(54) **High strength aluminum-based alloys.**

(57) The present invention provides aluminum-based alloys with high strength and toughness, the alloys having a composition consisting of the general formula (I) $Al_aM_bLn_c$ or the general formula (II) $Al_aM_bX_dLn_c$, wherein M is at least one metal element selected from the group consisting of Co, Ni, and Cu; X is at least one metal element selected from the group consisting of V, Mn, Fe, Mo, Ti and Zr; Ln is at least one element selected from the group consisting of Y, rare earth elements and Mm (misch metal) which is a composite of rare earth elements; and a, b, c and d are, in atomic percentage, $75 \leq a \leq 97$, $0.5 \leq b \leq 15$, $0.5 \leq c \leq 10$ and $0.5 \leq d \leq 3.5$. The alloys are composed of an aluminum matrix or an aluminum supersaturated solid solution matrix which has an average crystal grain size of 0.1 to 80 μm and contains therein a uniform dispersion of metastable or stable phase particles composed of intermetallic compounds formed between the host element (matrix element) and the above-mentioned alloying elements, the intermetallic compounds having an average particle size of 10 to 500 nm.

EP 0 475 101 A1

BACKGROUND OF THE INVENTION

1. Field of the Invention

5   The present invention relates to aluminum-based alloys having high strength together with high hardness, high wear resistance, high heat resistance and superior toughness.

2. Description of the Prior Art

10   Aluminum-based alloys having high strength and high heat resistance have heretofore been produced by a liquid quenching method. For instance, Japanese Patent Application Laid-Open No. 1-275732 discloses aluminum-based alloys produced by the liquid quenching method and the aluminum-based alloys have an amorphous or fine crystalline structure and are superior alloys characterized by an advantageous combination of properties of high strength, high heat resistance and high corrosion resistance.

15   The aluminum-based alloys disclosed in the above Japanese Patent Application Laid-Open No. 1-275732 are superior alloys having high strength, high heat resistance and high corrosion resistance and also exhibit a high degree of processability as high strength materials. However, the aluminum-based alloys should be still improved in their toughness for applications as materials where a high toughness is required.

20 SUMMARY OF THE INVENTION

      In view of the foregoing, it is an object of the present invention to provide materials having a superior toughness, while retaining an adequate strength, and, thereby, useful in structural component applications where a high reliability is required.

25   The present invention provides a high strength aluminum-based alloy having a composition consisting of the general formula (I) $Al_aM_bLn_c$ or the general formula (II) $Al_aM_bX_dLn_c$,
      wherein:
      M is at least one metal element selected from the group consisting of Co, Ni, and Cu;
      X is at least one metal element selected from the group consisting of V, Mn, Fe, Mo, Ti and Zr;
30   Ln is at least one element selected from the group consisting of Y, rare earth elements and Mm (misch metal) which is a composite of rare earth elements; and
      a, b, c and d are, in atomic percentage, $75 \leq a \leq 97$, $0.5 \leq b \leq 15$, $0.5 \leq c \leq 10$ and $0.5 \leq d \leq 3.5$,
      the alloy being composed of an aluminum matrix or an aluminum supersaturated solid solution matrix having an average crystal grain size of 0.1 to 80 μm and containing therein a uniform dispersion of
35   metastable or stable phase particles composed of intermetallic compounds, which are formed between the host element (matrix element) and the above-mentioned alloying elements and/or between the alloying elements the intermetallic compounds having an average particle size of 10 to 500 nm.

BRIEF DESCRIPTION OF THE DRAWINGS
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      FIG. 1 shows a schematic illustration of a single-roller melt spinning apparatus employed to prepare a thin ribbon by rapidly quenching and solidifying alloys of the present invention.
      FIG. 2 is a graph showing the test results of alloys of the present invention.

45 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

      The aluminum-based alloys of the present invention can be obtained by rapidly solidifying a melt of the alloy having the composition as specified above, employing liquid quenching techniques. The liquid quenching techniques are methods for rapidly cooling a molten alloy and, particularly, single-roller melt-
50   spinning, twin-roller melt-spinning and in-rotating-water melt-spinning are effective. In these techniques, a cooling rate of about 10^4 to 10^6 K/sec can be obtained. In order to produce thin ribbon materials by single-roller melt-spinning technique or twin-roller melt-spinning, the molten alloy is ejected from the bore of a nozzle onto a roll of, for example, copper or steel, with a diameter of about 30 - 300 mm, which is rotating at a constant rate within the range of about 300 - 10000 rpm. Thus, various thin ribbon materials with a
55   width of about 1 - 300 mm and a thickness of about 5 - 500 μm can be readily obtained. Alternatively, in order to produce wire materials by in-rotating-water melt-spinning, a jet of the molten alloy is directed, under application of a back pressure of argon gas, through a nozzle into a liquid refrigerant layer having a depth of about 1 to 10 cm which is held by centrifugal force in a drum rotating at a rate of about 50 to 500

rpm. In such a manner, fine wire materials can be readily obtained. In this process, the angle between the molten alloy ejecting from the nozzle and the liquid refrigerant surface is preferably in the range of about 60° to 90° and the relative velocity ratio of the ejected molten alloy to the liquid refrigerant surface is preferably in the range of about 0.7 to 0.9.

Besides the above processes, the alloy of the present invention can also be obtained in the form of a thin film by a sputtering process. Further, rapidly solidified powder of the alloy composition of the present invention can be obtained by various atomizing processes (for example, high pressure gas atomizing) or spray process.

Whether the resultant rapidly solidified aluminum alloys have an average crystal grain size of 0.1 to 80 μm can be examined using a transmission electron microscope. In detail, the grain sizes of individual crystals can be measured from the contrast resulting from the difference in crystal orientation of the respective crystals which contrast is observed in a bright-field of about 1000 to 100,000 magnifications. When the individual crystals can not be distinctly observed in the bright-field, they can be examined through observation in a dark-field of a certain electron diffraction spot. The average particle size of intermetallic compounds can be examined in the same way. The presence of intermetallic compounds can be confirmed through an ordinary electron diffraction. The intermetallic compounds can be easily distinguished from an aluminum matrix in the electron diffraction image.

As previously described, the alloys of the present invention can be obtained by the above-mentioned single-roller melt-spinning process, twin-roller melt spinning process, in-rotating-water melt spinning process, sputtering process, various atomizing processes, spraying process, mechanical alloying process, mechanical grinding process, etc. It is possible to control the average sizes of crystal grains and intermetallic compound particles of the resultant alloys by appropriately varying the processing conditions according to the need.

Further, depending on composition, alloys having an amorphous structure can be obtained but the amorphous structure decomposes into a crystalline structure when being heated to a certain temperature or higher. The alloys of the present invention can also be obtained by the thermal decomposition of the amorphous structure and, in this decomposition process, the average grain size can be controlled within the range of the present invention by properly adjusting the heating conditions.

In the aluminum-based alloys represented by the general formula (I) or (II), a, b, c and d are limited to the atomic percentages ranging from 75 to 97%, 0.5 to 15%, 0.5 to 10% and 0.5 to 3.5%, respectively. The reason for these limitations is that when a, b, c and d are outside the specified ranges, the resultant alloys become brittle and toughness and high strength can not be achieved. Consequently, alloys having properties contemplated by the present invention can not be obtained by industrial rapid quenching processes employing a liquid quenching or the like.

The M element is at least one metal element selected from the group consisting of Co, Ni and Cu. Although the M element has a relatively poor diffusion tendency in an aluminum matrix, it forms various stable or metastable fine intermetallic compounds in coexistence with the Ln element. The resultant intermetallic compounds are finely dispersed throughout the aluminum matrix, thereby effectively preventing an extraordinary grain coarsening as well as strengthening the matrix. Consequently, the M element considerably improves the hardness and strength of the alloys and stabilizes fine crystalline phases both at room temperature and at an elevated temperature, thereby providing an improved heat resistance.

The X element is at least one metal element selected from the group consisting of V, Mn, Fe, Zr, Ti and Mo. Although the X element exhibits a relatively low diffusion tendency in an aluminum matrix, it has an effect in retaining the room temperature hardness and strength up to elevated temperatures. Further, addition of the X element in amounts of 0.5 to 3.5 atomic percent is advantageous especially when processed materials are produced by a hot plastic forming, because the X element addition provides ductility.

The Ln element is at least one element selected from the group consisting of Y, rare earth elements and Mm (misch metal). The Ln element also has a low diffusion ability in an aluminum matrix but, when it is contained in coexistence with the foregoing M element, it forms stable intermetallic compounds and makes a great contribution to stabilization of the fine crystalline structure.

Within the alloy compositional ranges of the present invention, an amorphous phase or an average crystal grain size of less than 0.1 μm can also be obtained. However, in such a case, the ductility (i.e., toughness) is not sufficient for the intended use of the present invention, although the strength is high. In order to achieve the desired ductility, i.e., at least 0.5% tensile elongation, an average crystal grain size of 0.1 μm or greater is essential.

Further, an average crystal grain size exceeding 80 μm may be obtained by employing an excessively reduced cooling-rate or an excessively increased processing temperature for the thermal decomposition,

but, in such conditions, the strength will drastically reduce. Therefore, the object of the present invention can not be achieved.

Proper choice of the heating conditions provides an average crystal grain size controlled within the range contemplated by the present invention.

In the present invention, the particle size of intermetallic compounds is limited to the range of 10 to 500 nm because when the size is outside the specified range, the intermetallic compounds do not act as a matrix strengthening component. In detail, an excessively increased cooling rate or an inadequate processing temperature for the thermal decomposition results in intermetallic compounds having a particle size of less than 10 nm. Such fine intermetallic compounds have no effect in strengthening the aluminum matrix. Further, when the intermetallic compounds excessively dissolve in the matrix as solid solution, a problem of brittleness may arise. On the other hand, when the cooling rate is excessively reduced or the processing temperature of the thermal decomposition is too high, the resultant intermetallic compounds have an average particle size exceeding 500 nm and produce no strengthening effect. That is, the dispersed particles become too large and it does not exhibit any strengthening effect. Within the above-specified range, greatly improved Young's modulus, high-temperature strength and fatigue strength can be obtained.

As set forth above, in the production of the alloys of the invention, proper choice of the production conditions makes it possible to control the crystal grain size and the average particle size of intermetallic compounds. Therefore, when strength is important, the average crystal grain size and the intermetallic compound particle size are controlled to small sizes. Alternatively, when ductility is required, the crystal grain size and the intermetallic compound particle size are controlled to large sizes. In such a manner, the properties can be controlled according to the purposes.

When the crystal grain size is controlled within the range of 0.1 to 10 μm, properties desirable as superplastic forming materials can also be obtained.

The alloys of the present invention can be obtained in the form of ribbons, thin strips or powders and can be readily processed into bulk materials using hot plastic forming processes, such as extrusion, press forming or forging, within the temperature range of one-fifth (1/5) to one half (1/2) the melting point of the alloys. Also, bulk materials can also be readily obtained from the alloys having an amorphous structure or a supersaturated solid solution structure by appropriately controlling the powder consolidation conditions. The alloys of the present invention exhibit superior properties as highly tough and strong alloys and, thus, are especially useful as highly reliable structural materials.

Hereinafter, the present invention will be explained in more detail with reference to the following examples.

Examples

Molten alloy 3, having a predetermined composition, was prepared using a high-frequency melting furnace and charged into a quartz tube 1 having a small opening 5 (diameter: 0.5 mm) at the tip thereof, as shown in FIG. 1. After being heated to melt the alloy 3, the quartz tube 1 was disposed right above a copper roll 2. Then, the molten alloy 3 contained in the quartz tube 1 was ejected from the small opening 5 of the quartz tube 1 under the application of an argon gas pressure of 0.7 kg/cm^2 and brought into contact with the surface of the copper roll 2 rapidly rotating at a rate of 1,000 rpm. The molten alloy 3 was rapidly quenched and solidified into an alloy thin ribbon 4.

According to the processing conditions as described above, 14 different alloy thin ribbons (width: 1 mm, thickness: 20 μm) having the compositions (by at.%) as shown in Table 1 were obtained and test specimens were prepared. The average crystal grain size of each test specimen was measured through observation by transmission electron microscopy (TEM). The measurement results showed that all of the test specimens were composed of a crystalline matrix having an average crystal grain size of 0.1 to 60 μm and containing intermetallic compounds having an average particle size of 10 to 50 nm therein. It was found that no amorphous phase was contained in the test specimens.

The mechanical properties measured by a tensile test at room temperature, and microVickers hardness (under a load of 50g) are also set out in Table 1.

Table 1

	Composition (at. %)	Hv(DPN)	σ_{max}(MPa)	ε(%)
1	$Al_{85}Ni_5Fe_2Y_8$	275	920	2.5
2	$Al_{87}Ni_8Y_5$	273	890	2.7
3	$Al_{90}Ni_5La_5$	264	890	2.6
4	$Al_{92}Ni_5V_1Mm_2$	297	910	1.7
5	$Al_{88}Fe_2Co_2Ce_8$	312	915	2.2
6	$Al_{88}Fe_2Zr_2Mm_8$	305	927	1.8
7	$Al_{88}Cu_4Ni_2Mm_6$	267	945	1.7
8	$Al_{92}Cu_4Ni_2Y_2$	256	875	2.8
9	$Al_{90}Co_4Ni_2Y_4$	256	890	1.7
10	$Al_{87}Co_4Ti_2Mm_7$	275	920	1.6
11	$Al_{90}Ni_6Zr_1Mm_3$	273	930	2.9
12	$Al_{90}Ni_8Zr_{0.5}Mm_{1.5}$	278	928	2.3
13	$Al_{89.5}Ni_8Zr_1Fe_{0.5}Mm_1$	273	912	2.6
14	$Al_{87}Ni_8Cu_{1.5}Mg_2Mm_{1.5}$	287	945	1.8

Remark: Hv(DPN):   microVickers hardness

σ_{max}(MPa):   ultimate tensile strength

ε(%):   Tensile elongation

All of the samples were found to be superior alloys having an elongation of at least 1.6% coupled with a strength of at least 875 MPa.

Next, alloy powders, having an average particle size of not greater than 45 μm and consisting of an amorphous phase, were prepared by an atomizing process with a high-pressure gas (Ar) and consolidated into bulk materials by a powder extrusion process described below.

The powders were compacted at 230 °C in a vacuum to provide green compacts, 24 mm in diameter and 30 mm long, having relative densities of 75 to 85% and formed into billets for extrusion. The billets were extruded at 450 °C to produce extruded bars, about 6 mm in diameter, with an extrusion ratio of 15 and machined into test pieces for a tensile test. (measuring part: 3 mm in diameter and parallel parts: 15 mm). The test results are shown in Table 2.

Further test pieces were cut from the respective extruded bars for observation by TEM and average crystal grain size measurements were conducted. It was found that all of the test pieces had an average crystal grain size within the range of 5 to 60 μm and had a structure composed of a crystalline matrix containing uniformly dispersed intermetallic compounds of 20 to 50 nm.

Table 2

Composition (at. %)	Hv(DPN)	σ_{max}(MPa)	ε(%)
1 $Al_{87}Ni_8Y_5$	295	925	1.6
2 $Al_{90}Ni_5La_5$	272	910	1.8
3 $Al_{92}Cu_4Ni_2Y_2$	272	905	2.2
4 $Al_{90}Ni_6Zr_1Mm_3$	287	945	2.4
5 $Al_{90}Ni_8Zr_{0.5}Mm_{1.5}$	293	941	2.2
6 $Al_{89.5}Ni_8Zr_1Fe_{0.5}Mm_1$	285	937	1.9
7 $Al_{87}Ni_8Cu_{1.5}Mg_2Mm_{1.5}$	301	953	1.6

Remark: Hv(DPN):   microVickers hardness

σ_{max}(MPa):   ultimate tensile strength

ε(%):   Tensile elongation

It was found that all of the test pieces had high strength and ductility and were superior as structural materials.

A further billet of $Al_{87}Ni_6Mm_7$ for extrusion was prepared in the same manner as described above and extruded at various temperatures to produce extruded bars. The changes of the tensile strength, hardness and tensile elongation were examined with respect to the changes of the average crystal grain size. The results are shown in FIG. 2.

As shown in FIG. 2, when the average crystal grain size was at least 0.1 μm, the tensile elongation was at least 0.5%. Whereas an average grain size of not more than 80 μm provide a high hardness of 200 (DPN), which was more than 2 times the hardness (Hv: 50 to 100 DPN) of a commercial aluminum-based alloy, coupled with a high strength level of at least 650 (MPa). A strength of at least 800 (MPa), a hardness of at least 230 (DPN) and an elongation of at least 1.2 (%) are the most desirable conditions for structural materials and it will be noted that these conditions can be satisfied within the average crystal grain size range of 22 to 60 μm.

As described above, the alloys of the present invention have a high degree of hardness, strength, wear resistance and heat resistance together with a superior toughness and are useful as highly reliable materials for use in structural components, etc.

Claims

1. A high strength aluminum-based alloys having a composition consisting of the general formula (I) $Al_aM_bLn_c$,
   wherein:
   M is at least one metal element selected from the group consisting of Co, Ni, and Cu;
   Ln is at least one element selected from the group consisting of Y, rare earth elements and Mm (misch metal) which is a composite of rare earth elements; and
   a, b and c are, in atomic percentage, $75 \leq a \leq 97$, $0.5 \leq b \leq 15$ and $0.5 \leq c \leq 10$,
   the alloy being composed of an aluminum matrix or an aluminum supersaturated solid solution matrix having an average crystal grain size of 0.1 to 80 μm and containing therein a uniform dispersion of metastable or stable phase particles composed of intermetallic compounds, which are formed between the host element (matrix element) and the above-mentioned alloying elements and/or between the alloying elements, the intermetallic compounds having an average particle size of 10 to 500 nm.

2. A high strength aluminum-based alloy having a composition consisting of the general formula (II) $Al_aM_bX_dLn_c$,

    wherein:

    M is at least one metal element selected from the group consisting of Co, Ni, and Cu;

    X is at least one metal element selected from the group consisting of V, Mn, Fe, Mo, Ti and Zr;

    Ln is at least one element selected from the group consisting of Y, rare earth elements and Mm (misch metal) which is a composite of rare earth elements; and

    a, b, c and d are, in atomic percentage, $75 \leq a \leq 97$, $0.5 \leq b \leq 15$, $0.5 \leq c \leq 10$ and $0.5 \leq d \leq 3.5$,

    the alloy being composed of an aluminum matrix or an aluminum supersaturated solid solution matrix having an average crystal grain size of 0.1 to 80 μm and containing therein a uniform dispersion of metastable or stable phase particles composed of intermetallic compounds, which are formed between the host element (matrix element) and the above-mentioned alloying elements and/or between the alloying elements, the intermetallic compounds having an average particle size of 10 to 500 nm.
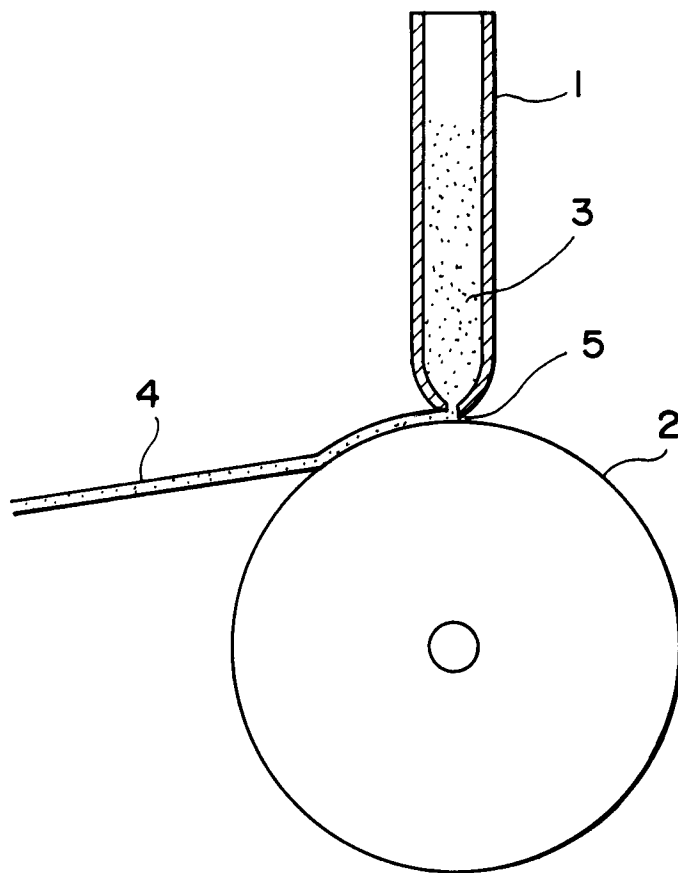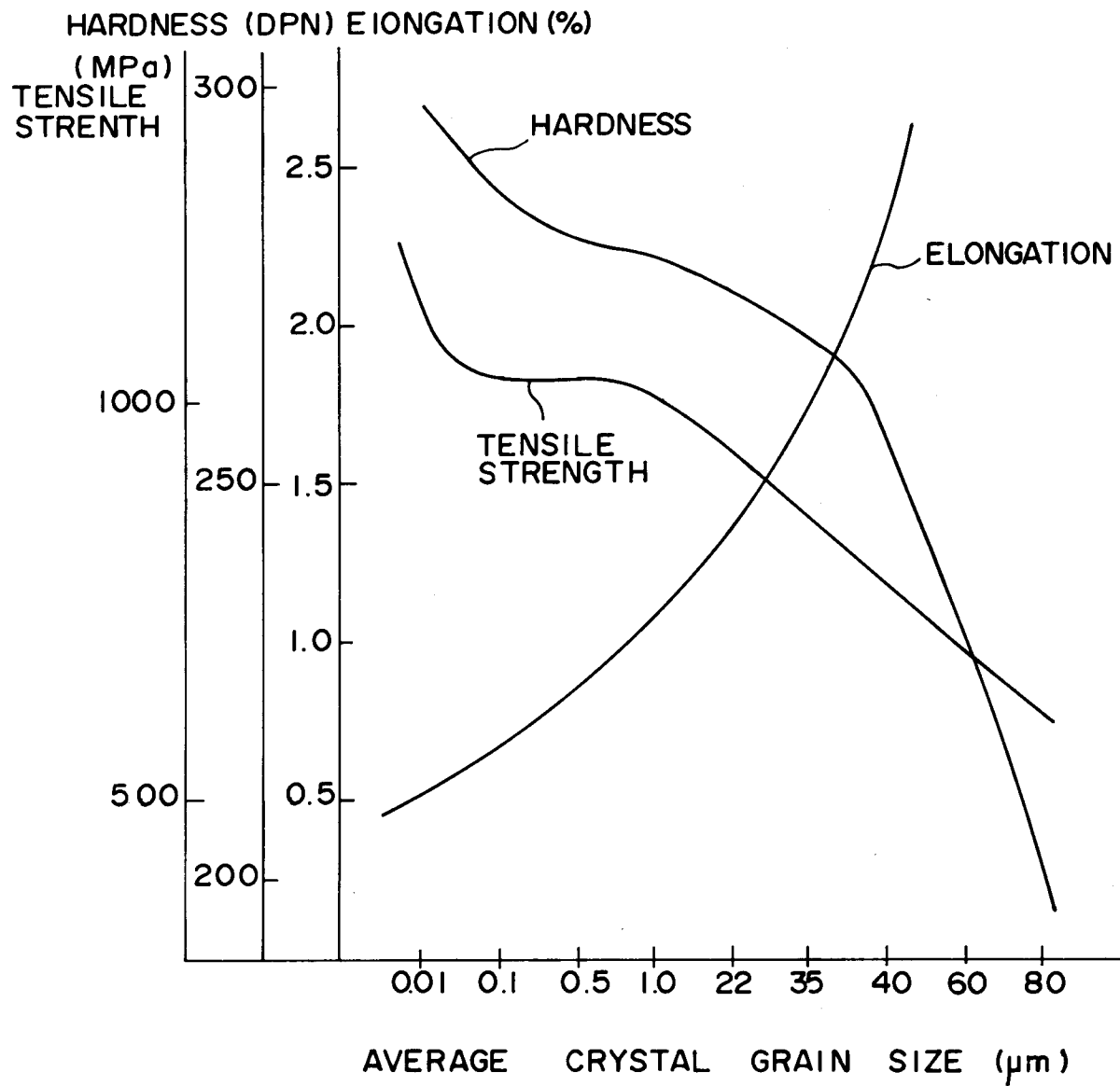
F I G. 1

F I G. 2

HARDNESS (DPN) EIONGATION (%)

(MPa)
TENSILE STRENTH

300
250
200

2.5
2.0
1.5
1.0
0.5

1000
500

HARDNESS

ELONGATION

TENSILE STRENGTH

0.01 0.1 0.5 1.0 22 35 40 60 80

AVERAGE   CRYSTAL   GRAIN   SIZE (μm)

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.5)
Y,D	EP-A-0 339 676 (YOSHIDA KOGYO K.K.) * claims 1,2 *	1,2	C22C1/00
Y	DE-A-3 524 276 (BBC AKTIENGESELLSCHAFT BROWN,BOVERI & CIE) *Claims 1 ,2 ;pages 5-7,"Ausführungsbeispiel 1"; page 10, 1.2-16*	1,2	
Y	EP-A-0 136 508 (ALLIED CORPORATION) * claims 1-9 *	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 NOVEMBER 1991	LIPPENS M.H.