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(54) **AL-NB-B MASTER ALLOY FOR GRAIN REFINING**

AL-NB-B-VORLEGIERUNG FÜR KORNFEINEN

ALLIAGE MÈRE AL-NB-B POUR RAFFINEMENT DU GRAIN

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(56) References cited:
WO-A2-2012/110788

- **B. S. MURTY ET AL: "Grain refinement of aluminium and its alloys by heterogeneous nucleation and alloying", INTERNATIONAL MATERIALS REVIEWS, vol. 47, no. 1, 1 February 2002 (2002-02-01), pages 3-29, XP055086865, ISSN: 0950-6608, DOI: 10.1179/095066001225001049**

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Description

[0001] The present application relates to a method of making a master alloy (also known as a masterbatch alloy) for refining the grain size of a metal alloy, and to the subsequent use as a grain refiner of the metal alloy. In particular, it relates to the preparation of a master alloy for refining the grain size of aluminium-silicon alloys and magnesium alloys (both including and excluding aluminium).

[0002] An important objective in the production of metal alloys is the reduction in grain size of the final product. This is known as "grain refinement" and is commonly addressed by adding so-called "grain refiners" which are substances thought to promote inoculation of metal alloy crystals. Grain refinement by inoculation brings many benefits in the casting process and has significant influence on improving mechanical properties. The fine equiaxed grain structure imparts high yield strength, high toughness, good extrudability, uniform distribution of the second phase and micro-porosity on a fine scale. This in turn results in improved machinability, good surface finish and resistance to hot tearing (along with various other desirable properties).

[0003] The present applicant has filed International Patent Application No. PCT/GB2012/050300 (published as WO 2012/110788 after the priority date of the present application) which relates to method of refining the grain size of (i) an alloy comprising aluminium and at least 3% w/w silicon or (ii) an alloy comprising magnesium, comprises the steps of:

- (a) adding sufficient niobium and boron to the alloy in order to form niobium diboride or Al_3Nb or both, or
- (b) adding niobium diboride to the alloy, or
- (c) adding Al_3Nb to the alloy, or
- (d) any combination thereof.

[0004] The addition of Al-Ti-B based grain refiner in the form of a master alloy with a chemical composition of 94wt%Al-5wt%Ti-1wt%B is a common practice for the industry to manufacture aluminium wrought alloys. Master alloy addition avoids use of the corrosive KBF_4 salt in the casting process. The addition of the elemental form of boron is not advisable due to the practical difficulty of dispersing it in the melt as a result of its poor wetting nature with liquid Al or Mg alloys. Master alloy addition overcomes these problems.

[0005] In WO 2012/110788, it is disclosed that, instead of salt addition, one can add the niobium diboride grain refiner in the form of a small metal piece of Al-Nb-B master alloy to an Al-Si based liquid alloy to obtain a fine grain size. Addition of concentrated Al-Nb-B alloy ensures the uniform dispersion of NbB_2 into the aluminium melt.

[0006] In particular, WO 2012/110788 discloses that a commercial pure Al ingot was melted in an electric furnace at the temperature range 800-850 °C and held for 2 hours. 5wt % NbB_2 (mixture of Nb and KBF_4) was added to the melt in order to form an NbB_2 phase. After stirring and removing dross, the liquid metal was cast into a mould in order to result in an Al-Nb-B grain refiner master alloy.

[0007] In another example, WO 2012/110788 discloses that a commercial Al-10Nb master alloy was melted at 900 °C and added to pure Al to dilute the alloy to form Al-2Nb master alloy. Then the 1wt% Boron is added to the melt to result in a master alloy composition of Al-2Nb-B.

[0008] US 3,933,476 (Union Carbide Corporation) discloses a method for the grain refining of aluminium using an addition of titanium, aluminium and KBF_4 .

[0009] GB 1 244 082 (Kawecki Berylco Industries, Inc.) discloses a method for adding an alloying or grain refining constituent in the form of a wire or strip to a main metal, wherein the constituent consists of aluminium and one or more of boron, titanium or zirconium.

[0010] In accordance with a first aspect of the present invention, there is provided a method of producing a master alloy for refining the grain size of a bulk alloy, comprising the step of providing an Al-B alloy and adding Nb in elemental form to form an Al-Nb-B master alloy.

[0011] The technical advantages of a master alloy in accordance with the invention are first that it can be produced without using a corrosive salt such as KBF_4 ; secondly that the addition of a concentrated Al-Nb-B alloy to the bulk alloy ensures the uniform dispersion of Nb-based phases into the melt; and thirdly that the it results in a finer grain size in the final alloy (in other words, it is a more effective grain refiner).

[0012] In a preferred embodiment, the Al-B alloy is prepared by providing an Al-B alloy with a higher boron content than is required and diluting it with elemental aluminium. For example, to prepare the 97wt%Al-2wt%Nb-1wt% B alloy, the commercially available 95wt%Al-5wt%B alloy is diluted by adding pure aluminium to produce a 99wt%Al-1wt%B alloy. Sufficient elemental niobium is then added until the desired 97wt%Al-2wt%Nb-1wt%B alloy is obtained.

[0013] The masterbatch (also called a master alloy) may comprise niobium and boron in amounts sufficient to form sufficient niobium diboride in the final alloy product so that when this master alloy is added to the Al-Si or Mg alloy melt, it can refine the grain size of solidified structures. It is conventional when representing the formula of an alloy to omit the weight percent of the highest alloy component. Thus a masterbatch alloy for adding to an aluminium alloy may have the general formula $\text{Al-Xwt}\%\text{Nb-Ywt}\%\text{B}$ where X can be from 0.01 to 99 and Y can be from 0.002 to 25 and the weight

percent of the aluminium component is the balance to take the total to 100.

[0014] A number of preferred embodiments of the invention will now be described with reference to the drawings, in which:

5 Fig.1 Typical microstructural features in Al-SB master alloy. The boride phase particles (AlB_{12}) are dark in contrast.

Fig.2: Al-4.05Nb-0.9B master alloy microstructure, showing NbB_2 phase particles

10 Fig. 3 Al-2Nb-2B master alloy microstructure, showing NbB_2 phase particles

Fig.4 Al-2Nb-B master alloy microstructure, showing NbB_2 phase particles

15 Fig. 5. Photograph of macro-etched surfaces of cross-sections of Al-10Si cast samples. Photo on left is Al-10Si alloy and the photo on right is for the sample produced after the addition of Al-2Nb-2B to the melt.

Fig.6: Optical micrographs of samples shown in Fig.5. (a) & (b) are for Al-10Si and (c) & (d) are for Al-10Si with Al-2Nb-2B addition. Finer primary Aluminium and finer eutectic particles can be seen in the sample with Al-2Nb-2B addition.

20 Fig.7. Photographs of top surfaces of A380 ingots cast from liquid metal (a) without and (b) with the addition of Al-2Nb-B.

25 Fig. 8. Schematic illustration of spatial variation of grain structure in Al-10Si alloy billets processed without and with Al-2Nb-B master alloy addition.

Fig. 9. Photographs of Al-10Si alloy billets produced without and with Al-2Nb-B master alloy addition.

30 Fig.10. Schematic illustration of cross-section of wedge mould. T1, T2, T3 represents positions of thermocouples in the mould. Microstructures of etched surfaces at these three different positions are also shown.

Fig.11. Microstructures of cross-sections of tensile bars produced using high pressure die casting process for AM50 alloys (a) without and (b) with addition of Al-2Nb-B master alloy.

35 Fig. 12. Sketch of the moulds used in the experiment of Example 7. Typical cooling rates obtained in these moulds are depicted in these sketches. Cooling rate decreases as the thickness of cast structure increases.

Fig. 13 Macroetched cross-sections of Alloy A wedge shape and cylindrical specimens: a) without and b) with addition of Al-2Nb-2B master alloy.

40 Fig. 14. Macroetched cross-sections of Alloy B wedge shape and cylindrical specimens: a) without and b) with addition of Al-2Nb-2B master alloy.

45 Fig. 15. Macroetched cross-sections of Alloy C wedge shape and cylindrical specimens: a) without and b) with addition of Al-2Nb-2B master alloy.

Fig. 16. Microstructures of Alloy D. (a) without and (b) with 0.1wt of Nb equivalent master alloy addition with Al-2Nb-2B composition. Al-2Nb-2B addition refined grain structures significantly both Al grains and eutectic Si needle size.

50 Fig. 17. Microstructures of Alloy E. (a) without and (b) with addition of Al-2Nb-2B master alloy. Grain structure is significantly refined for both Al grains and eutectic Si needle size.

Fig. 18. Anodised microstructures of Alloy F. Microstructure on left is for cylindrical mould specimen without grain refiner addition. Microstructure on right is with Al-2Nb-2B addition.

55 Fig. 19 Macroetched cross-sections of Alloy G wedge shape and cylindrical specimens: a) without and b) with addition of Al-2Nb-2B master alloy.

Fig. 20. Comparison of microstructures in cylindrical cast samples (a) Alloy G without addition. (b) Alloy G with Al-

2Nb-2B master alloy addition. Grain refiner in the form of Al-2Nb-2B master alloy addition resulted in very fine (~150 microns) grain structure in comparison to large dendrite structures seen in reference samples. Finer primary Si size particles (dark contrast particles) are after Al-2Nb-2B addition.

5 Example 1: Processing of Al-Nb-B master alloys

[0015] In this example source for Boron is commercially available Al-5wt%B master alloy. Nb is in the form of elemental powder, procured from Alfa Aesar, A Johnson Matthey Company. Figure 1 shows the microstructure of Al-B master alloy. The particles which are dark in contrast and spherically shaped are aluminium borides. This master alloy together with commercial pure Al ingot with required contents were melted in an electric furnace at the temperature range 800-850 °C and held for 2 hours with appropriate concentrations listed in Table 1. The melt was stirred with a non-reactive ceramic rod. We then introduced Nb metallic powder, either in compacted form or in discrete particle form, in to the melt. It is important to note that, in addition to NbB₂ phase formation, (Al,Nb)B₂, Al₃Nb phase inclusions may also form depending on location chemical concentrations in the melt. The melt is cast in to a mould. The cast metal is referred as Al-Nb-B master alloy. The microstructure of various master alloys is shown in Figures 2, 3 and 4. These consist of fine Nb based particles distributed in Al matrix.

Example 2: Application of Al-2Nb-2B master alloy to Al-10Si alloy

[0016] Al-10Si alloy was melted in an electric furnace at 800 °C and held for 2 hours. A reference sample is cast in a conical shaped mould. The mould was pre-heated to 250 °C and temperature of the melt was maintained at 740 °C, prior to pouring into a conical mould. A small piece of Al-2Nb-2B master alloy (equivalent to 0.05wt%NbB₂ w.r.t weight of Al in Al-10Si alloy) was added to the remaining melt. 15 minutes later, the melt was stirred for about 1 minute and cast into a conical mould. Figure 5 reveals the grain size of Al-10Si alloy without addition and with addition of Al-2Nb-1B master alloy. Refined grain structure is obtained through the addition of Al-Nb-B master alloy. The casting process is repeated for Al-Si with various types of master alloys and their corresponding grain sizes are shown in Table 1. All the master alloys with compositions shown in Table 1, are shown to refine the grain size of Al-Si alloy. In addition finer grain size, as shown in Fig. 6 (c) & (d), finer eutectic Si is observed.

Table 1 Master alloy compositions, addition levels and the corresponding average grain size in Al-10Si alloy

Master alloy composition	Nb addition level (wt. %)				
	0	0.01	0.025	0.05	0.1
Al-2Nb-1B	3-4 mm	1 mm	0.55 mm	0.5 mm	0.2 mm
Al-2Nb-2B	3-4 mm	-	0.4 mm	0.2 mm	0.2mm
Al- 3Nb-1B	3-4 mm	-	0.4 mm	0.2 mm	0.25 mm
Al- 4.05Nb-0.9B	3-4 mm	-	0.4 mm	0.3 mm	0.25mm

Example 3: Application of Al-2Nb-1B master alloy to A380 alloy

[0017] 3 Kg of A380 alloy was melted in an electric furnace at 750 °C and held for 1 hours and cast into a steel mould. Another batch of 3 Kg was melted and a small piece of Al-2Nb-B master alloy (equivalent to 0.05wt%NbB₂ w.r.t weight of A380 alloy) was added to the melt. 15 minutes later, the melt was stirred for about 1 minute and cast into a mould. Figure 7(a) shows the grain size of this alloy and Fig 7(b) shows the alloy added with Al-Nb-B master alloy. The detailed analysis of the ingots revealed that addition of Al-Nb-B mater alloy reduced the grain size from 1 cm to 0.4 mm. The macro-porosity is also significantly reduced.

Example 4: Processing of Al-10Si billets with the addition of Al-2Nb-B (A simulation of Direct Chill casting process)

[0018] Al-10Si alloy melt is prepared in a graphite crucible with electric resistance furnace. The melt temperature is maintained at 800 °C. Both ends opened cylindrical steel mould is placed in a vertical tube furnace. The hot zone for this furnace is controlled by three zone heating system to maintain uniform temperature along longitudinal direction of the tube. The temperature along the axis of the steel mould is maintained at 720 °C. The bottom part of the steel tube is closed with a Cu block. The melt temperature is reduced to 740 °C and then the melt is poured into steel mould. Prior to pouring the melt, the Cu block is cooled by water jet with flow rate of 4 l/min. The time taken to fill the steel tube with

melt is ~ 5 seconds. Due to cooling provided by the water jet, the melt starts to solidify from bottom. Ten seconds after completion of pouring, Cu block is removed and the water jet is placed directly underneath the solidified block of Al-Si alloy. As a result, the heat is extracted unidirectional from the melt. The cooling conditions along the longitudinal direction in this experiment are similar to that of transverse direction in industrial scale direct-chill casting process. Figure 8 (a) shows schematic illustration of billet produced by this method. Huge columnar grain structure forms in the melt. Figure 8(b), shows a schematic illustration of billet produced from the melt added with 0.05wt% of NbB₂ in the form of Al-2Nb-B addition. Columnar grain structure is absent after Al-Nb-B addition and only fine equi-axed grain structure can be seen. Macro-etched surfaces of cylindrical billets cast in unidirectional solidification are shown in Fig. 9. Much needed elimination of columnar growth is achieved through the addition of Al-Nb-B master alloy.

Example 5: Application of Al-2Nb-B master alloy to Magnesium (AM50) alloy

[0019] AM50 alloy was melted in an electric furnace at 690°C and held for 2 hours. SF₆+N₂ gas mixture was used to protect the melt from oxidation. Approximately 0.1wt% of Al-2Nb-B master alloy w.r.t to weight of AM50 was added to the melt and stirred for 1 minute with steel rod. The melt containing NbB₂ was poured into the wedge shaped mould. For comparative purpose an experiment without any NbB₂ addition was also carried out. This wedge shaped mould provides wide range of cooling rate depending on the thickness of casting. The cooling rate between position T1 and tip, the cooling rate could range between 80 °C/s to 1000 °C/s. Both cast samples were polished and chemically etched. Microstructures at various positions (T1, T2, and T3) are compared in Figure 10. Grain refinement is observed, as shown in Figure 10, when Al-2Nb-B is added to the melt.

Example 6: High pressure die casting of Magnesium (AM50) alloy with Al-2Nb-B master alloy addition

[0020] High pressure die casting (HPDC) is a commonly used process to produce variety of large structures/components for automotive, electronics and construction sector applications. It is a mass production technology. It provides higher cooling rates to the melt and finer grain structure is obtained during solidification process. AM50 alloy melt is prepared as described in Example 5. Melt with and without addition of 0.1wt% of Al-2Nb-B is fed to the shot-sleeve of high pressure die casting machine, followed by injecting the melt in to a permanent mould with a plunger and then solidifying it under pressure. At least 15 castings are produced. Each cast structure consists of three cylindrical and three flat bars. Microstructure of cross-sections of a typical cylindrical sample is shown in Fig. 11. Since the cooling rate in HPDC process ~1000 °C/s, very fine grain structure is expected to form. However, during pouring, when the melt is in contact with cold wall of shot-sleeve, heterogeneous nuclei at these walls takes place and they grow into the melt. In the literature, these crystals are known as "early solidified crystals" (ESC). The ESC size is measured to be ~250 μm in size. When the grain refiner is added, as shown in Fig 11(b), the size of these crystals significantly reduced and the overall grain size appears to be similar in whole sample. Tensile tests were conducted on at least 40 cylindrical specimens each. Statistically, the elongation is observed to improve by 11%, when the Al-2Nb-B is added.

Example 7: Application of Al-2Nb-2B master alloys to various commercially sourced Al-Si alloys

[0021] The alloys compositions used to perform the study of the influence of the Al-2Nb-2B master alloy are given in Table 2. These alloys are near eutectic (Alloys A); hypo-eutectic alloy (Alloys B-F) and Hyper-Eutectic (Alloy G) commercially used alloys.

Table 2. List of alloys investigated

Alloy	Si	Mg	Mn	Cu	Ni	Zn	Fe
Alloy A	11-12	0.1	0.5	0.1	0.1	0.1	0.6
Alloy B	7.5-9.5	3	0.5	3.0	0.5	3	1.3
Alloy C	6.5-7.5	0.4	0.3	0.2	0.1	0.1	0.5
Alloy D	9.99	0.005	0.005	0.0017	0.0044	0.005	0.09
Alloy E	10.98	0.268	0.21	2.134	0.068	0.778	0.83
Alloy F	6.06	0.275	0.265	2.725	0.0257	0.305	0.356
Alloy G	13.0	0.4	0.5	0.7	1.5	0.1	1

[0022] The alloys were placed in a clay graphite crucible, melted and, prior to casting, kept at a processing temperature

of 790°C at least for 1 hour. At this point, the reference alloy was left to cool down to approximately 740 (± 3) °C and cast into a cylindrical mould and wedge shaped copper moulds pre-heated at 250 °C. These moulds are a 30 mm diameter steel mould and a copper wedge shaped mould. In the wedge mould, the cooling rate studied by means of this configuration ranges between 2°C/s to 150°C/s as it can be seen in the sketch presented in Figure 12.

[0023] In the case of grain refiner addition, in the form of Al-2Nb-2B master alloy addition (0.1wt% of Nb and 0.1wt% B addition rate), after holding the melt for 60 minutes at 790°C, the master alloy is added to the melt and a minimum time of 30 minutes was left for the novel grain refinement to dissolve inside the melt to ensure a homogeneous distribution of the grain refining phases. Chemical etching to reveal the microconstituents was performed by immersing the polished surfaces in Tucker's solution (25 ml H₂O + 15 ml HF + 15 ml HNO₃ + 45 ml HCl) for 20 to 30 seconds.

[0024] The macroetched cross-section of the Alloy A wedge-shaped samples without and with the addition of Al-2Nb-2B are shown in Fig. 13 where it can be seen that the alloy A without grain refiner addition is characterised by an important spatial variation of the grain size of the primary α -Al grains since it ranges from approximately 200 μ m (tip) up to almost 1mm (top of the sample). From Fig. 13b, it can be noticed that the addition of the master alloy significantly decreases the mean primary α -Al grain size as well as the spatial variation reducing this latter to between 100 μ m and 200 μ m. Similarly, the final primary α -Al grain size is less sensitive to the cooling rate and, therefore, industrial components based on Alloy A with fine and uniform grain size could be obtained with a great range of casting processes.

[0025] Macroetched cross-section of the Alloy A cylindrical samples without and with the addition of the Al-2Nb-2B master alloy are also shown in the figure (right side). It can be seen that as in the case of the wedge-shaped sample, the microstructure of the reference material is composed of coarse primary α -Al grains and there is an spatial variation in size. In particular, the grain size is fine in the outer diameter, which corresponds to the material solidified in contact with the mould, and then increases noticeably and, finally, slightly decreases in the centre of the cylindrical samples. The addition of the master alloy led to much finer primary α -Al grains and levels. The alloy microstructure is also less sensitive to the local variation of the cooling rate which is of paramount importance when casting products with different wall thicknesses are manufactured.

[0026] Similar refinement is observed for all other alloys listed in Table 2. The macro or microstructures are presented in Fig 14 to 20.

Claims

1. A method of producing a master alloy for refining the grain size of a bulk alloy, comprising the step of providing an Al-B alloy and adding Nb in elemental form to form an Al-Nb-B master alloy.
2. A method as claimed in claim 1, wherein said Al-B alloy is prepared by providing an Al-B alloy with a higher boron content than is required and diluting it with elemental aluminium.
3. A method as claimed in claim 2, wherein the Al-B alloy with a higher boron content is Al-5B.

Patentansprüche

1. Verfahren zur Herstellung einer Masterlegierung zum Verfeinern der Korngröße einer Massenlegierung, umfassend den Schritt des Bereitstellens einer Al-B-Legierung und des Zusetzens von Nb in elementarer Form zur Bildung einer Al-Nb-B-Masterlegierung.
2. Verfahren nach Anspruch 1, wobei die Al-B-Legierung bereitgestellt wird, indem eine Al-B-Legierung mit einem höheren Borgehalt als erforderlich bereitgestellt und mit elementarem Aluminium verdünnt wird.
3. Verfahren nach Anspruch 2, wobei die Al-B-Legierung mit einem höheren Borgehalt Al-5B ist.

Revendications

1. Procédé de production d'un alliage mère pour raffiner la taille des grains d'un alliage massif, comprenant l'étape de disposition d'un alliage Al-B et d'ajout de Nb sous forme élémentaire pour former un alliage mère Al-Nb-B.
2. Procédé selon la revendication 1, dans lequel ledit alliage Al-B est préparé par disposition d'un alliage Al-B avec une teneur en bore plus élevée que ce qui est requis et par dilution de celui-ci avec de l'aluminium élémentaire.

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3. Procédé selon la revendication 2, dans lequel l'alliage Al-B avec une teneur en bore plus élevée est Al-5B.

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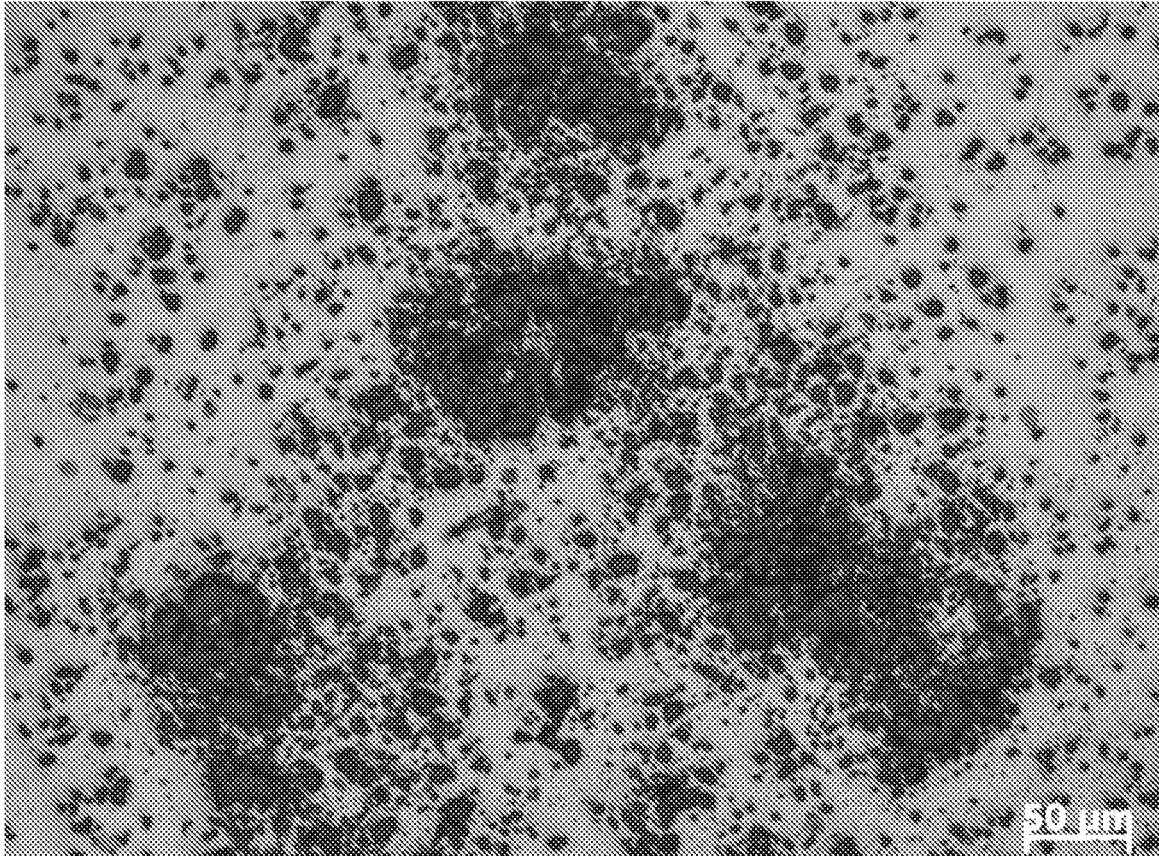


Fig.1

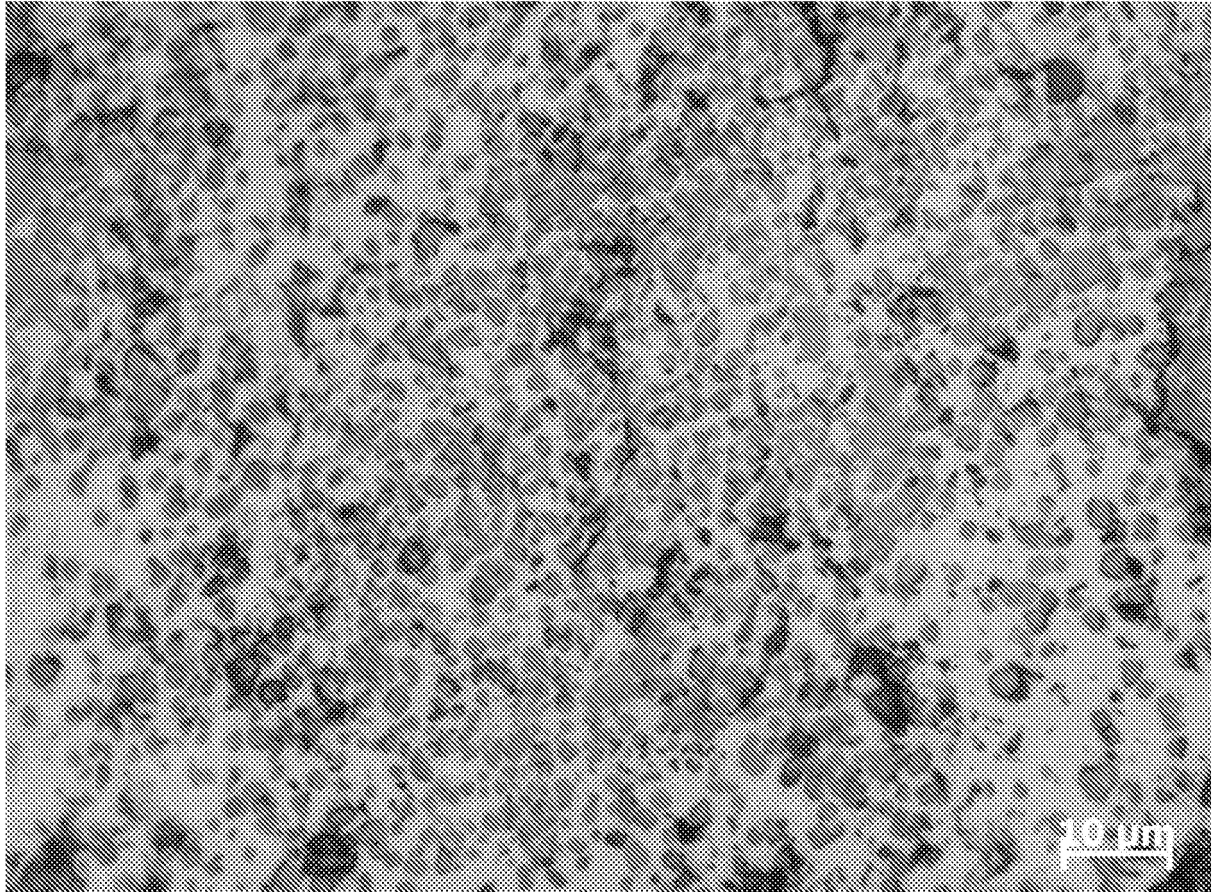


Fig.2

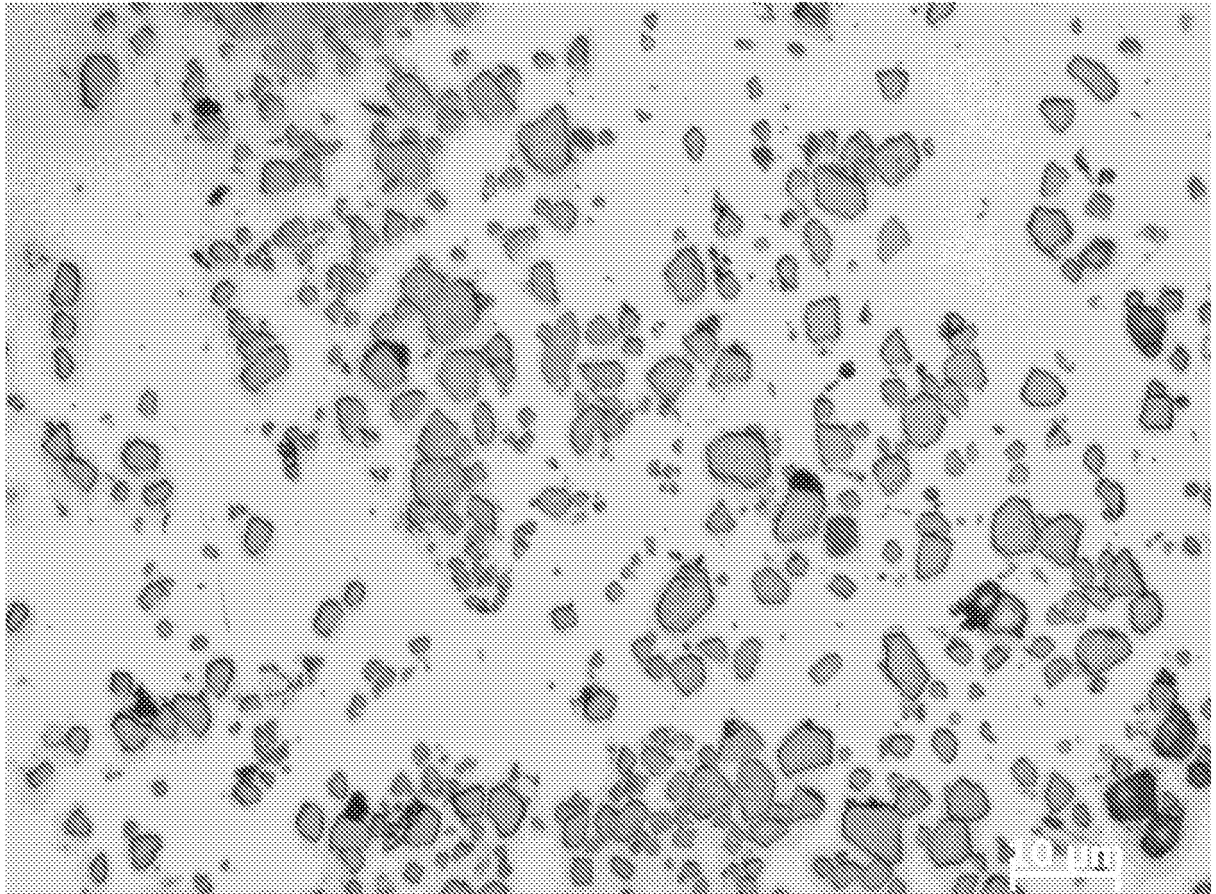


Fig.3

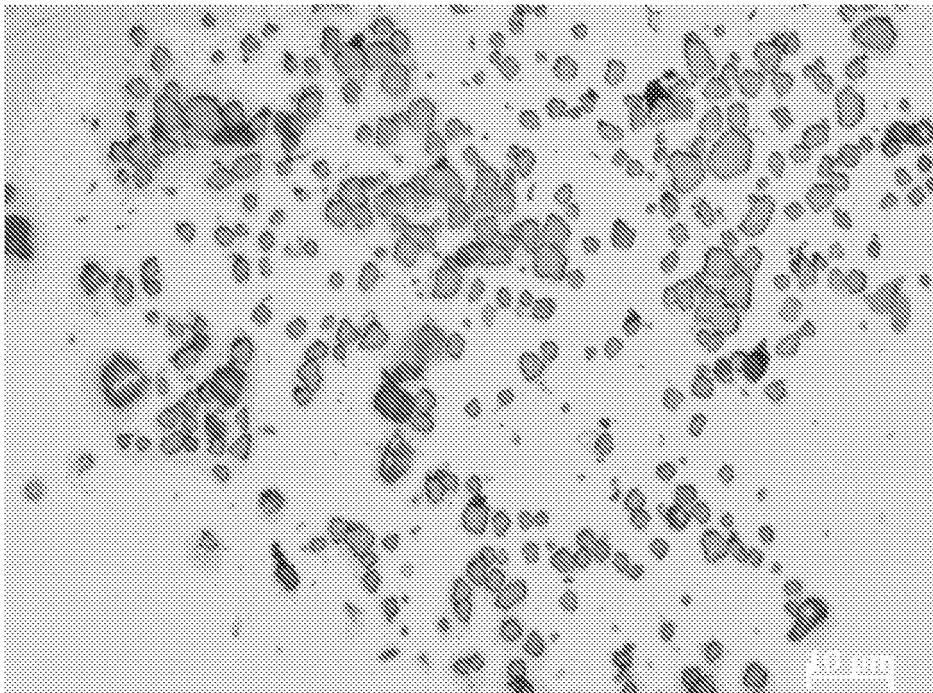


Fig.4

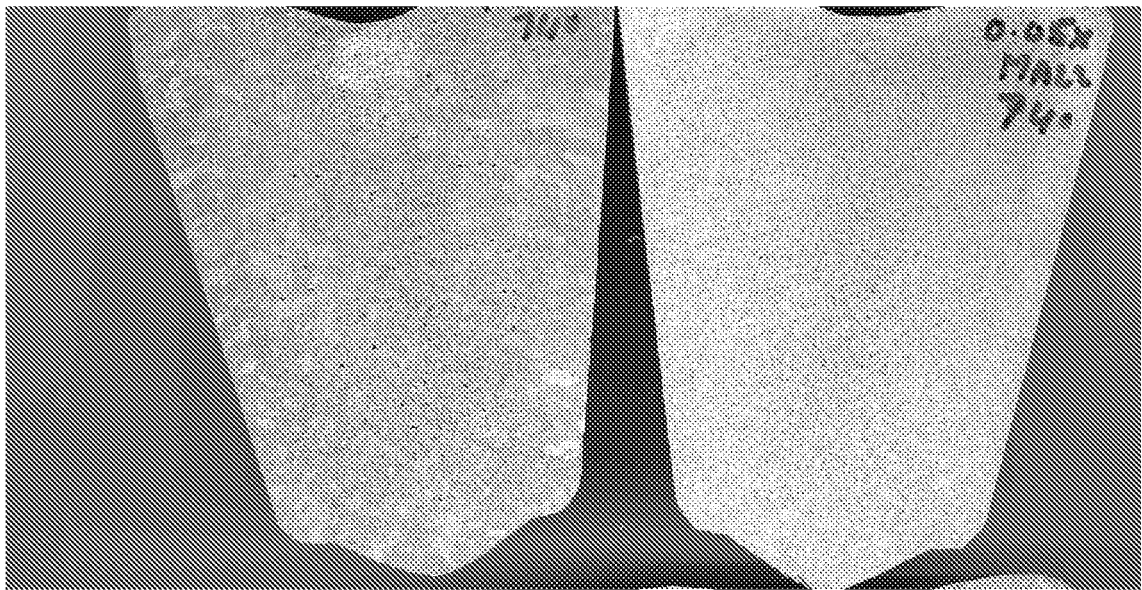


Fig.5

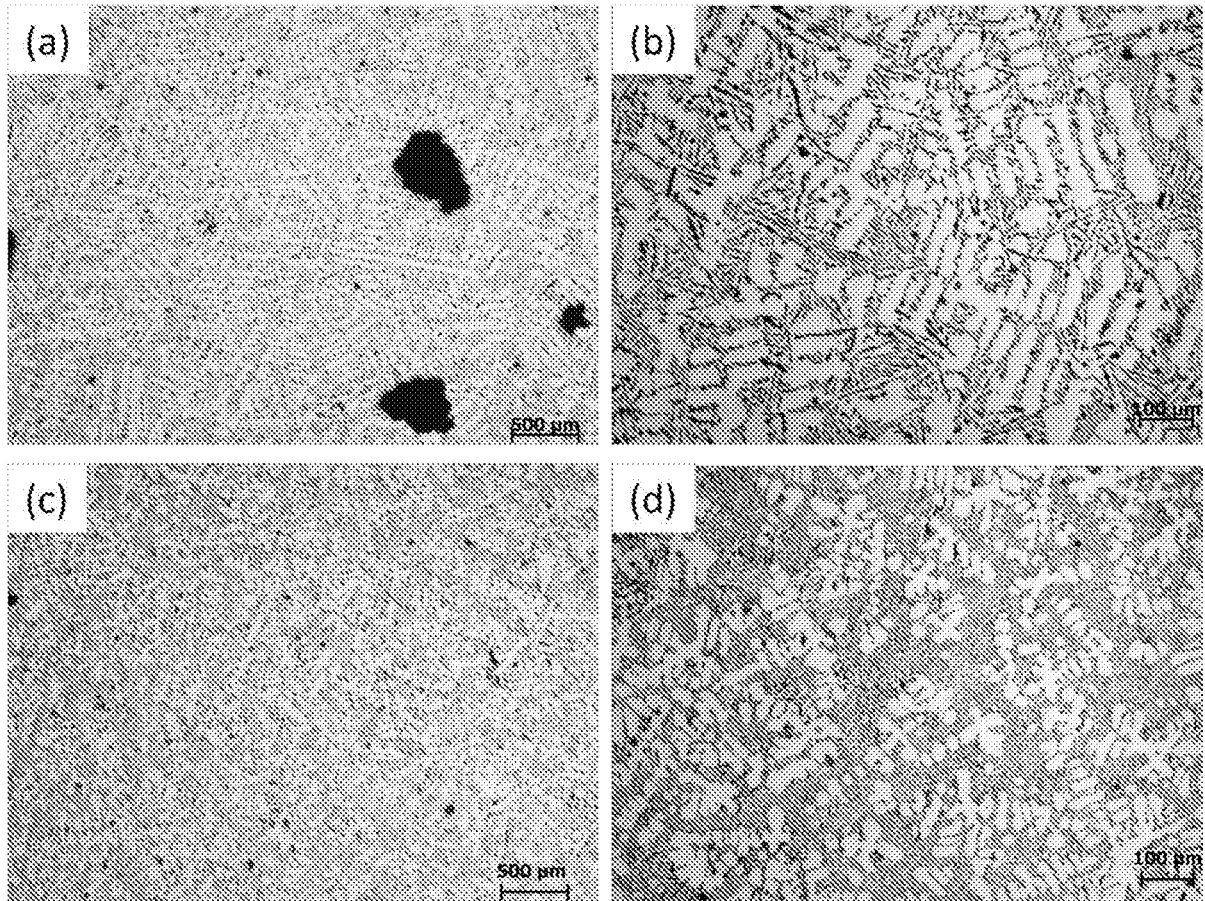


Fig.6

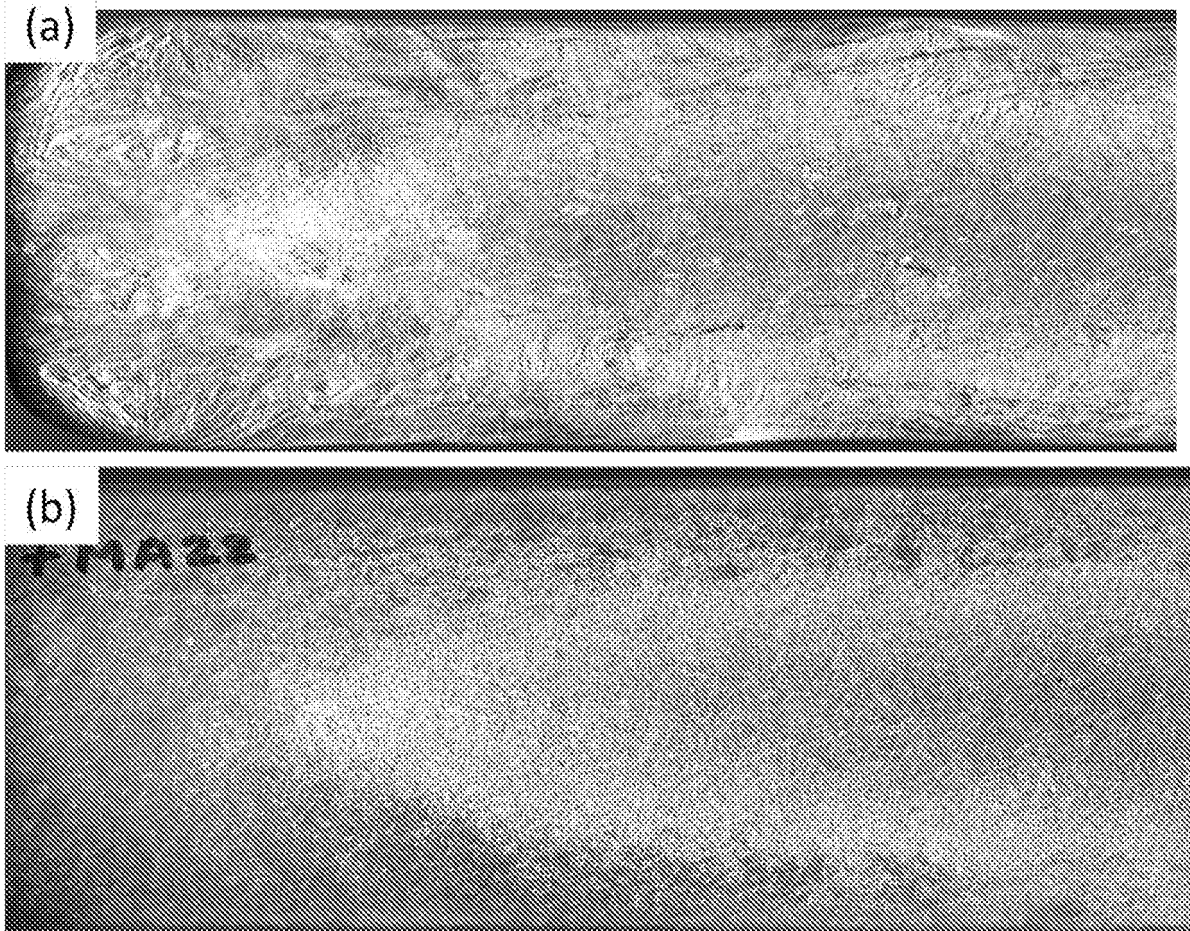


Fig.7

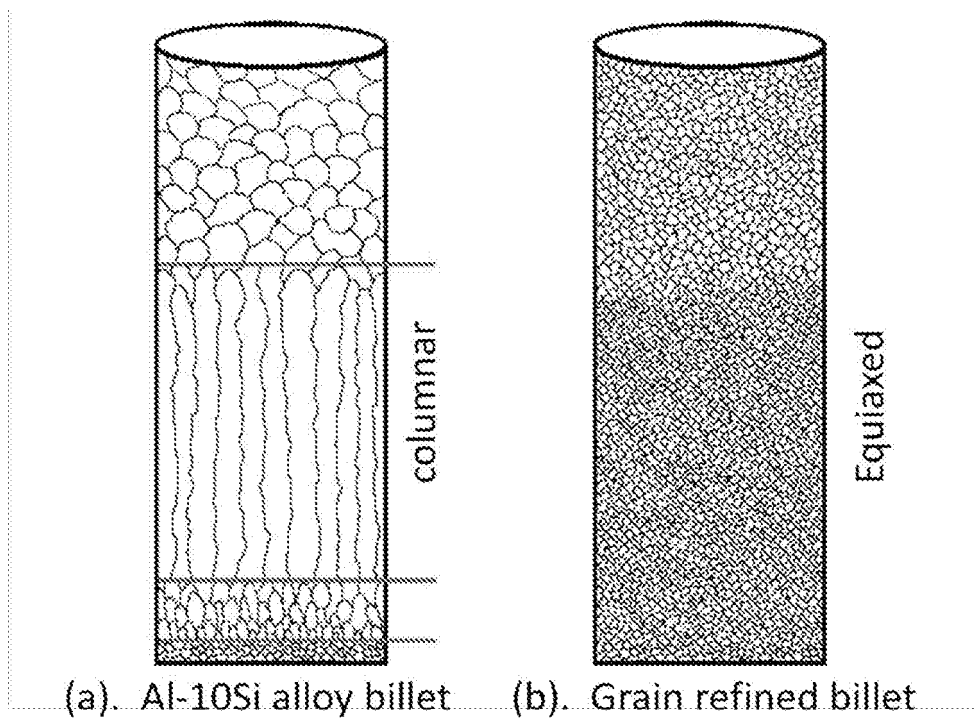


Fig.8

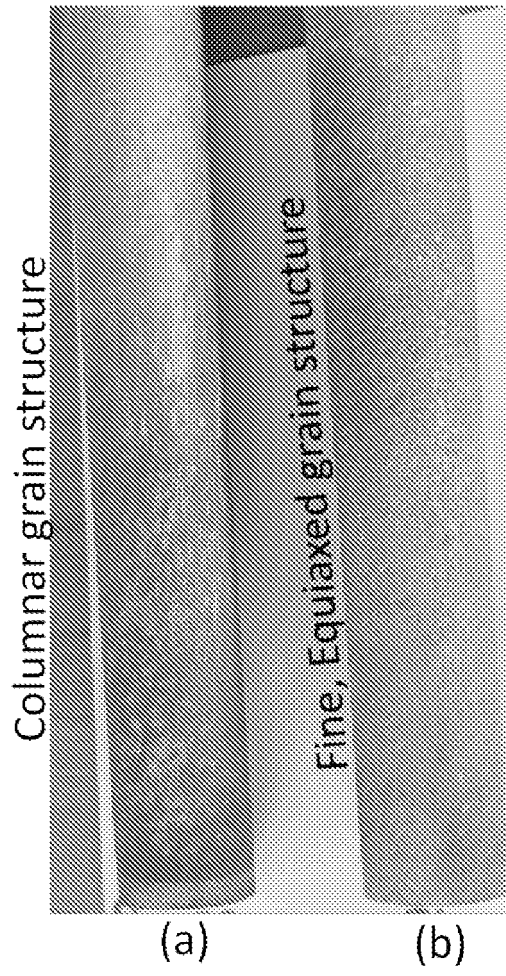


Fig.9

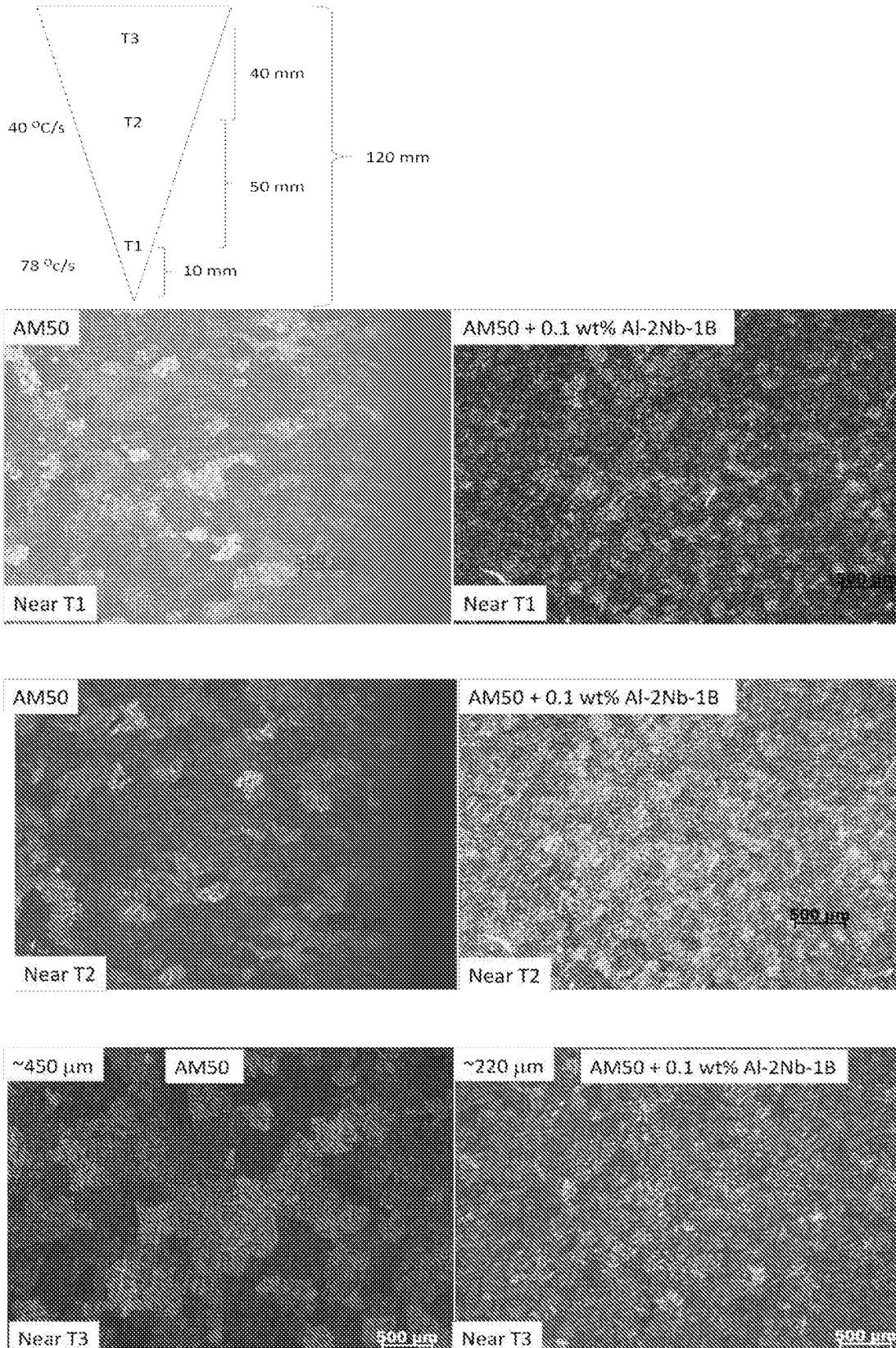


Fig.10

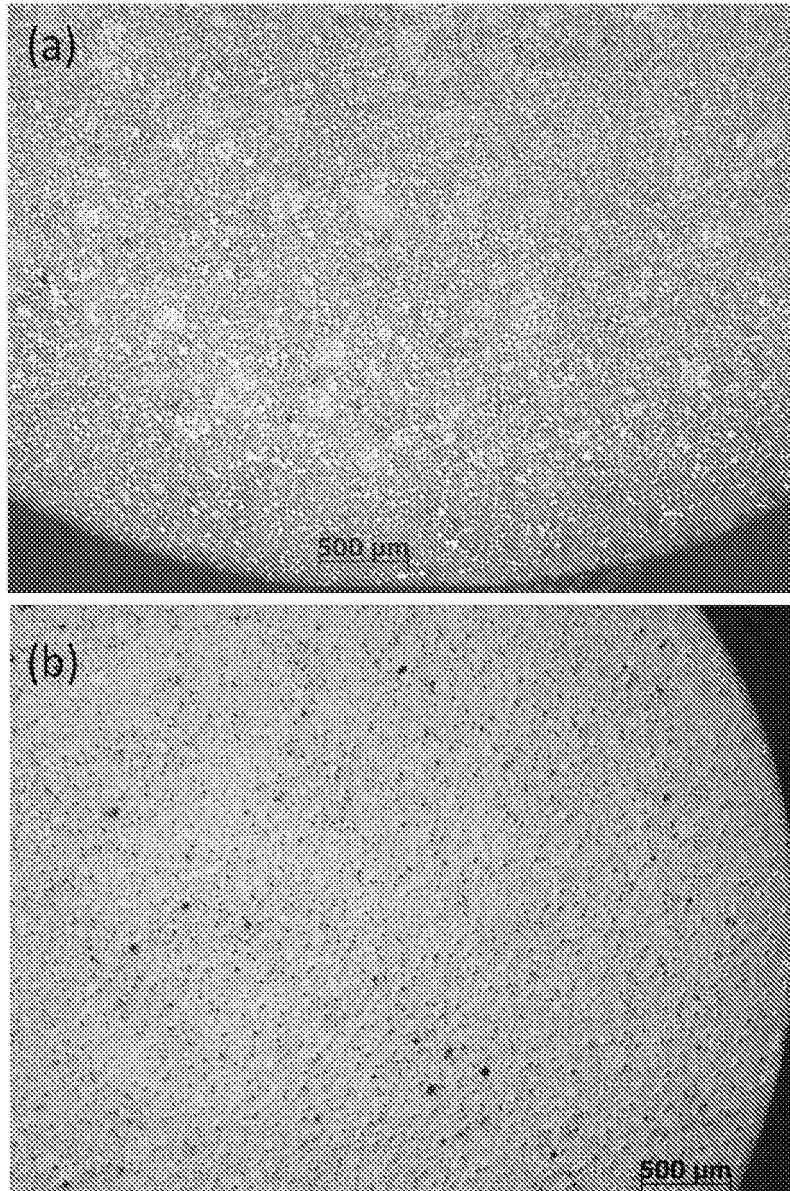


Fig.11

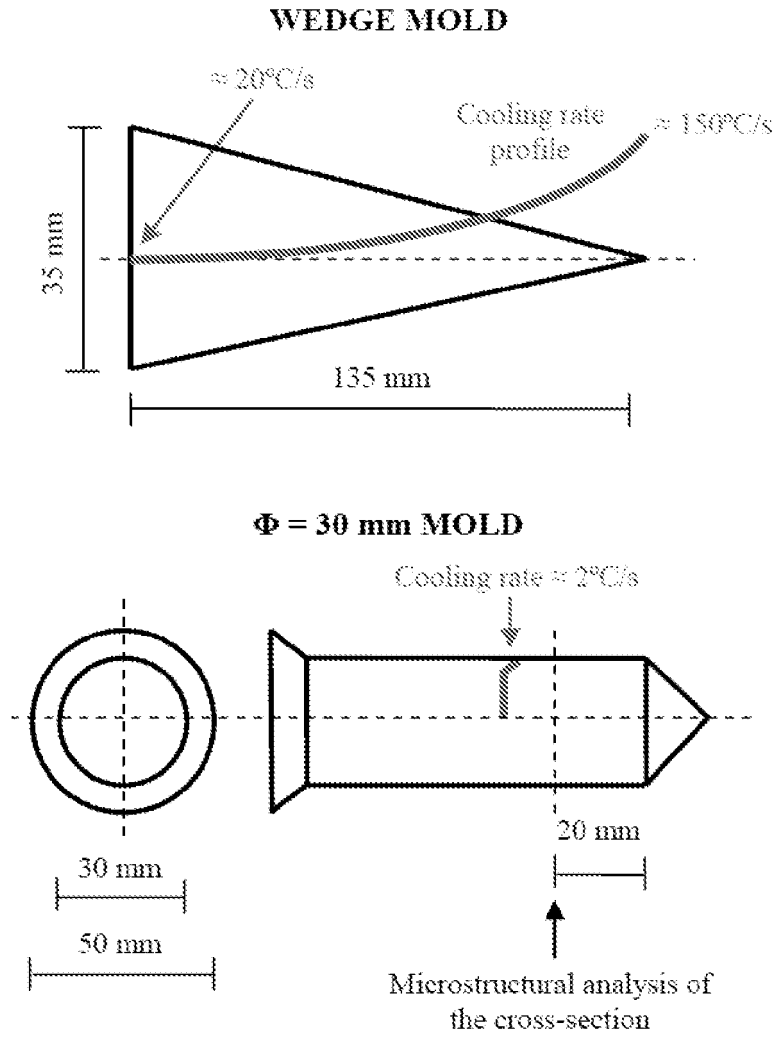


Fig. 12

Alloy A

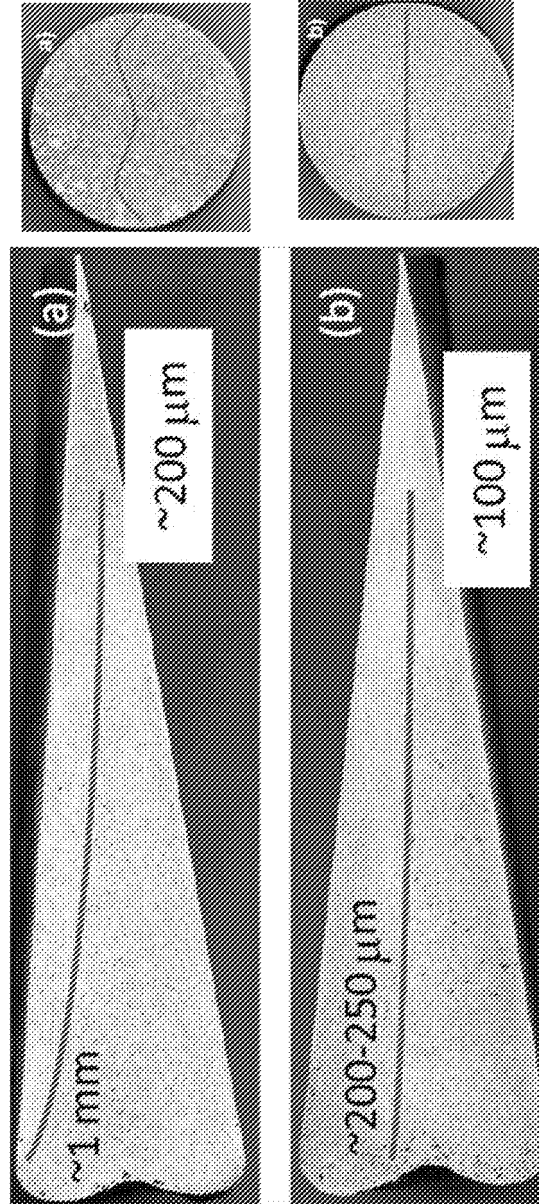


Fig.13

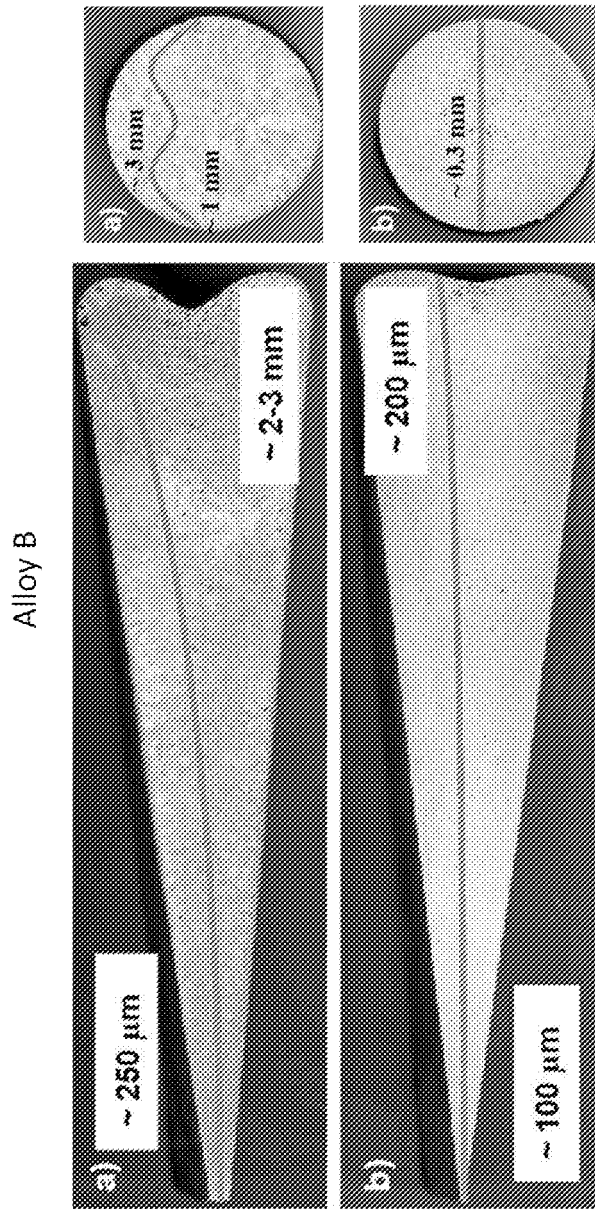


Fig.14

Alloy C

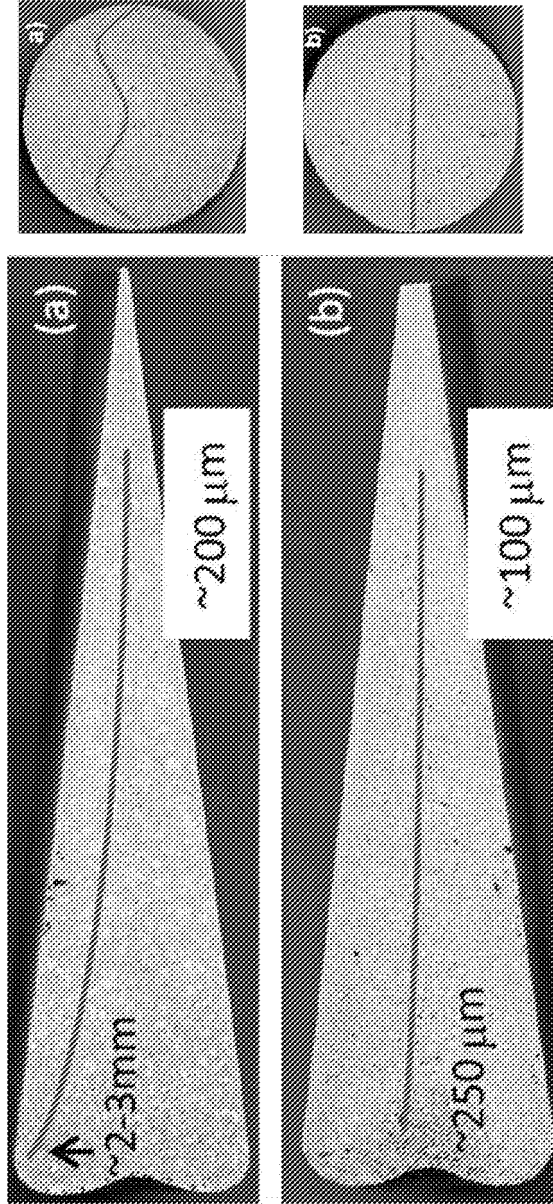


Fig. 15

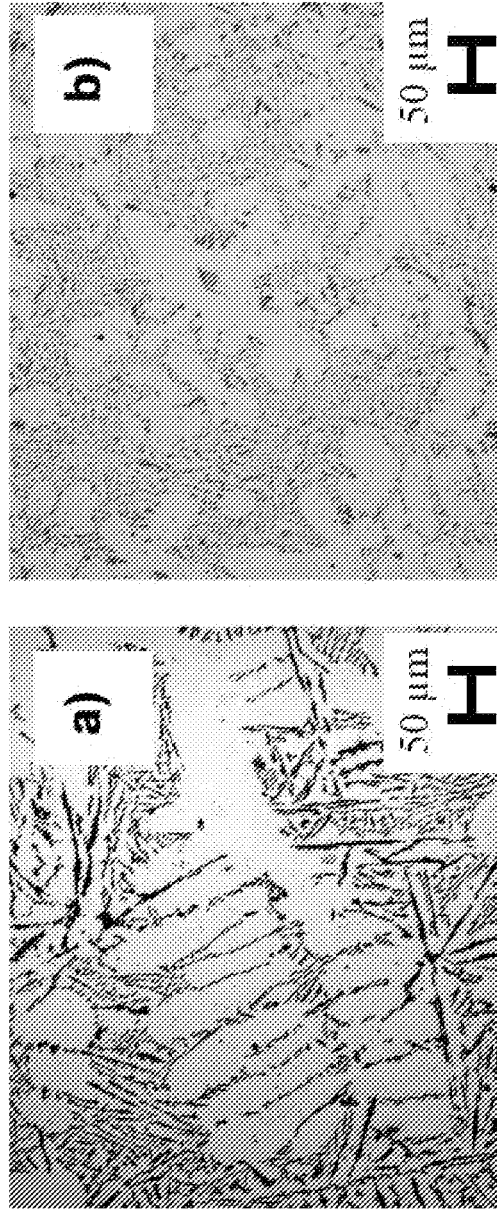


Fig.16

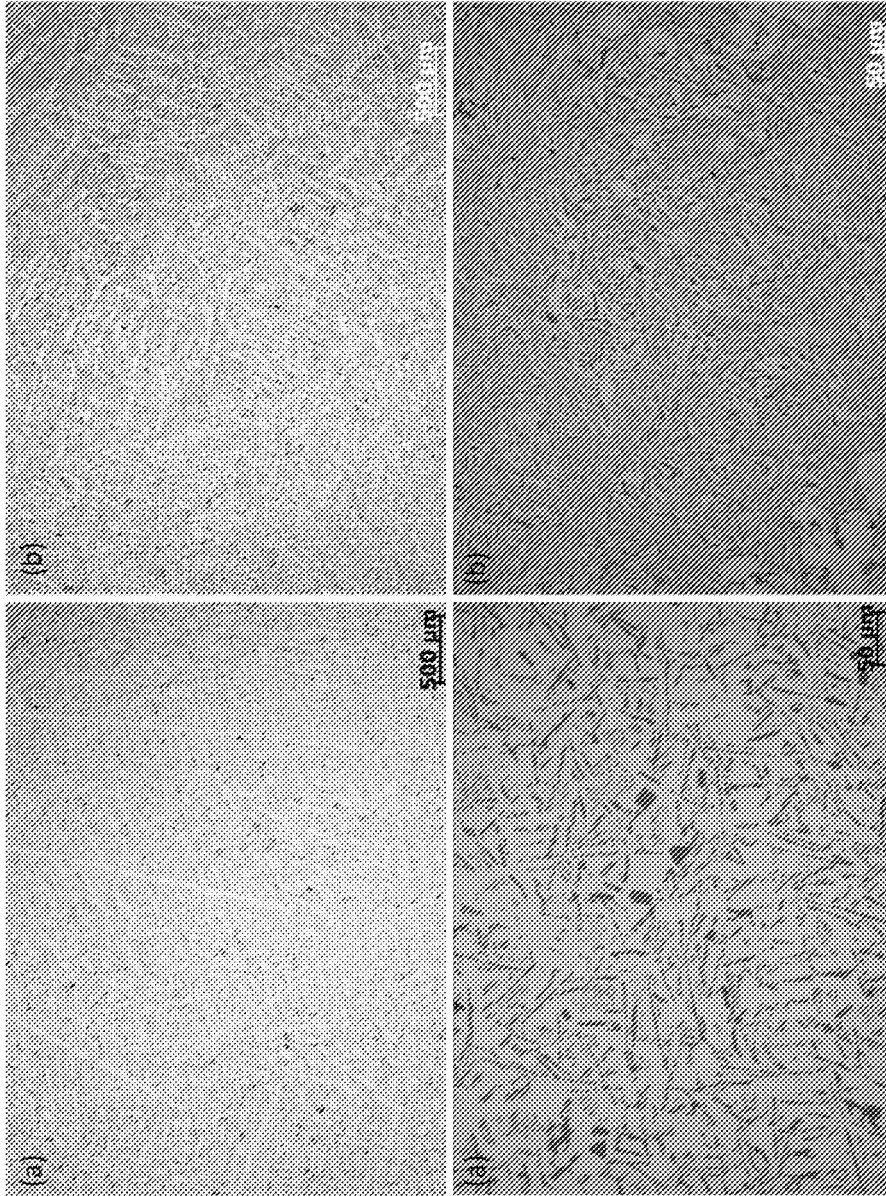


Fig.17

Alloy F

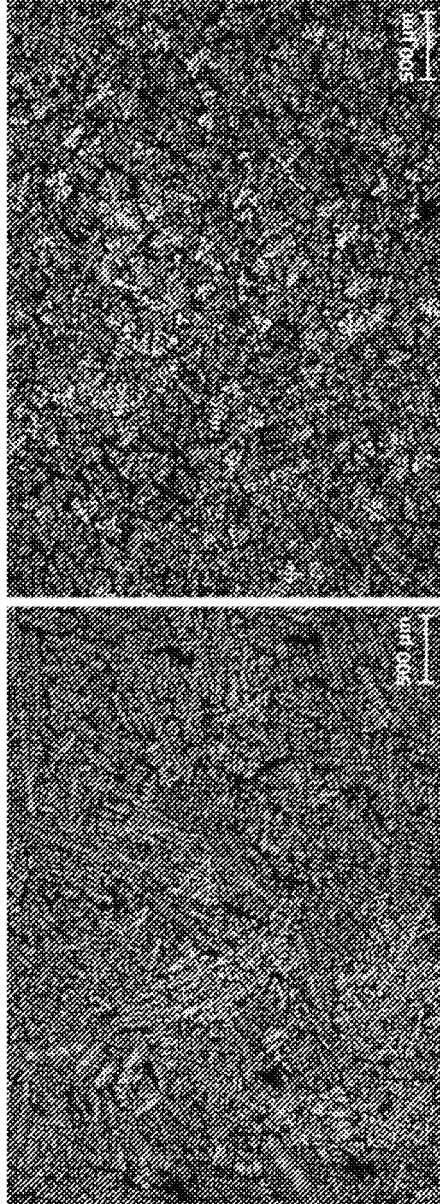


Fig. 18

Alloy G

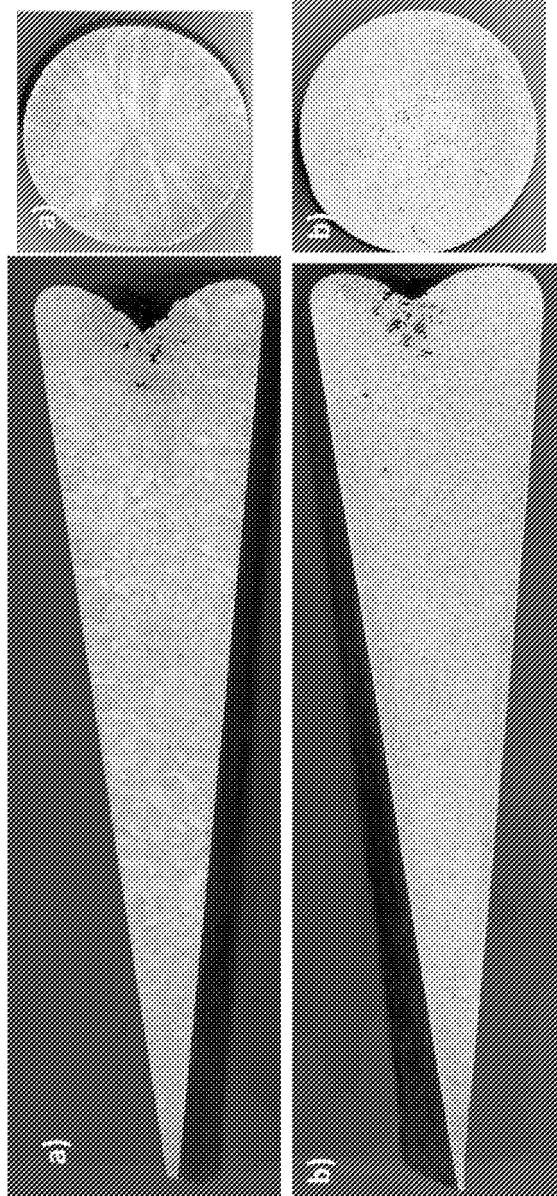


Fig.19

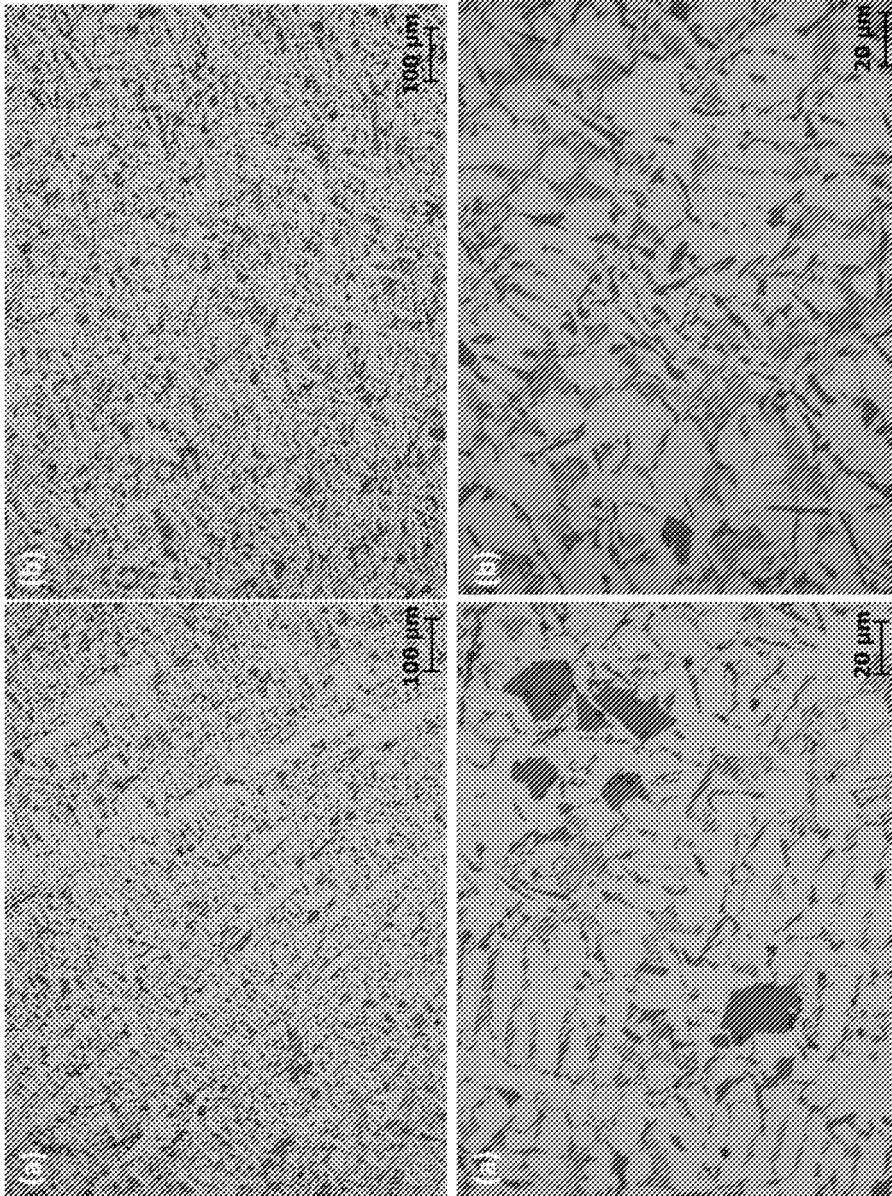


Fig. 20

REFERENCES CITED IN THE DESCRIPTION

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