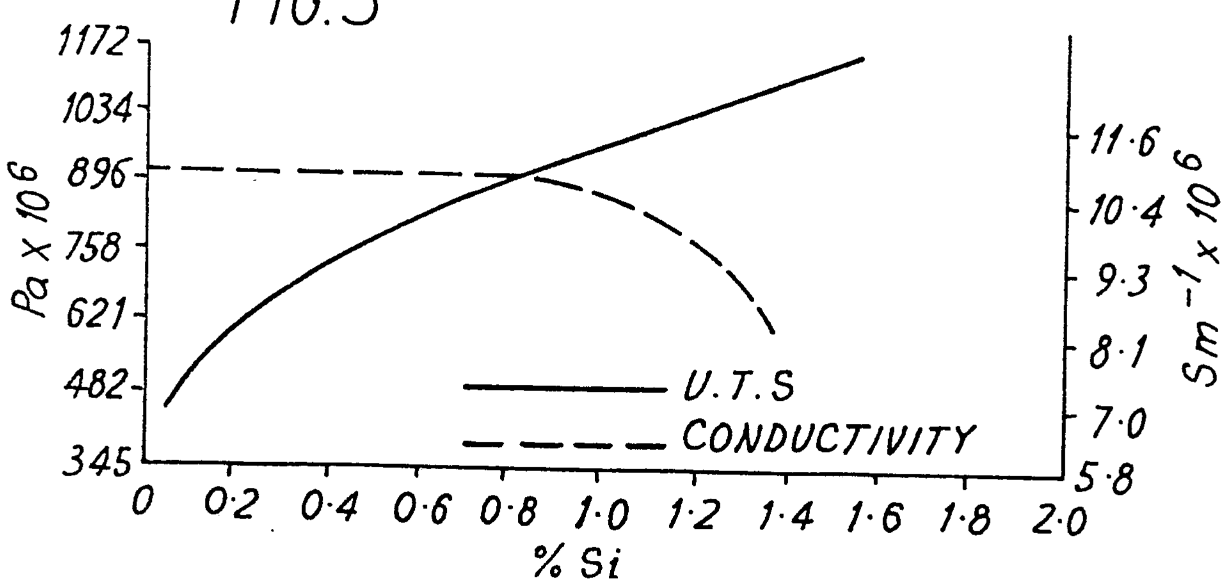


FIG.4

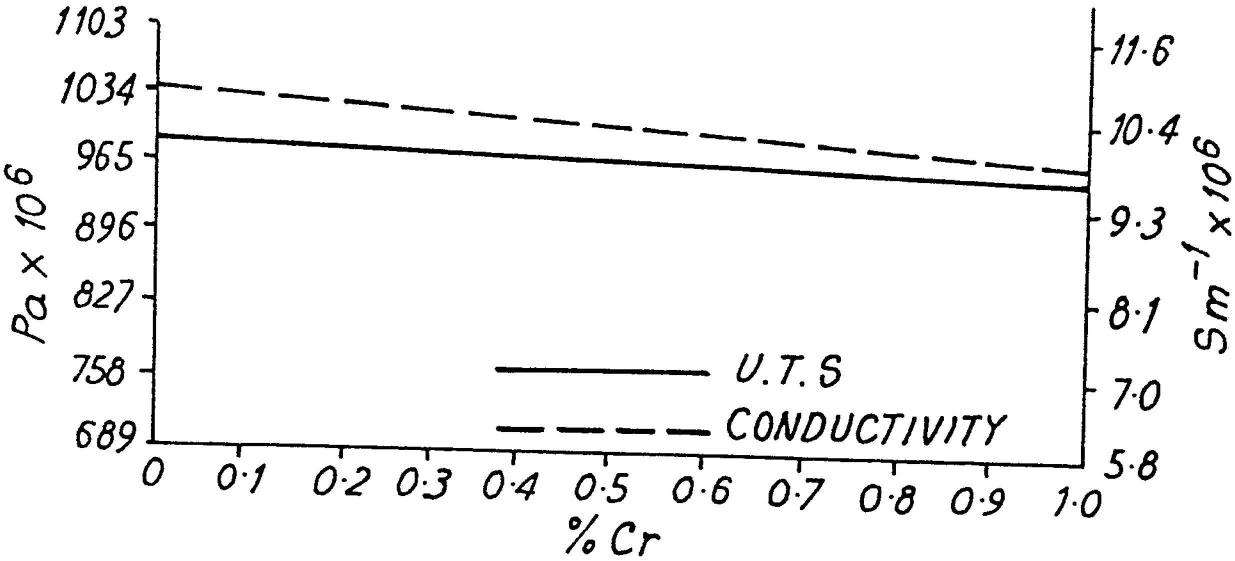
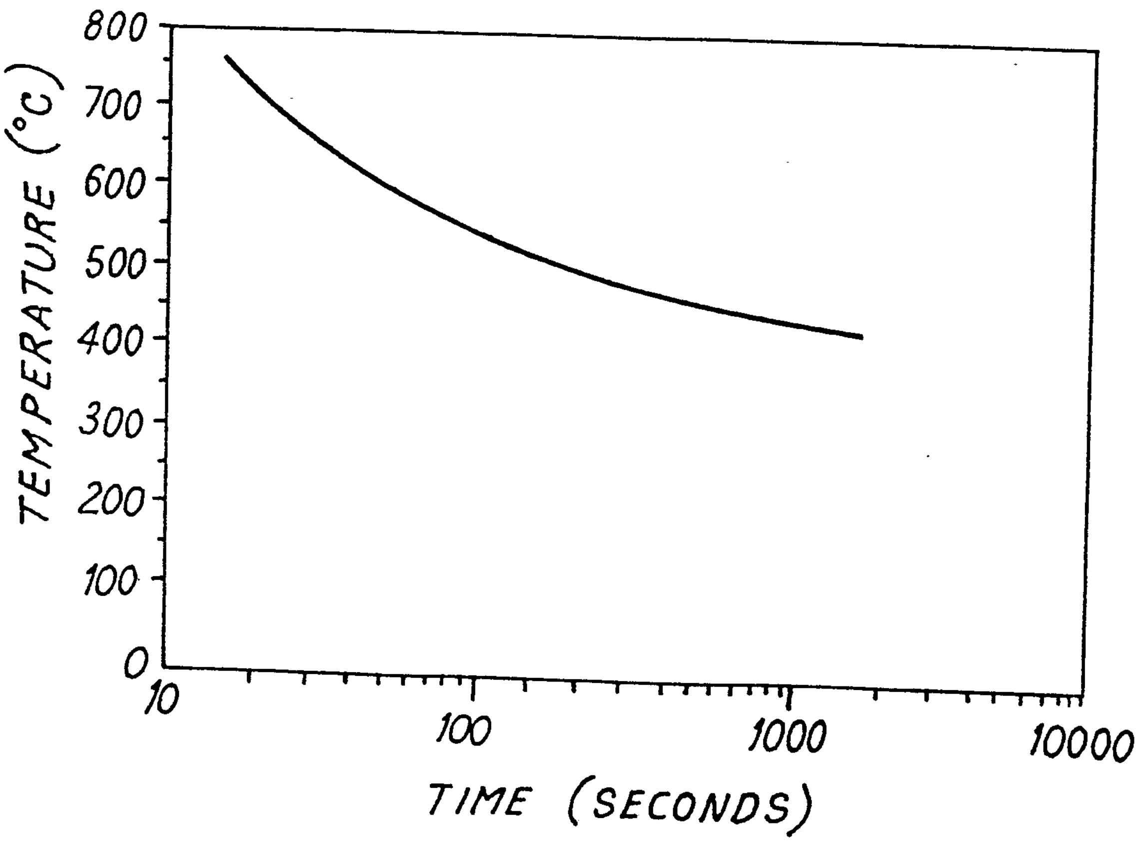

1103
1034
965
896
827
758
689
Pa x 10^6
11·6
10·4
9·3
8·1
7·0
5·8
Sm^-1 x 10^6
U.T.S
CONDUCTIVITY
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
% Cr

FIG.5


800
700
600
500
400
300
200
100
0
TEMPERATURE (°C)
10
100
1000
10000
TIME (SECONDS)

European Patent Office

0018818

EUROPEAN SEARCH REPORT

Application number

EP 80 30 1407

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	GB - A - 1 408 343 (GOSUDARSTVENNY NAUCHNOISSLEDOVATELSKY I PROEKTNY) INSTITUT SPLAVOV I OBRABOTKI TSVETNYKH METALLOV) * Claim 1 * --	1,6
	GB - A - 1 422 215 (GOSUDARSTVENNY NAUCHNOISSLEDOVATELSKY I PROEKTNY INSTITUT SPLAVOV I OBRABOTKI TSVETNYKH METALLOV) * Claim 1 * --	1
	DE - A - 1 558 474 (DIES) * Claims 1,2 * --	1
A	US - A - 2 851 353 (ROACH et al.) * Claim 1 * --	1
A	GB - A - 1 161 610 (LANGLEY ALLOYS) * Claims 1,2 * ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 22 C 9/06

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 22 C 9/06

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10-06-1980	LIPPENS

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