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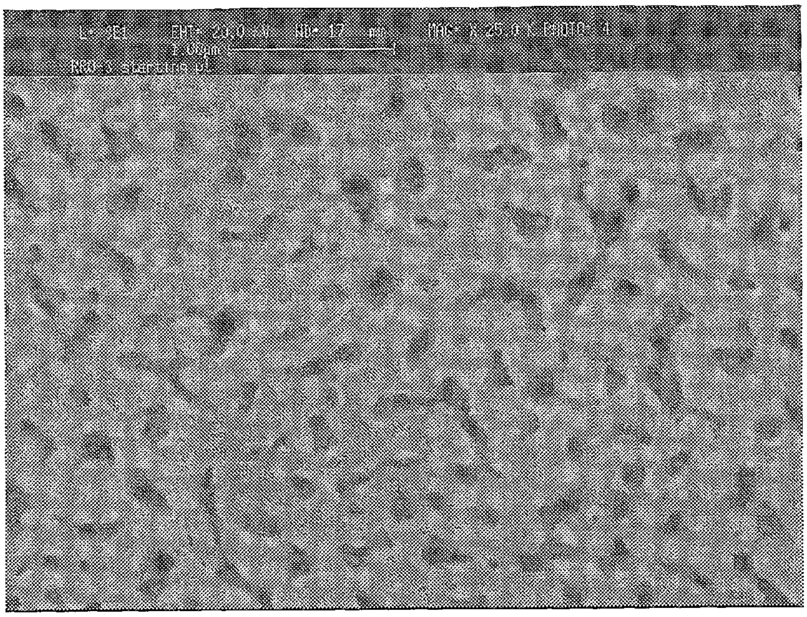
(54) Title: METAL COMPOSITES AND METHODS FOR FORMING SAME



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(57) Abstract: A metal composite comprising a spinodal structure having at least one ductile phase and method of making same is disclosed. The metal composite is formed by forming an alloy comprising a positive heat of mixing in the liquid state; purifying the alloy; and forming a network structure of the alloy comprising at least one ductile sub-network.

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METAL COMPOSITES AND METHODS FOR FORMING SAME

Field of Invention

This invention relates generally to a metal composite and methods for forming same and, more particularly, to a metal composite having a network structure with at least one ductile sub-network.

Background

Nanostructured materials are defined as materials having a grain size diameter of between and including 1 nm and 1,000 nm. The presence of nanostrutures in a material improves mechanical properties when compared to the same material formed without nanostructures.

Nanostructured materials have typically been synthesized by powder sintering or thermal annealing of glassy metals, and fluxing. In powder sintering, nanometer size powders are compacted together, and may be annealed, to produce nanostructured materials. Nanostructured materials produced by powder sintering are typically disk shaped, having a diameter of about 1 cm, and a thickness of 1 mm to 2 mm. The powdered sintered materials are typically brittle and exhibit voids and non-uniform grain growth.

Alternatively, thermal annealing of an amorphous metal produces nanocrystals in an amorphous matrix. A metallic melt is quenched into a glass or amorphous metal, which is then annealed at a temperature near its glass transition temperature, resulting in uniformly distributed nanocrystals in an amorphous matrix. When the amorphous matrix also crystallizes, a crystalline nanostructure may be produced.

A fluxing technique has more recently been used to prepare nanostructured materials. In this method, liquid-state spinodal decomposition occurs resulting in brittle solid spinodals. A typical Pd-Si nanostructure is shown in FIG. 1. As seen in FIG. 1, discrete Pd precipitates (shown in white) are located inside solid spinodals. However, the discrete Pd precipitates are at a negligible volume fraction so that the solid spinodals remain brittle.

As such, the major constituent phases of conventional nanostructures are brittle, and have a broad grain size distribution. Conventional nanostructures also have low strength and low impact fracture energy. Moreover, conventional amorphous metals typically have a small overall dimension, such as ribbon or foil forms having a thickness of 30-50 microns that renders them inappropriate for commercial applications.

SUMMARY OF INVENTION

In one embodiment, the present invention is directed to a method comprising forming an alloy with the constituents, purifying the alloy, and forming a network structure of the alloy comprising at least one ductile sub-network structure.

Another embodiment is directed to a metal composite comprising a ductile spinodal structure. Another embodiment is directed to a metal article comprising the metal composite. In another embodiment, the metal article is a nanostructure composite.

Another embodiment is directed to a method of forming a metal composite comprising forming an alloy, purifying the alloy, forming one or more spinodals, and heating the one or more spinodals causing at least one of the one or more spinodals to transform into one or more ductile phases.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting disclosure, the present specification shall control.

BRIEF DESCRIPTION OF DRAWINGS

In the figures:

FIG. 1 is a TEM micrograph of a conventional Pd-Si nanostructure at a magnification of 75,000X.

FIG. 2 is a SEM micrograph showing the microstructure of a conventional steel ball at a magnification of 9,500X.

FIG. 3A is a SEM micrograph showing a portion of a two phase spinodal microstructure of $Fe_{80}C_{15}Si_5$ at a magnification of 35,000X.

FIG. 3B is a SEM micrograph showing another portion of the two phase spinodal microstructure of FIG. 3A at a magnification of 6,000X.

FIG. 3C is a SEM micrograph showing another portion of the two phase spinodal microstructure of FIG. 3A at a magnification of 34,000X.

FIG. 3D is a SEM micrograph showing another fracture surface of the two phase spinodal microstructure of FIG. 3A at a magnification of 8,500X.

FIG. 3E is a SEM micrograph showing a fracture surface of the two phase spinodal microstructure of FIG. 3A at a magnification of 9,400X.

FIG. 4A is a SEM micrograph showing a portion of a spinodal structure of $Fe_{40.5}Co_{40.5}C_{14}Si_5$ at magnification of 34,000X.

FIG. 4B is a SEM micrograph showing another portion of the spinodal structure of FIG.4A at a magnification of 5,400X.

FIG. 4C is a SEM micrograph showing a fracture surface of the spinodal structure of FIG. 4A at a magnification of 13,500X.

FIG. 4D is a SEM micrograph showing another fracture surface of the spinodal structure of FIG. 4A at a magnification of 4,100X.

FIG. 5A is a SEM micrograph showing a portion of a spinodal structure of $Co_{75}Si_{15}B_{10}$ at a magnification of 34,000X.

FIG. 5B is a SEM micrograph showing another portion of the spinodal structure of FIG. 5A at a magnification of 2,000X.

FIG. 5C is a SEM micrograph showing another portion of the spinodal structure of FIG. 5A at a magnification of 5,400X.

FIG. 5D is a SEM micrograph showing a fracture surface of the spinodal structure of FIG. 5A at a magnification of 1,400X.

FIG. 6A is a SEM micrograph showing a portion of a spinodal structure of $Fe_{82}C_{18}$ at a magnification of 4,100X.

FIG. 6B is a SEM micrograph of a fracture surface of the spinodal structure of FIG. 6A at a magnification of 9,500X.

DETAILED DESCRIPTION

This invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description or illustrated in the figures. The invention is capable of other embodiments and of being practiced or of being carried out in various ways. Also, the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of "including," "comprising," or "having," “containing,” “involving,” and variations thereof herein, is meant to encompass the items listed thereafter and equivalents thereof as well as additional items.

The present invention provides a metal composite comprising a network of at least two spinodals, or sub-networks, and methods for forming same. The terms “spinodal” and “sub-network” are used interchangeably herein, to define a solid morphology of isolated clusters and/or interconnected regions following liquid state spinodal decomposition and subsequent solidification. For example, spinodal decomposition and subsequent solidification of a binary alloy results in two sub-networks. Similarly, spinodal decomposition of a tertiary alloy results in two or three sub-networks. Sub-networks may include discrete precipitates, but not in an appreciable amount.

In one embodiment, at least one spinodal or sub-network of the metal composite is a ductile phase. As used herein the phrase “ductile phase” is defined as a malleable phase. The ductile spinodal may be isolated clusters, partially interconnected, substantially interconnected, and combinations thereof. That is to say that the degree of interconnection of the ductile spinodal may vary throughout the metal composite. In one embodiment, the metal composite comprises a ductile spinodal and a brittle spinodal. In another embodiment, the metal composite comprises a first ductile spinodal and a second ductile spinodal. In one embodiment of the invention, relative volume fractions of the ductile and brittle phases may be changed to vary any desired property, such as but not limited to, hardness, fatigue strength, compressive yield strength, wear resistance, and maximum operating temperature.

The metal composite may be formed from any alloy for which a predominant constituent has a positive heat of mixing with at least one other constituent in the liquid state. As used herein, the phrase “heat of mixing” is defined as an enthalpy change when 1 mol of a mixture is formed from its pure components at a temperature, T. As used herein, the term "predominant" is defined as an intended primary constituent of the alloy. The liquid state may be either stable or metastable. Examples of alloys having constituents with a positive heat of mixing of include: monotectic, eutectic, and peritectic alloys. Other examples of alloys having constituents with a positive heat of mixing are noted in the text "Thermodynamics of Solids," by Richard A. Swalin, Published by John Wiley & Sons, Inc.(1962), which is incorporated herein by reference for all purposed. In one embodiment, the alloy may comprise a metal and a metalloid.

In one embodiment, the overall heat of mixing of all constituents in the alloy may be positive. In another embodiment, the overall heat of mixing in the liquid state of all constituents in the alloy may be negative. For example, an alloy comprised of first, second, and third components may have an overall negative heat of mixing in the liquid state, although the first constituent (the major constituent) has a positive heat of mixing in the liquid state with the second component, and also has a positive heat of mixing in the liquid state with the third component. In this example, an overall negative heat of mixing may arise from a very negative heat of mixing in the liquid state for the second and third constituents, which overwhelms the positive heats of mixing in the liquid state for the first major constituent with the second and third constituents.

Any metal may be used to obtain desired composite properties as long as the selected metal has a positive heat of mixing when combined with at least one other constituent of the alloy in the liquid state. For example, the metal may be a Group VIII metal, such as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, and combinations thereof. In one embodiment, the metal may be selected from the group consisting of Fe, Co, Ni, Cu, Pd, Pt, Mn, Al, T, Zr, Cr, W, and combinations thereof. In one embodiment, the metal is Co. In another embodiment, the metal is Fe. In yet another embodiment, the metal is Ni.

Any metalloid may be used to obtain desired composite properties, as long as the selected metalloid has a positive heat of mixing when combined with other predominant constituents in the liquid state. For example, the metalloid may be any of B, C, Si, As, Sb, Te, Po and combinations thereof. In one embodiment, the metalloid may be any of B, C, Si, and combinations thereof. In another embodiment, the metalloid is C.

In another embodiment, the alloy comprises Fe and at least one of Si and C. In this embodiment, Fe may range between and including about 70 atomic % and about 92 atomic %, Si may range between and including about 0 atomic % and about 20 atomic %, and C may range between and including about 0 atomic % and about 30 atomic %. The ranges used represent minimums and maximums of individual components, though it is understood that individual components are combined in such a way to result in an atomic percent of the alloy of 100 %. It is believed that these ranges of Fe, Si, and C will result in a ductile spinodal network when processed according to the methods disclosed herein. Although compositions outside these ranges may produce the desired ductile nanostructure, it is believed these ranges may be more effective under processing conditions.

In one embodiment, the Fe-C-Si composition may range between and including $Fe_{76}C_{24}Si_0$; $Fe_{81}C_{19}Si_0$; $Fe_{85.5}C_0Si_{14.5}$; $Fe_{88.5}C_0Si_{11.5}$ and all compositions in between. It has been found that this range, and all points therein, result in a nanostructure comprising ductile spinodals upon air cooling, and substantial undercooling.

In another embodiment, the Fe-C-Si composition may range between and including $Fe_{81}C_{19}Si_0$; $Fe_{84}C_{16}Si_0$; $Fe_{90}C_0Si_{10}$; $Fe_{88.5}C_0Si_{11.5}$ and all points in between. In yet another embodiment, the Fe-C-Si composition of another embodiment ranges between and including $Fe_{73}C_{27}Si_0$; $Fe_{76}C_{24}Si_0$; $Fe_{84}C_0Si_{16}$; $Fe_{85.5}C_0Si_{14.5}$ and all points therein. It has been found that within these ranges, and all points there between, portions of the composite formed from these compositions form nanostructures comprising ductile spinodals upon air cooling. However, increased cooling rates may be used so that the entire sample of these compositions may form the desired nanostructures.

In another embodiment, the Fe-C-Si composition may range between and including $Fe_{84}C_{16}Si_0$; $Fe_{87}C_{13}Si_0$; $Fe_{90}C_0Si_{10}$; $Fe_{92}C_0Si_8$ and all points in between. In another embodiment, the Fe-C-Si composition of another embodiment ranges between and including $Fe_{70}C_{30}Si_0$; $Fe_{73}C_{27}Si_0$; $Fe_{82}C_0Si_{18}$; $Fe_{84}C_0Si_{16}$ and all points therein. It is believed that with these ranges, the desired nanostructures may form in a drop tower filled with a gaseous medium.

In another embodiment, B may be added to the Fe-C-Si alloy. For example, B may be added in a range of between and including about 0 atomic % and about 5 atomic % without significantly impacting the formation of the spinodal structures.

In yet another embodiment, the alloy may comprise any non-metal selected from the group Ge, P, S and combinations thereof. In one embodiment, Ge may replace, or be used in addition to Si, without significantly affecting the nanostructure, However, in some instances, the presence of Ge resulted in the formation of voids. In another embodiment, P may be added to the alloy to increase the formation of spinodal structures. For example, between and including about 0.5 atomic % and about 4 atomic % of P may be added to the Fe-C-Si alloy so that the entire composite may comprise a spinodal structure. It has been found that the addition of P in the Fe-C-Si alloy reduces or eliminates the presence of eutectic structures, thereby increasing the amount of spinodal structures.

In another embodiment, Ni may be added to the Fe-C-Si ally to increase the volume fraction of the ductile phase. For example, about 1 atomic % to more that about 3 atomic % Ni may be added to the Fe-C-Si alloy to increase the volume fraction of the ductile phase.

The alloy may have a glass forming ability (GFA) defined herein as a ratio of a glass transition temperature (T_g) to a liquidus temperature (T_l), greater than or equal to about 0.35 so that the nanostructures formed are sufficiently large to impart the desired physical properties to the composite. In one embodiment, the GFA is greater than or equal to about 0.49. For example, $Fe_{82.5}B_{17.5}$ has a GFA of about 0.35; $Fe_{80}B_{20}$ has a GFA of about 0.49; $Fe_{80}C_7P_{13}$ has a GFA of about 0.58; $Fe_{79}Si_{10}B_{11}$ has a GFA of about 0.58, and $Co_{75}Si_{15}B_{10}$ has a GFA of about 0.56.

The alloy may be formed by heating a selected composition of constituents in a desired proportion. Heating may be carried out under normal alloying conditions with conventional equipment, such as a radio frequency induction furnace or high temperature furnace.

Optionally, the formed alloy may be divided into smaller portions of the alloy for further processing. The alloy may be placed in a first portion of a container which also has a second portion smaller than the first portion. A vacuum may drawn on the container. The container may be heated allowing the alloy to melt forming a first molten alloy. The first molten alloy may be forced into the second portion of the container with a pressurized gas.

The container and the first molten alloy may be cooled forming a solidified alloy. The solidified alloy may be removed from the second portion of the container and may be apportioned into a desired size or mass.

In one embodiment, the first portion of the container may have a cross sectional area smaller than a cross sectional area of the second portion. Accordingly, the second portion may be sufficiently long to accommodate the entirety of the molten alloy in the narrower cross sectional area. Upon cooling the first molten alloy and the container, the solidified alloy may be cut into various thicknesses, suitable for a desired application.

The alloy not further divided or the solidified alloy further divided into smaller portions may be further processed to remove impurities according to conventional methods. For example, the solidified alloy may be heated to a temperature greater than or equal to its liquidus (T_l) in the presence of a flux to form a second molten alloy. In one embodiment, the solidified alloy and flux material may be heated to a temperature greater than about1,000 °C.

Any flux may be used so long as it does not react with the second molten alloy. For example, the flux may be boron oxide, glass, calcium oxide, barium oxide, aluminum oxide, magnesium oxide, lithium oxide, and mixtures thereof. In one embodiment, the flux is glass. In another embodiment the flux is boron oxide. Boron oxide (B_2O_3), nominally anhydrous, is available from Atomergic Chemetals Corporation (Farmingdale, NY).

The second molten alloy may then be cooled to a temperature sufficient to form a second solidified alloy. In one embodiment, the second molten alloy may be undercooled by cooling the second molten alloy below its liquidus. The second molten alloy may be cooled to or below a critical temperature, T_c, typically below the liquidus to allow liquid state spinodal decomposition, thereby forming liquid spinodals. Without being bound by any particular theory, it is believed that the fluxing process purifies the second molten alloy, allowing the second molten alloy to remain in its liquid state well below it liquidus. By allowing the second molten alloy to remain in its liquid state below its liquidus, the second molten alloy is a metastable liquid that undergoes spinodal decomposition upon entering the metastable miscibility gap (critical temperature T_c), which is often substantially below the liquidus of the alloy. During spinodal decomposition, the molten alloy splits into a number of metastable liquid spinodals having a liquid phase wavelength λ. As used herein, the wavelength (λ) is defined as a lateral dimension, or diameter, of the spinodal. In one embodiment, the metastable liquid may have a liquid phase λ of less than about 300 nm, preferably less than about 100 nm.

Upon cooling, the second molten alloy solidifies to form an undercooled specimen having a spinodal or sub-network structure. The solid spinodals may be crystalline, amorphous, quasi-crystalline, and mixtures thereof. In one embodiment, the alloy is cooled to a ΔT of about 100 °K to about 500 °K. As used herein the term ΔT is defined as the difference between the liquidus temperature and actual temperature ($T_l - T$).

The solid phase wavelengths (λ) formed by the liquid state spinodal decomposition of the second molten alloy typically range from microns to nanometers. The resultant composite may have a fine microstructure defined as a material having a grain size diameter, or wavelength, of between and including 1 nm and 100,000 nm. The composite may include nanostructures, wherein one physical dimension of one constituent phase is about 1,000 nm or less. Each spinodal, or sub-network, within the entire networked structure my have solid phase wavelengths that are similar to or differing from one another.

In one embodiment, the spinodal or sub-network structure formed may have a solid phase λ of less than about 50 microns. In another embodiment, the spinodal or sub-network structure formed may have a solid phase λ of about 10 microns or less. In yet another embodiment, the spinodal structure formed has a solid phase λ of about 300 nm or less, preferably less than about 100 nm.

The solid phase wavelength may vary throughout a specimen. For example, the solid phase wavelength may change during crystallization. During crystallization, a crystallization front moves across the molten so that the solid phase λ increases, effectively creating a coarser spinodal structure. Therefore, the solid phase wavelength may be smallest at a site where crystallization is initiated, and increase as crystallization proceeds further from the initiation site. The wavelength of the solid spinodal at the site where crystallization is initiated may be similar to the wavelength of the liquid spinodal. In one embodiment, the spinodal morphology at a distance from the site where crystallization is initiated may be replaced (partially or entirely) by other structures, including dendrite and eutectic.

If crystallization is bypassed after the metastable liquid alloy undergoes metastable liquid spinodal decomposition, the liquid spinodals may solidify into amorphous spinodals upon further cooling. The solidification may occur homogeneously, that is, hardening does not begin at any single location. The hardening continues on further cooling, until all the liquid spinodals become amorphous solids. It is expected that the solid phase λ is substantially uniform in this mode of solidification, so that the liquid phase λ of the liquid spinodals may be similar to the solid phase λ of the amorphous spinodals. Solid spinodals may also form as a mixture of amorphous and crystalline spinodals, so that λ may vary through out the solid.

The phases in the spinodals, if crystalline, may, but need not, form a microstructure comprising a coherent grain boundary. As used herein, the term “coherent grain boundary” is defined as a coherent interface and/or a semi-coherent interface. A coherent interface has interfacial energies of about 10 to about 100 mJ/m^2, and occurs when two crystals perfectly match at an interface plane so that the two lattices are continuous across the interface. A semi coherent interface occurs when the interface has a series of edge or screw dislocations and has an interfacial energy of about 200 mJ/m^2 to about 500 mJ/m^2.

In another embodiment of the invention, any brittle spinodals present in a specimen may be further treated to undergo phase transformation into one or more ductile spinodals. For example, on annealing, Fe_3Si decomposes into Fe and graphite, thereby further increasing the strength and impact fracture of the specimen. In one embodiment, one or more brittle spinodals may be annealed to form ductile phases. The resultant ductile phases may be isolated clusters, partially or substantially completely interconnected, and combinations thereof. The ductile phases may be interconnected with other ductile phases, and or with brittle phases.

The metal composite may be a bulk material having any shape suitable for a particular purpose. As used herein, the phrase “bulk material” is defined as a material having a shape with a cross sectional dimension greater than or equal to about 1mm in all directions. For example, the composite may be a sphere, cone, pyramid, square, rectangle or irregular shape. In one embodiment, the composite is a sphere. In another embodiment, the bulk material has at least one cross sectional dimension of about 2.54 cm, preferably about 1 cm. In yet another embodiment, the metal composite may be a sphere having any diameter suitable for a particular purpose. For example, the metal composite may be a sphere having a diameter less than about 1 inch, less than or equal to about 2 cm, less than or equal to about 1.0 cm, and less than or equal to about 5 mm respectively. In another embodiment, the spherical metal composite may have a diameter of about 0.1 mm. The process for forming the metal composite into spheres, such as ball bearings, is advantageous when compared to conventional process of making steel balls. For example, the typical expensive process may be replaced with a simple and inexpensive fluxing process, and the conventional heat treating process may be eliminated.

EXAMPLES

The invention may be further understood with reference to the following examples, which are intended to serve as illustrations only, and not as limitations of the present invention as defined in the claims herein.

Alloys for each of the compositions listed below were prepared as follows:

A desired composition of raw materials, selected from Fe, Co, Ni, C, Si, B, Ge, and P, were alloyed in an RF induction furnace at a minimum temperature of about 1,000 °C. The alloy was air cooled to solidify, and then positioned in a large portion of a fused silica tube. The fused silica tube comprised a large portion with an inner diameter of about 10 mm to 30 mm, and a long small portion having an inner diameter of about 2 mm to about 8 mm. The small portion had a length of about 10 mm to about 600 mm. The silica tube containing the alloy was evacuated by a mechanical pump and placed in a furnace at a sufficient temperature and for a sufficient time to melt the alloy. When the alloy was completely melted, a pressurized gas was introduced into the large portion of the silica tube forcing the molten alloy into the small portion of the tube. The tube and alloy were cooled, forming a rod shaped alloy. The rod shaped alloy was removed from the tube and cut into smaller disk shaped pieces each having a thickness in the range of between and including about 1 mm to about 10 mm.

Each disk was positioned with anhydrous B_2O_3 in individual fused silica tubes, having inner diameters between about 3 mm and about 15 mm, and a length of about 10 mm to about 100 mm. A number of fused silica tubes containing an alloy disk and anhydrous B_2O_3 were placed in a larger fused silica tube having a diameter of about 20 mm to about 100 mm. A vacuum was drawn on the larger silica tube, which created a vacuum in the individual tubes containing each alloy disk and anhydrous B_2O_3. The large tube was then heated at sufficient temperature and for a specified time period, ranging from about 15 minutes to about 8 hours to completely melt the alloys. The molten alloys were cooled and allowed to crystallize at the ΔT temperatures noted below.

Example I.	Fe:	80 atomic %
	C:	15 atomic %
	Si:	5 atomic %

This alloy was prepared by purifying molten $Fe_{80}C_{15}Si_5$ in a flux above its liquidus, and subsequent undercooling below its liquidus.

The Fe-C-Si system was formed into a precision ball bearing with some of its properties listed in Table 1. Also listed in Table are comparative results for conventional chrome steel balls (available from FAG Bearing, Danbury, CT).

Table 1

Property	Fe-C-Si system	Chrome steel balls (available from FAG Bearing, Danbury, CT)
Hardness (HV)	750-850	
Fatigue strength (Maximum compressive pressure (MPA))*	>3,600**	<2,600***
Compressive yield strength (MPA)	About 7,000	About 3,600
Maximum operating temperature	550 °C	150 °C

*Fatigue strength was determined by using a cyclic compressive force, with a minimum compressive pressure of bout 0 MPA and a maximum cyclic compressive pressure of about 3,600 MPA for 10^7 cycles.

** Samples remained in tact after completion of the test.

***Samples did not survive the test.

It was found that the Fe-C-Si system had about the same wear resistance and hardness as the conventional steel ball. However, balls made from the Fe-C-Si system exhibited a compressive yield strength almost double that of the conventional steel ball (7,000 MPA compared to 3,600 MPA). The balls made from the Fe-C-Si system also exhibited a greater fatigue strength of 3,600 MPA without failure, compared to the conventional balls which failed at 2,600 MPA. Similarly, the balls of the Fe-C-Si system exhibited a greater Young's modulus and greater thermal stability than the conventional steel balls. In addition, the Fe-C-Si system balls exhibited an impact fracture energy that approached that of a ceramic precision ball bearing made of SiN.

FIG. 3A is a SEM of a two phase spinodal microstructure of the $Fe_{80}C_{15}Si_5$ ball. The $Fe_{80}C_{15}Si_5$ was analyzed at various locations within the ball. The micrograph in FIG. 3A shows a two-phase spinodal structure having an interconnected microstructure. Both phases are crystalline, and have an average wavelength of about 300 nm. The randomness of the microstructure indicates that this is the site where crystallization was initiated. FIG. 3B is a micrograph of a center of the specimen of FIG. 3A. FIG. 3B shows alignments and differing orientation of the alignments of the spinodal structure near the center of the specimen. FIG. 3C is a micrograph of the specimen at an end opposite to the site of initiation. FIG. 3C shows the formation of eutectic structures at the end opposite to the site of initiation. FIG. 3D shows the fracture behavior of this system, in which the fracture surface is scale-like or cloud-like. The white curves in FIG. 3D are ridges, illustrating that ductile fracture has occurred. FIG. 3E is another micrograph of the specimen of FIG. 3A showing the microstructure on a fracture surface of the specimen. The two solid spinodals in the metal composite are Fe_3Si and body centered cubic (BCC) Fe, or solid solution of Fe. The former spinodal is brittle, while the latter is ductile. Upon fracturing, the ductile spinodal forms ridges on a fracture surface. Without being bound by any particular theory, it is believed that the high strength and high impact fracture energy are due to BCC Fe (or solid solution Fe).

At a very large ΔT, for example 100 -500 °K, the melt split into two liquid spinodals. These two liquid spinodal were metastable and were, therefore, prone to crystallization. Crystallization started at a point on the surface of the molten specimen (called the site of initial crystallization). The crystallization front then spread out until the entire molten specimen became a crystal. During crystallization, heat was released (heat of crystallization) that may have been partly responsible for the change in microstructures at increasing distances from the site of initial crystallization. At the site of initial crystallization, since crystal growth was fast and heat released is relatively small, the morphology of the liquid spinodals may have been similar to the morphology of the solid spinodals. Moving away from the site of initial crystallization, the spinodal morphology evolved.

In comparison, FIG. 2 is a SEM of a microstructure of a conventional steel ball, typically a mixture of austenite and martensite, produced by conventional methods. Typically, steel in the form of a wire coil (still austenite, which is soft) is manufactured. Short cylindrical pieces are cut form the wire and cold forged in a heading machine. The surface of the headed balls are ground by a flashing machine. The balls are then hardened in a furnace, transforming more than half of the austentite into martensite, which is hard. After hardening, the balls go though two more grinding processes (grinding and lapping) to produce a desire surface finish. The balls are then cleaned and polished. Drawbacks to the conventional method of preparing steel balls include the necessity of using a high quality wire coil, and ensuring the heat treatment does not convert all the austenite into martensite. Moreover, because not all the austenite is converted, the conventional steel balls may not be suitable for high temperature application, such as those greater than 150 °C.

Although not being bound by any one particular theory, it is believed that the microstructure including the ductile phase of the present invention provides a micro- or nano-structured object with unique physical properties when compared to similar objects made with conventional methods, such as: greater compressive yield strength, greater Young's modulus, greater fatigue resistance, and greater thermal stability, while maintaining similar wear resistance and hardness, while also exhibiting similar impact fracture energy similar to that of ceramic balls.

Example II. Fe: 40.5 atomic %
CO: 40.5 atomic %
C: 14 atomic %

Si: 5 atomic %

The crystallization temperature was about 800 °C. The microstructures of an as formed $Fe_{40.5}CO_{40.5}C_{14}Si_5$ ingot (the specimen) are shown in Figs. 4A-4D. FIG. 4A shows the microstructure of a portion of the specimen that crystallized first, locating the free surface of the specimen. In FIG. 4A, there are two solid spinodals, of different phases, which together form a random network. FIG. 4B shows the microstructure of a portion of the specimen that crystallized last, at the opposite end of the specimen. As seen in FIG. 4b, the microstructure is a mixture of spinodal morphology and eutectic structure. FIG. 4c shows the fracture surface of the specimen, in which bright ridges indicate ductile fracture had take place in one of the two spinodals. The distribution of the ridges is consistent with the prediction of a spinodal mechanism. In regions dominated by eutectics, the eutectic morphology is exhibited on the fracture surface shown in FIG. 4D.

Example III. CO: 75 atomic %
Si: 15 atomic %
B: 10 atomic %

Crystallization occurred at about 800 °C. The microstructures of an as formed $CO_{75}Si_{15}B_{10}$ ingot (specimen) are shown in Figs. 5A-5D. FIG. 5A shows the microstructures of a portion of the specimen which crystallized first, located at the free surface of the ingot. In FIG. 5A, there are two solid spinodals of different phases, forming a network. The network morphology changes as the location in the specimen moves away from the site where crystallization was initiated. Toward the center of the specimen, one solid spinodal shown apparently breaks into elongated grains, as shown in FIG. 5B. The elongated grains may be over about 20 microns. A layer of multiple phases separates the elongated grains. FIG. 5C shows microstructures at a location further from the site of initial crystallization. As shown in FIG. 5C, the layer surrounding the elongated grains of the portion of the specimen that crystallized last appear to be substantially homogeneous. FIG. 5D shows a fracture surface of the specimen which illustrates that the layers surrounding the elongated grains are ductile.

Without being bound to any particular theory, it is believed that the ductile layers provide the specimen with impact fracture energy and strength.

Example IV. Fe: 82 atomic %
C: 18 atomic %

Crystallization temperature was about 650 °C. The microstructure of an as prepared ingot of $Fe_{82}C_{18}$ specimen is shown in FIG. 6A. In FIG. 6A, there are many domains, each of which is occupied by a network-like structure that is aligned. The boundaries between the domains are relatively flat, and the alignments of the network close to the boundaries are sharp. Apparently, a form of rearrangement of the network branches occurred during crystallization forming the boundaries. FIG. 6B shows the microstructure of a fracture surface of the specimen of FIG. 6A. As seen in FIG. 6A, two vertical lines are found near the center of the micrograph, and represent the boundaries described above. Attached to these boundaries are aligned features, similar to that of a dendrite. Further away from the boundaries, scale-like or cloud-like structures again dominate the microstructure. The lighted parts of FIG. 6B represent ridges which have undergone a ductile fracture.

Having thus described several aspects of at least one embodiment of this invention, it is to be appreciated various alterations, modifications, and improvements will readily occur to those skilled in the art. Such alterations, modifications, and improvements are intended to be part of this disclosure, and are intended to be within the spirit and scope of the invention. Accordingly, the foregoing description and drawings are by way of example only.

CLAIMS

1. A method comprising:
   forming an alloy;
   purifying the alloy; and
   forming a network structure of the alloy comprising at least one ductile sub-network structure.

2. The method of claim 1 wherein the alloy formed comprises a ratio of T_g to T_l greater than or equal to about 0.35.

3. The method of claim 2, wherein the alloy formed comprises a ratio of T_g to T_l greater than or equal to about 0.49.

4. The method of claim 2, wherein the alloy formed comprises a metal and a metalloid.

5. The method of claim 4, wherein purifying the alloy comprises:
   heating the alloy to form a molten alloy; and
   contacting the molten alloy with a flux material.

6. The method of claim 2, wherein forming a network structure comprises cooling the molten alloy.

7. The method of claim 6, wherein cooling the molten alloy comprises undercooling the molten alloy.

8. The method of claim 7, wherein the molten alloy is cooled to a ΔT of about 100°K to about 500°K

9. The method of claim 4, wherein the alloy formed comprises a metal selected from the group consisting of Fe, Co, Cu, Ni, Pd, Pt, Mn, Al, Ti, Zr, Cr, W, and combinations thereof.

10. The method of claim 9, wherein the alloy formed comprises a metal selected from the group consisting of Fe, Co, Ni, and combinations thereof.

11. The method of claim 10, wherein the alloy formed comprises Ni.

12. The method of claim 10, wherein the alloy formed comprises Co

13. The method of claim 10, wherein the alloy formed comprises Fe.

14. The method of claim 4, wherein the alloy formed comprises a metalloid selected from the group consisting of B, Si, C and combinations thereof.

15. The method of claim 4, wherein the alloy formed further comprises a non-metal selected from the group consisting of Ge, P, S and combinations thereof.

16. The method of claim 14, wherein the metalloid is C.

17. The method of claim 10, wherein the alloy formed comprises an element selected from the group consisting of C, Si, and combinations thereof.

18. The method of claim 15, wherein the alloy formed further comprises Ge.

19. The method of claim 5, wherein the alloy is contacted with a flux material selected from the group consisting of B_2O_3, glass, calcium oxide, barium oxide, aluminum oxide, magnesium oxide, lithium oxide, and combinations thereof.

20. The method of claim 19, wherein the alloy is contacted with a flux material selected from the group consisting B_2O_3, glass, and combinations thereof.

21. The method of claim 20, wherein the alloy is contacted with B_2O_3.

22. The method of claim 20, wherein the alloy is contacted with glass.

23. The method of claim 4, further comprising heating the alloy and the flux material to a temperature greater than about 1,000°C.

24. The method of claim 1, further comprising:

placing the alloy in a first portion of a vessel;

heating the first portion of the vessel under a vacuum causing the alloy to melt and flow into a second portion of the vessel; and

cooling the second portion of the vessel.

25. The method of claim 1, wherein the network structure is formed having a solid phase λ of about 50 microns or less.

26. The method of claim 25, wherein the network structure is formed having a solid phase λ of about 10 microns or less.

27. The method of claim 26, wherein the network structure is formed having a solid phase λ of about 300 nm or less.

28. The method of claim 27, wherein the network structure is formed having a solid phase λ of about 100 nm or less.

29. The method of claim 1, wherein the alloy comprising a positive heat of mixing in a liquid state is one of a monotectic alloy, a eutectic alloy, and a peritectic alloy.

30. The method of claim 25, wherein the spinodal structure is formed having a liquid phase λ and a solid phase λ that are substantially equal.

31. The method of claim 30, wherein the liquid phase λ and a solid phase λ that are substantially equal are at a location where crystallization is initiated.

32. The method of claim 1, wherein the alloy is formed from at least 2 constituents comprising a positive heat of mixing in the liquid state.

33. The method of claim 32, wherein the liquid state is metastable.

34. The method of claim 32, wherein the liquid state is stable.

35. A metal composite comprising a ductile spinodal structure.

36. The metal composite of claim 35, wherein the spinodal structure comprises a coherent grain boundary.

37. The metal composite of claim 35, wherein the composite is a bulk material.

38. The metal composite of claim 37, wherein the spinodal structure has a liquid phase λ of about 50 microns or less.

39. The metal composite of claim 37, wherein the spinodal structure has solid phase λ of about 50 microns or less.

40. The metal composite of claim 38, wherein the spinodal structure has a liquid phase λ and a solid phase λ that are substantially equal.

41. The metal composite of claim 35, further comprising a metal and a metalloid.

42. The metal composite of claim 41, wherein the metal is selected from the group consisting of Fe, Co, Cu, Ni, Pd, Pt, Mn, Al, Ti, Zr, Cr, W, combinations thereof.

43. The metal composite of claim 42, wherein the metal is selected from the group consisting of Fe, Co, Ni, and combinations thereof.

44. The metal composite of claim 43, wherein the metal is Ni.

45. The metal composite of claim 43, wherein the metal is Co.

46. The metal composite of claim 43, wherein the metal is Fe.

47. The metal composite of claim 41, wherein the metalloid is selected from the group consisting of B, Si, C and combinations thereof.

48. The metal composite of claim 41, further comprising Ge, P, S, and combinations thereof.

49. The metal composite of claim 47, wherein the metalloid is selected from the group consisting of C, Si, and combinations thereof.

50. The metal composite of claim 42, further comprising Si.

51. The metal composite of claim 42, further comprising C.

52. The metal composite of claim 42, further comprising a ratio of T_g to T_l greater than or equal to about 0.35.

53. The metal composite of claim 52, further comprising a ratio of T_g to T_l greater than or equal to about 0.49.

54. A metal article comprising the metal composite of claim 34.

55. The metal article of claim 54, wherein the article has a spherical shape.

56. The metal article of claim 55, wherein the spherical shape has a diameter of about 1 inch or less.

57. The metal article of claim 56, wherein the spherical shape has a diameter of about 2 cm or less.

58. The metal article of claim 57, wherein the spherical shape has a diameter of about 1 cm or less.

59. The metal article of claim 58, wherein the spherical shape has a diameter of about 5 mm or less.

60. The metal article of claim 59, wherein the spherical shape has a diameter of about 0.1 mm.

61. The metal article of claim 54, wherein the article further comprises a eutectic structure.

62. The metal article of claim 54, wherein the metal article is a nanostructure composite.

63. A method of forming a metal composite comprising:
forming an alloy;
purifying the alloy;
forming one or more spinodals; and

heating the one or more spinodals causing at least one of the one or more brittle spinodals to transform into one or more ductile phases.

64. The method of claim 63, wherein forming one or more spinodals comprises forming one or more brittle spinodals.

65. The method of claim 63, wherein the one or more ductile phases are interconnected.

66. The method of claim 65, wherein the one or more ductile phases are partially interconnected.

67. The method of claim 65, wherein the one or more ductile phases are substantially completely interconnected.

68. The method of claim 65, wherein the one or more ductile phases are interconnected with brittle phases.

69. The method of claim 63, wherein the one or more ductile phases are isolated clusters .

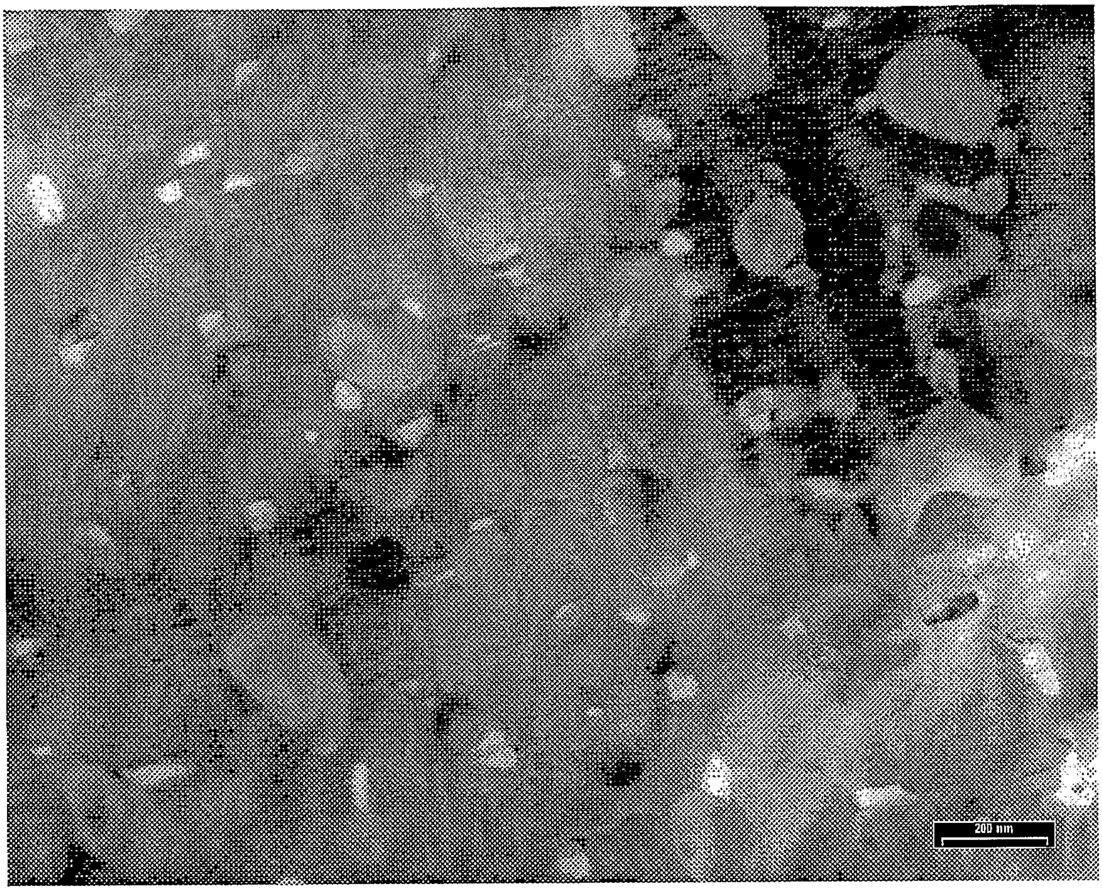

FIG. 1 Mag: X 75k (Prior Art)

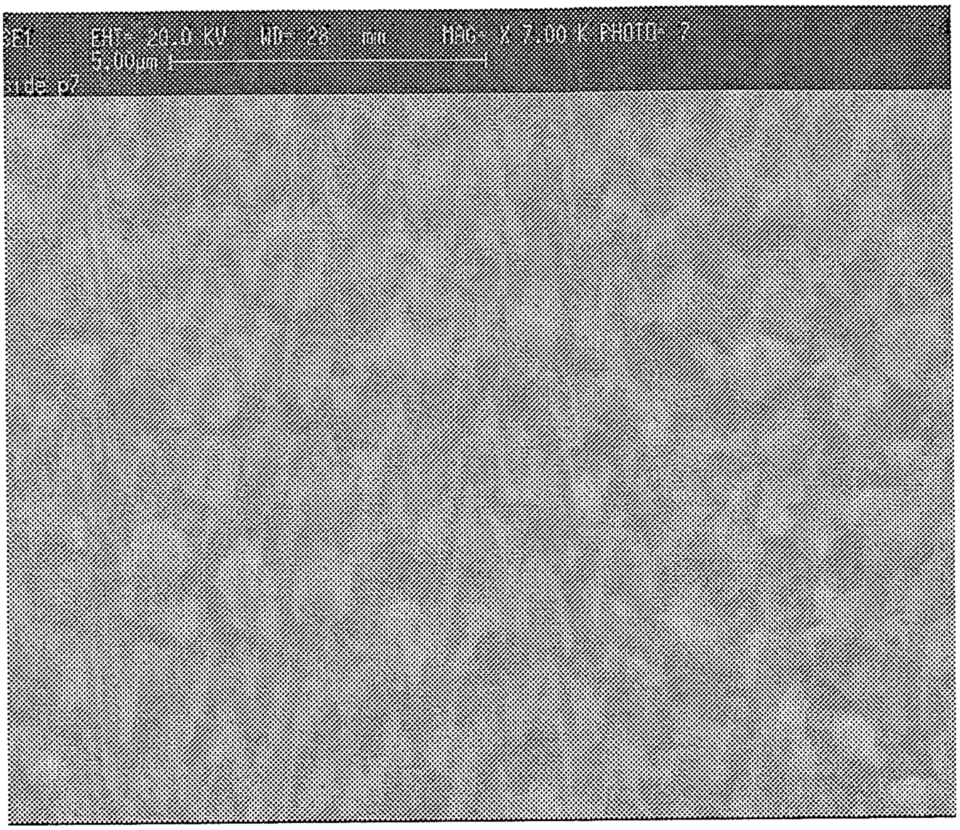

FIG. 2 Mag: X 9.5k (Prior Art)

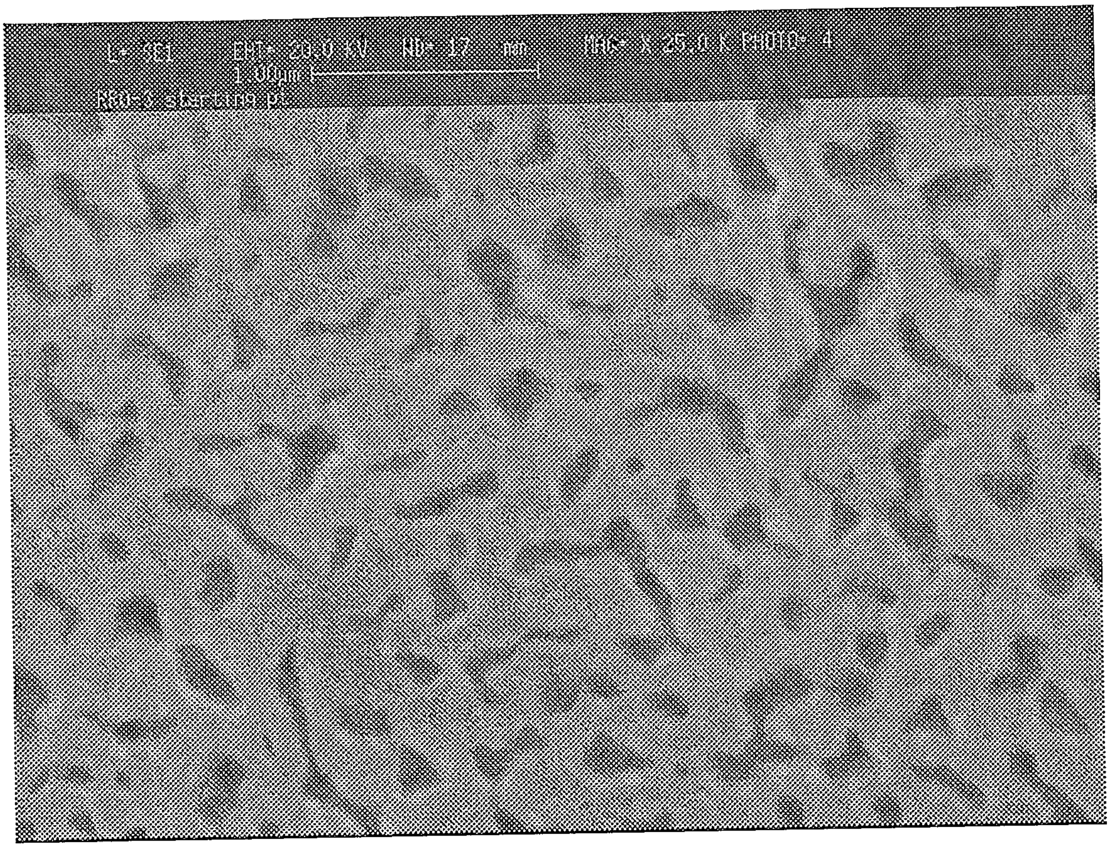

FIG. 3a Mag: X 35k

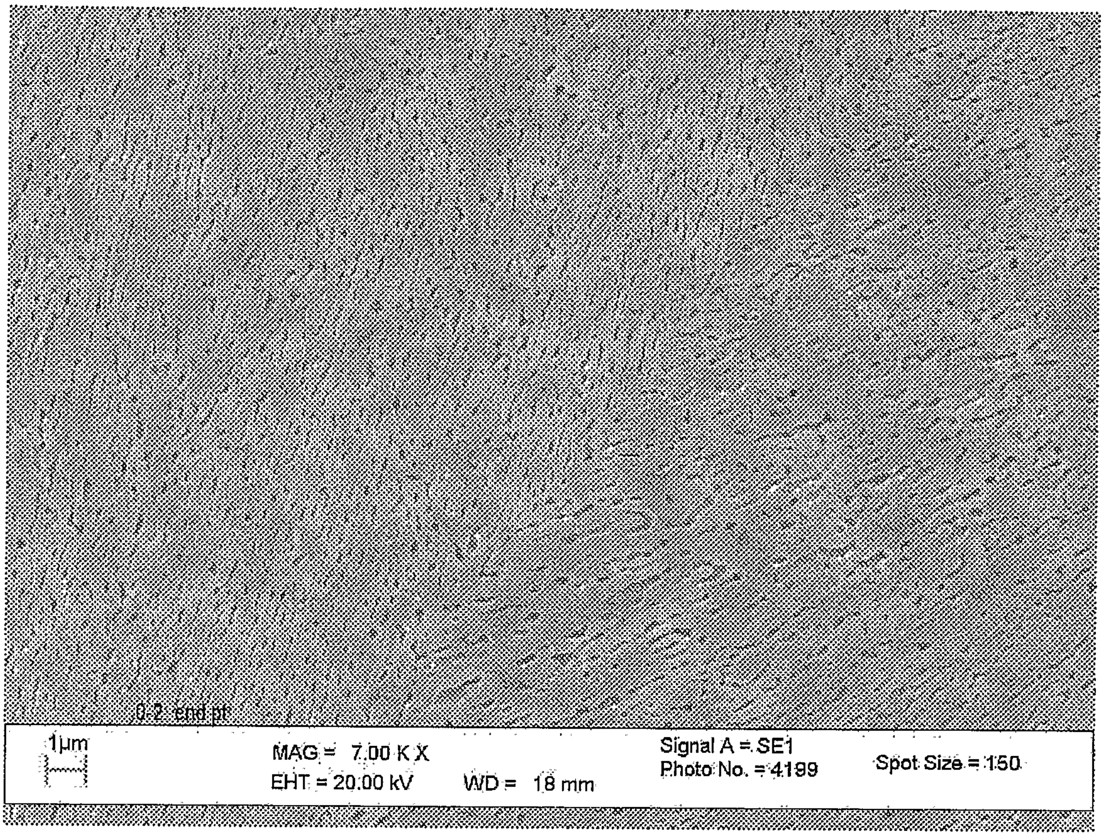

FIG. 3b Mag: X 6k

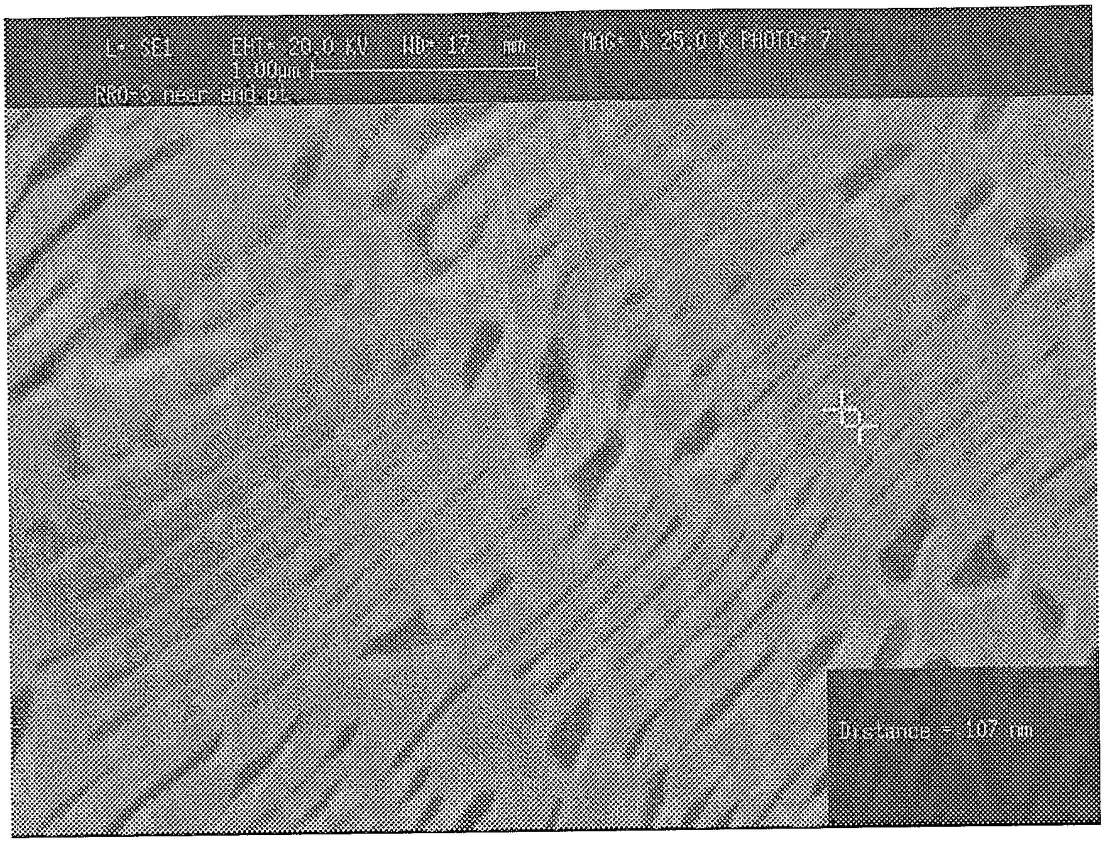

FIG. 3c Mag: X 34k

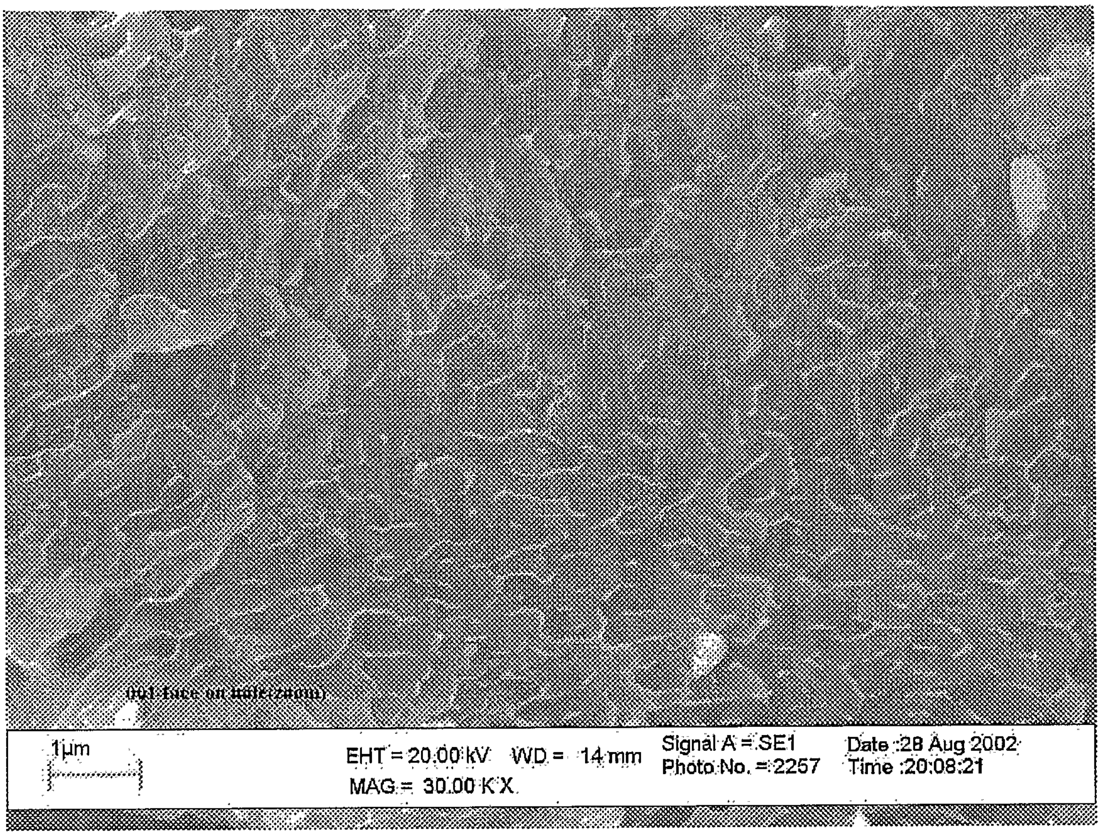

FIG. 3d Mag: X 8.5k

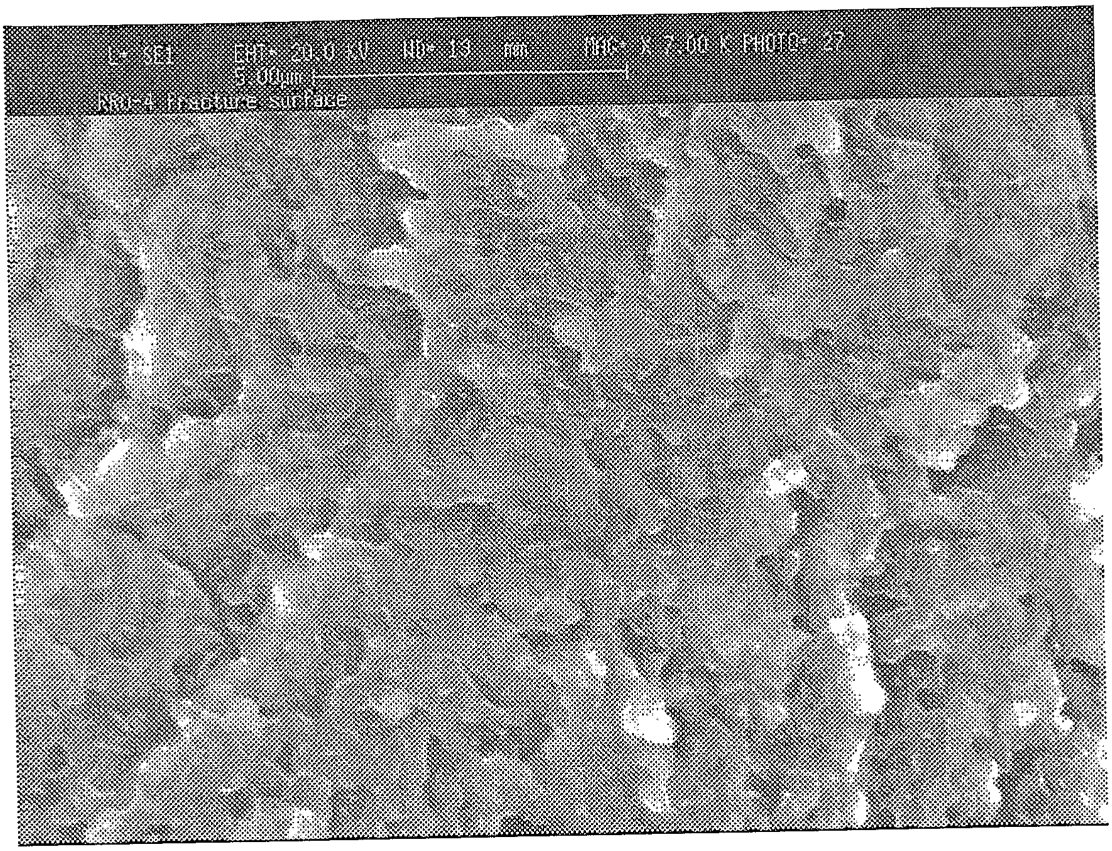

FIG. 3e Mag: X 9.4k

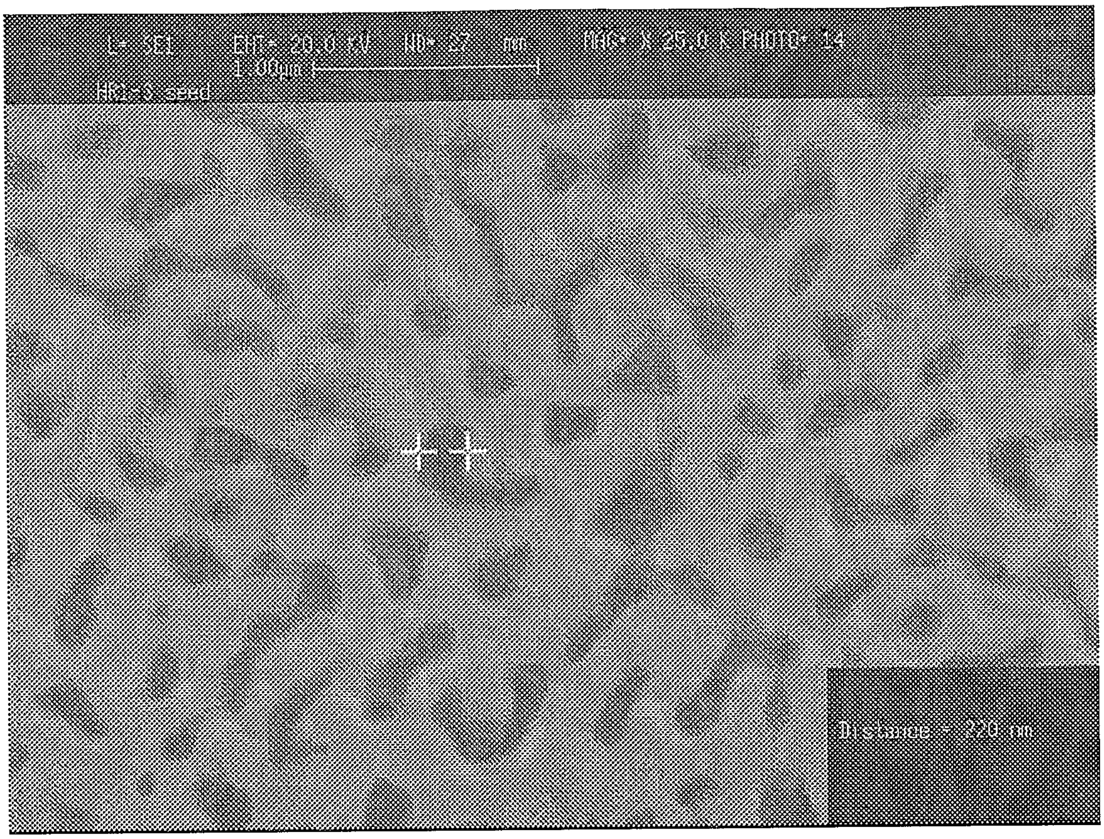

FIG. 4a Mag: X 34k

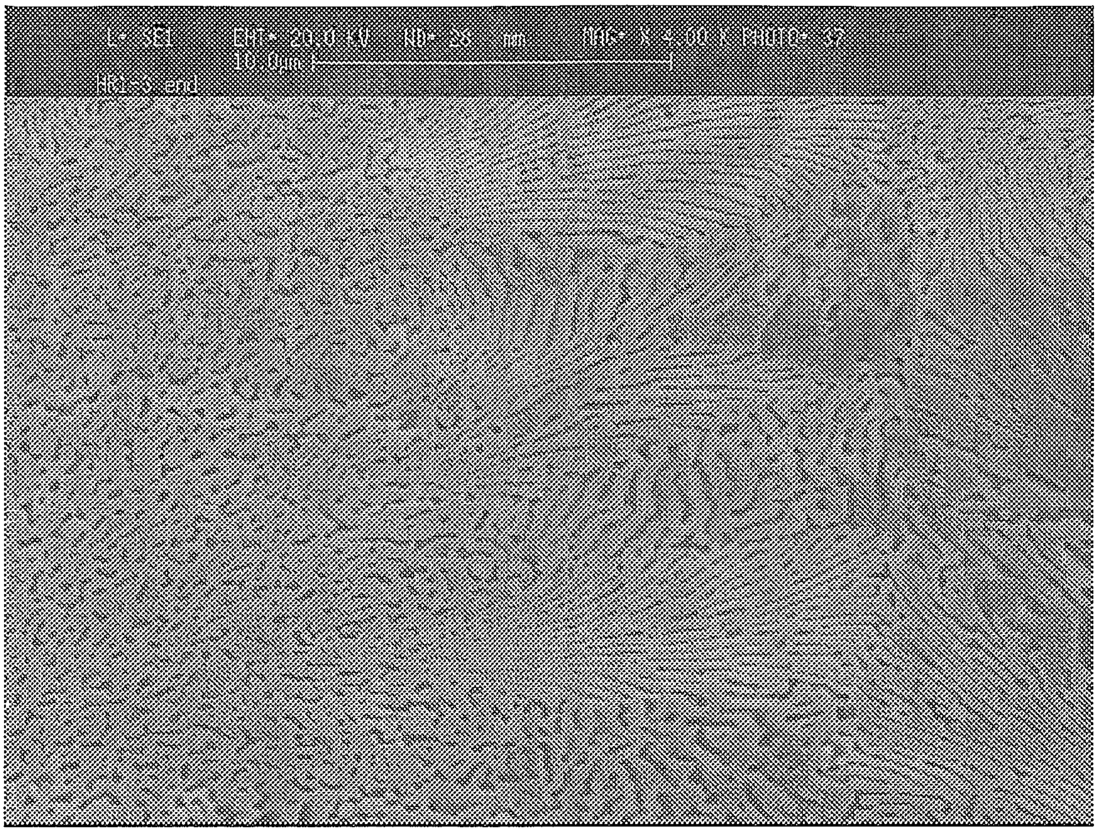

FIG. 4b Mag: X 5.4k

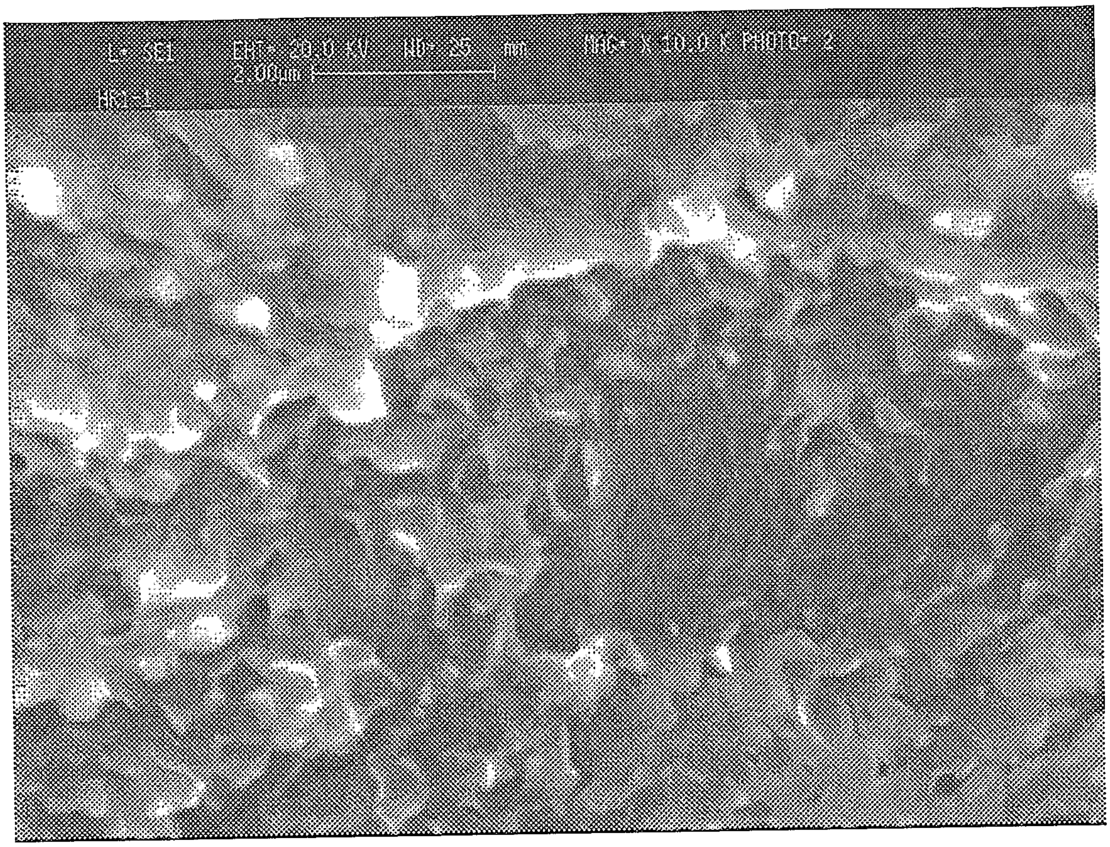

FIG. 4c Mag: X 13.5k

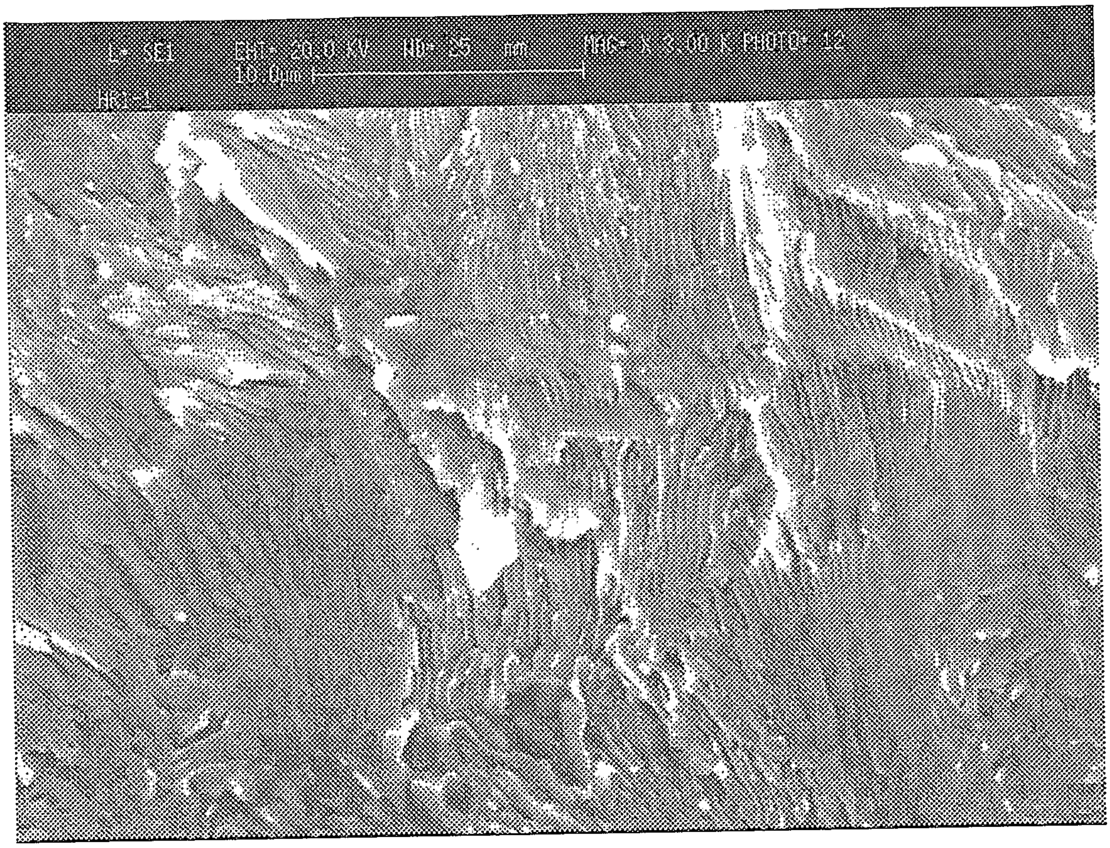

FIG. 4d Mag: X 4.1k

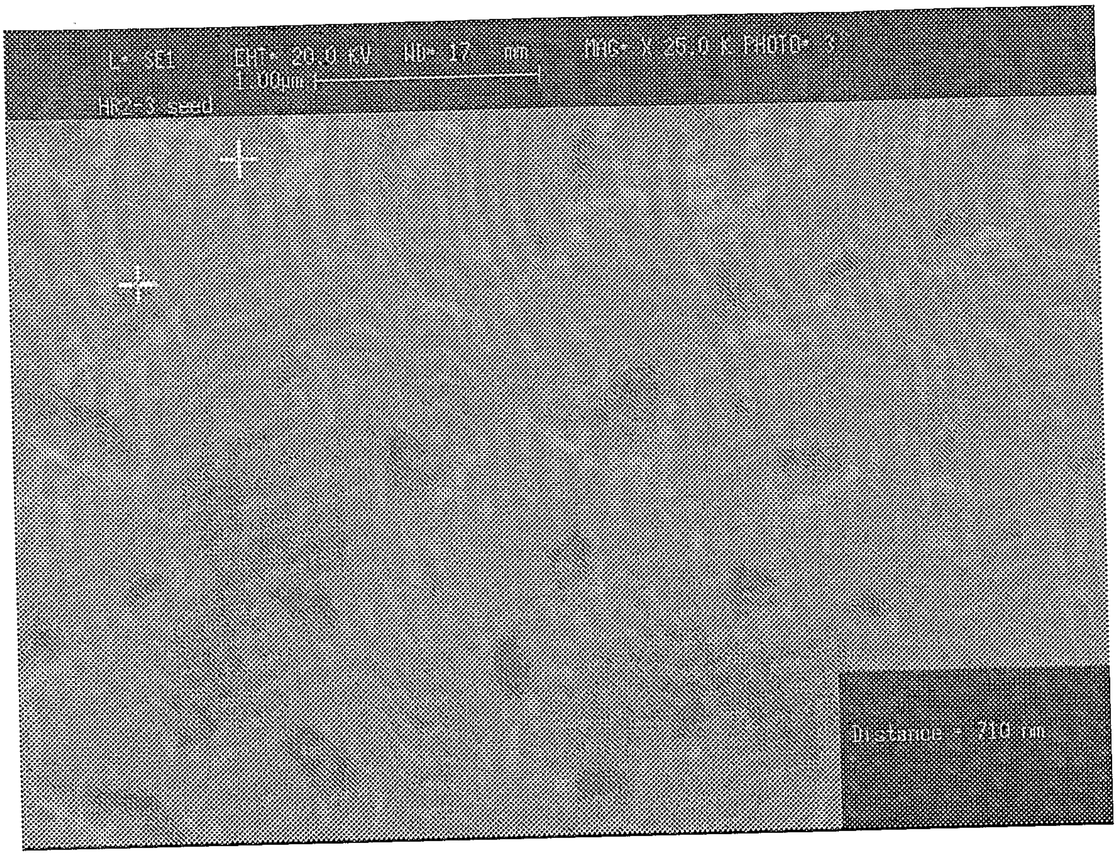

FIG. 5a Mag: X 34k

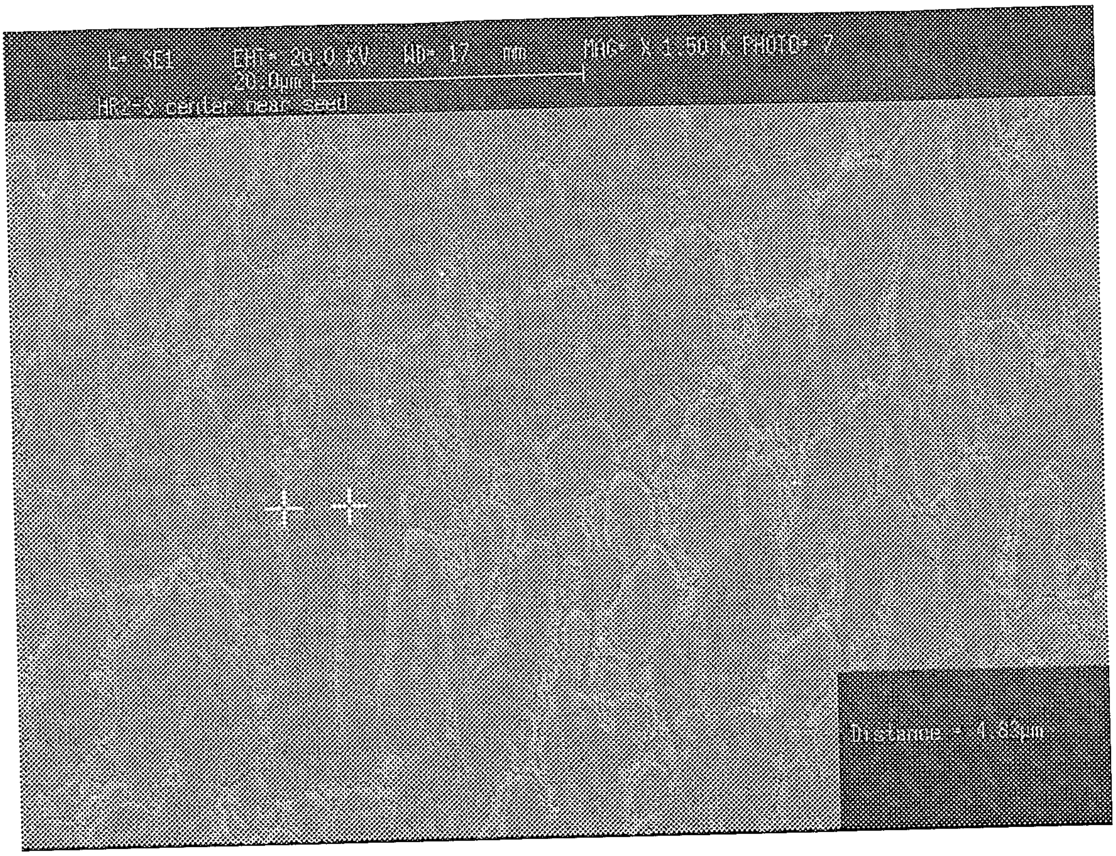

FIG. 5b Mag: X 2k

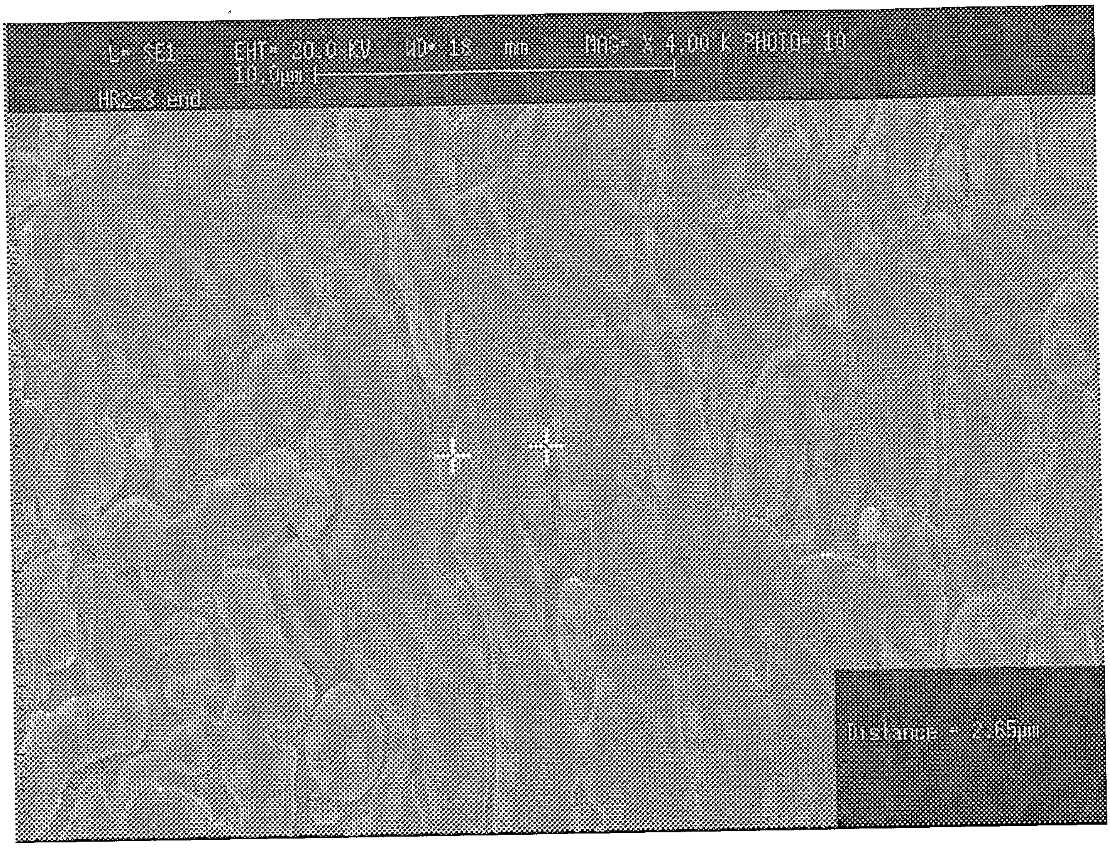

FIG. 5c Mag: X 5.4k

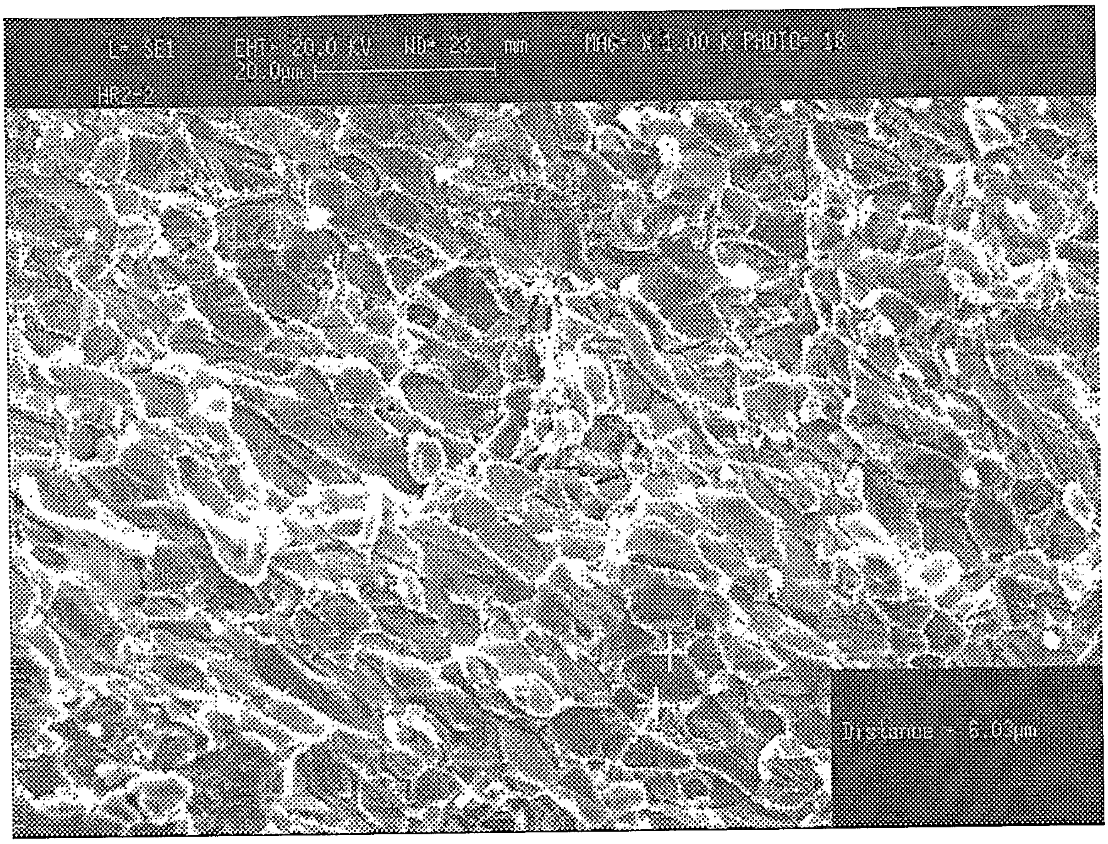

FIG. 5d Mag: X 1.4k

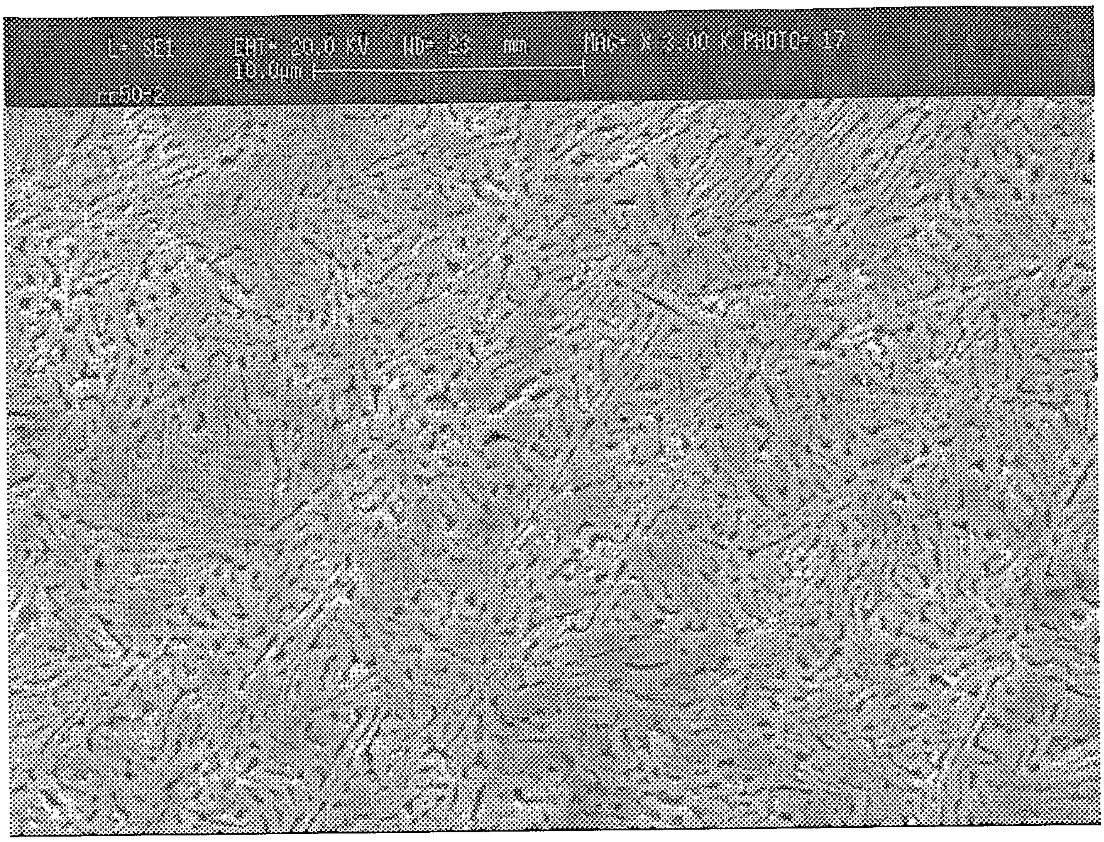

FIG. 6a Mag: X 4.1k

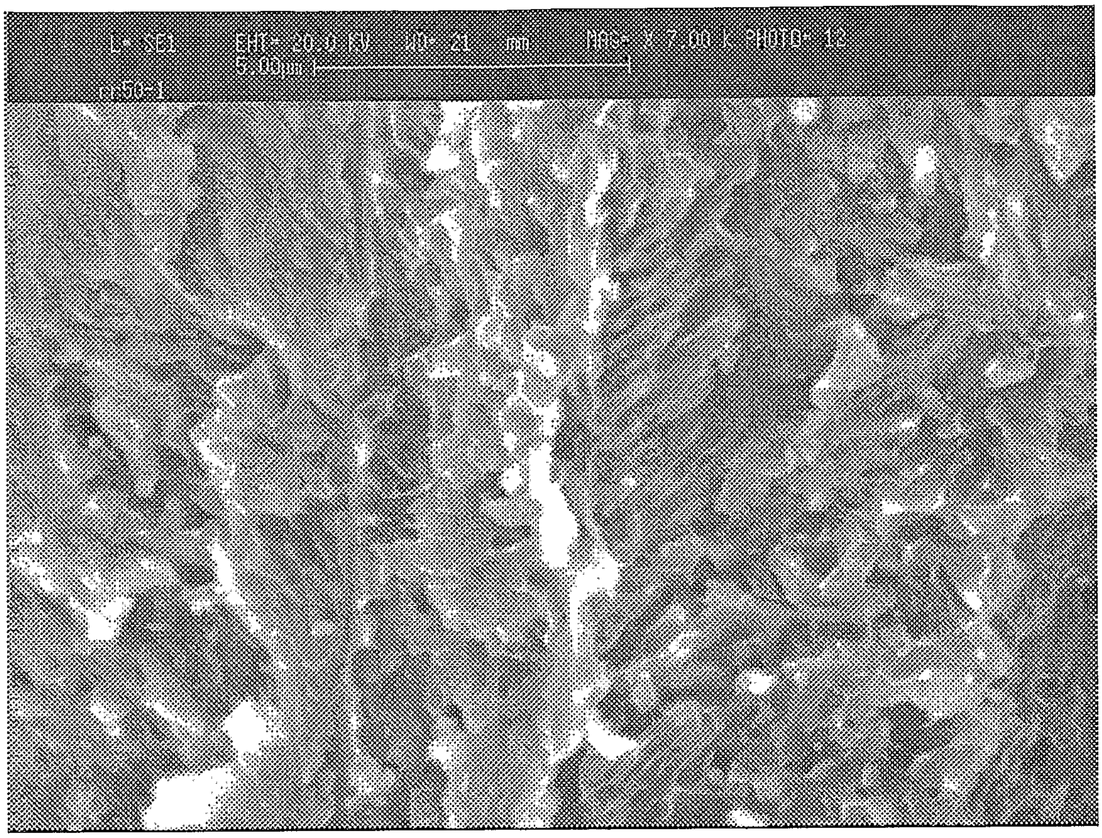

FIG. 6b Mag: X 9.5k

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2006/000483

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC 8 C22C C22F B01J

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)

CNPAT,WPI,EPODC,PAJ,CNKI
SUBNETWORK? SPINODAL? ALLOY?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US4406712 A (BELL TELEPHONE LABOR INC) 27 Sep. 1983(27.09.1983) Whole document	1-69
A	US6716292 B2 (CASTECH INC. Et al.) 06 Apr.2004(06.04. 2004) Whole document	1-69

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search
14 Jun.2006(14.06.2006)

Date of mailing of the international search report
13 · JUL 2006 (13·07·2006)

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Facsimile No. 86-10-62019451

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2006/000483

CLASSIFICATION OF SUBJECT MATTER

C22C1/04 (2006.01) i
C22C33/04 (2006.01) i
C22F1/00 (2006.01) i
B01J19/00 (2006.01) n

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2006/000483

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
US4406712 A	1983-09-27	NONE	
US6716292 B2	2004-04-06		
		WO9641033 A	1996-12-19
		CA2223839 C	1996-12-19
		AU5929196 A	1996-12-30
		EP0833954 A	1998-04-08
		ES2116250T T	1998-07-16
		DE833954T T	1998-10-22
		JP11506804T T	1999-06-15
		NZ309290 A	2000-02-28