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(54) Title: THERMO-MECHANICAL PROCESS TO ENHANCE THE QUALITY OF GRAIN BOUNDARY NETWORKS IN METAL ALLOYS

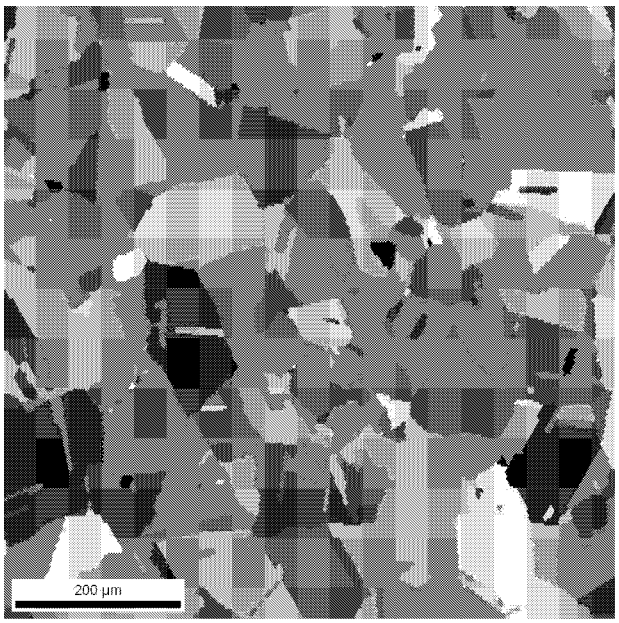


FIG. 1

(57) Abstract: Methods to enhance the quality of grain boundary networks are described. The process can result in the production of a metal including a relatively large fraction of special grain boundaries (e.g., a fraction of special grain boundaries of at least about 55%).

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THERMO-MECHANICAL PROCESS TO ENHANCE THE QUALITY OF GRAIN BOUNDARY NETWORKS IN METAL ALLOYS

RELATED APPLICATIONS

This application claims priority to U.S. Patent Application Serial No. 13/019,124, filed February 1, 2011, and entitled "Thermo-Mechanical Process to Enhance the Quality of Grain Boundary Networks in Metal Alloys," which is incorporated herein by reference in its entirety for all purposes.

NAMES OF PARTIES TO A JOINT RESEARCH AGREEMENT

This invention was made pursuant to a joint research agreement between Massachusetts Institute of Technology and Mitsubishi Materials Corporation.

FIELD OF INVENTION

The present invention relates generally to methods for processing metal alloys to enhance the quality of grain boundary networks.

BACKGROUND

Polycrystalline materials such as metal alloys include multiple crystalline grains, the perimeters of which are defined by discontinuities called grain boundaries. Grain boundaries are generally less energetically stable than the interior regions of crystal grains. The level of instability depends upon the crystallographic type of the grain boundary, of which many exist. Certain types of grain boundaries, referred to in the art as "special" grain boundaries, exhibit improved properties compared to "general" grain boundaries. Grain Boundary Engineering (GBE) refers to a family of techniques involving the processing, evaluation, and classification of grain boundaries within polycrystalline materials, which can be used to manipulate or optimize the morphology and network of grain boundaries to produce a larger fraction of special grain boundaries, and hence, desirable bulk properties.

SUMMARY OF INVENTION

Methods for processing metal alloys to enhance the quality of grain boundary networks are provided.

In one aspect, a method of processing a metal alloy is described. In one set of embodiments, the method comprises, while maintaining the metal alloy at a temperature expressed in Kelvins of at least about 0.95 times the solvus temperature of the metal alloy expressed in Kelvins: applying a force to strain the metal alloy over a first period of time; and reducing the applied force over a second period of time subsequent to the first period of time; wherein the metal alloy is processed to have a special grain boundary fraction of at least about 55%.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1 includes an exemplary image outlining grain boundaries in Sample 3 of Example 1; and

FIG. 2 is an exemplary image outlining grain boundaries in Sample 4 of Example 1.

DETAILED DESCRIPTION

Methods to enhance the quality of grain boundary networks of a metal alloy are described. The inventors have discovered, within the context of the invention, that the grain boundary network of a metal alloy can be improved by heating and/or maintaining the alloy to a temperature close to its solvus temperature, and straining the alloy at the elevated temperature by applying a force. After the force is applied, the force can be reduced (e.g., so that the alloy is no longer strained) and remain so over a second period of time while maintaining the metal alloy close to the solvus temperature. The force application and force reduction steps can be repeated for one or more cycles, in some

cases. This process can produce metal alloys including a relatively large fraction of special grain boundaries, which can improve one or more physical properties of the alloy.

The solvus temperature of a metal alloy with a fixed composition is known to those of ordinary skill in the art, and refers to the temperature at which a metal alloy transforms between a state in which two or more phases are present and a state in which a homogeneous solid solution is present. One of ordinary skill in the art would be capable of determining the solvus temperature of a metal alloy using a phase diagram, given the composition of the alloy.

Performing force application and force reduction steps at an elevated temperature can eliminate the need to substantially heat and cool the metal alloy between processing steps. This can result in significant energy and time savings, which can, in some embodiments, render the process industrially feasible.

Metal alloys with an increased fraction of special grain boundaries (and hence, a variety of desirable properties) can be produced using the methods described herein. For example, the methods can be used to produce metal alloys with high fractions of special grain boundaries, which may dissolve uniformly in solvents. Such metal alloys might find particular use as anode materials, for example, in electrodeposition systems. In addition, the metal alloys treated using the methods described herein can exhibit relatively high mechanical strength and/or weldability. The treated metal alloys may also exhibit high resistance to softening, hot cracking, stress-corrosion cracking, creep, electromigration, and/or corrosion.

In some embodiments, the treatment process can include the step of maintaining the metal alloy at a temperature above a selected value. For example, the metal alloy can be maintained, in some instances, at a temperature of at least about 0.9 times the solvus temperature of the metal alloy (wherein the temperature and the solvus temperature, T_S, are expressed in Kelvins). In some instances, $0.9T_S$ of a metal alloy (expressed in Kelvins) is above ambient temperature. In some instances, the metal alloy can be maintained at a temperature above about 750 °C (1023 K), above about 800 °C (1073 K), above about 850 °C (1123 K), above about 900 °C (1173 K), or above about 950 °C (1223 K). In some cases, the metal alloy may be maintained at a temperature of above about 0.9 T_S, above about 0.95 T_S, or above about 0.98 T_S (wherein the temperature and the solvus temperature, T_S, are expressed in Kelvins).

In some embodiments, maintaining a metal alloy at or above a given temperature may comprise applying energy (e.g., in the form of heat) to the metal alloy to ensure that it does not cool below the given temperature. In some instances, a substantially uniform temperature may be maintained throughout the bulk of the metal alloy. The temperature of a metal alloy described herein may be maintained, for example, using a furnace, via resistive heating, induction heating, gas burners or by any other suitable method known in the art.

The temperature of the metal may be maintained within a range, in some instances. The range may be absolute in some cases (e.g., between about 750 °C and about 1200 °C, or between about 800 °C and about 1000 °C). In some embodiments, the range may be measured as a fraction of the solvus temperature (e.g., between about between about 0.9 T_S and about 1.1 T_S, between about 0.95 T_S and about 1.05 T_S, or between about 0.98 T_S and about 1.02 T_S (wherein the temperature and the solvus temperature are expressed in Kelvins)).

The methods described herein can involve heating the metal alloy to a temperature above the selected value at which the metal is maintained (e.g., above the values noted above). The heating step can occur prior to the above-described step of maintaining the metal above the selected value. The metal may be heated, in some cases, above about 750 °C (1023 K), above about 800 °C (1073 K), above about 850 °C (1123 K), above about 900 °C (1173 K), or above about 950 °C (1223 K). In some cases, the metal may be heated above a temperature of about 0.9 T_S, about 0.95 T_S, or about 0.98 T_S (wherein the temperature and the solvus temperature, T_S, are expressed in Kelvins).

Heating the metal alloy can also comprise heating the metal alloy to a temperature within a range. The range can be absolute in some cases (e.g., between about 750 °C and about 1200 °C, or between about 800 °C and about 1000 °C). In some instances, the range may be measured as a fraction of the solvus temperature (e.g., between about between about 0.9 T_S and about 1.1 T_S, between about 0.95 T_S and about 1.05 T_S, or between about 0.98 T_S and about 1.02 T_S (wherein the temperature and the solvus temperature are expressed in Kelvins)).

In some preferred embodiments, the metal alloy is heated (and, in some cases, also maintained) above a temperature suitable to anneal the metal. Such temperatures may include those described above. Annealing generally involves heat treating a metal

to alter its microstructure, resulting, in some embodiments, in the recrystallization of at least a portion (or, in some cases, substantially all) of the annealed metal.

The metal alloy may be heated in any suitable atmosphere. For example, in some cases, the metal alloy can be exposed to ambient air (i.e., about 80% nitrogen and about 20% oxygen) while it is annealed. In some embodiments, the metal alloy can be exposed to an inert atmosphere while being annealed (e.g., helium, argon, nitrogen, etc.). In some embodiments a working gas environment or reducing atmosphere would be desirable. For example, in some embodiments, the atmosphere may consist of nitrogen with a small amount (e.g., up to about 3%) of hydrogen, which may react with any undesired oxygen in the atmosphere.

While maintaining the metal alloy at an elevated temperature (e.g., above a temperature or within a temperature range), a force may be applied to the metal alloy. The applied force may be applied to plastically strain the metal alloy, in some cases, over a period of time. Plastically straining a metal alloy can comprise any process which alters the shape of the metal alloy, i.e., plastically deforms the metal alloy. In some embodiments, straining may comprise compressing the metal alloy on one or more axes (e.g., forging the metal alloy), stretching the metal alloy, rolling the metal alloy, extruding the metal alloy, stamping the metal alloy, drawing, deep-drawing, or blanking the metal alloy, or any other method of deformation or shape forming known in the art.

When the applied force is along one axis, the extent of change in the dimension of the metal alloy (e.g., along the length of the metal alloy) along that axis, divided by the original dimension of the metal alloy along that axis, is referred to as the engineering strain. Engineering strain is expressed as a percentage of the change in dimension along that axis as compared to the original dimension along that axis. In some cases, the applied force produces an engineering strain of at least about 3%, at least about 5%, at least about 10%, at least about 25%, at least about 50%, at least about 80%, at least about 95%, at least about 99%, or at least about 99.8%. Applying a force to strain a metal alloy may also produce an engineering strain between about 3% and about 99.8%, or between about 50% and about 95%.

In some cases, the strain may be expressed as a true strain. True strain is also known to those of ordinary skill in the art of shape forming and deforming. When the force deforming a metal alloy is applied along one axis, the true strain refers to the extent of change in the dimension of the metal alloy, divided by the instantaneous dimension of

the metal alloy along that axis. True strain can also be expressed as a percentage change in dimension as compared with the instantaneous dimension along the axis. In some embodiments, the applied force may produce a true strain of at least about 3%, at least about 4.8%, at least about 9.5%, at least about 22.3%, at least about 40%, at least about 58%, or at least about 70%. Applying a force to strain a metal alloy may also produce a true strain between about 3% and about 70%, or between about 40% and about 58%.

In some cases, when the force applied is complex and/or multiaxial, the change in dimension along one axis may not completely describe the resulting strain. In these cases, the von Mises strain, which is known to those of ordinary skill in the art of shape forming and deforming, may be used to quantify the strain. In some embodiments, the applied force may produce a von Mises strain of at least about 3%, at least about 5%, at least about 10%, at least about 25%, at least about 50%, or at least about 80%. The applied force may produce a von Mises strain of between about 3% and between about 80%, or between about 50% and about 70%.

It should be understood that the strain values described above may relate to strains produced during the application of a force in a single cycle process, or the strain produced during each application of force during a multi-cycle process.

The force may be applied (e.g., to plastically strain a metal alloy) over any suitable period of time. In some instances, the force is applied within a range of time. For example, in some embodiments, the lower end of the range may be at least about 0.01 seconds, at least about 0.1 seconds, at least about 1 second, at least about 5 seconds, at least about 10 seconds, or at least about 1 minute while the upper end of the range may be about 10 seconds, about 1 minute, about 5 minutes, or about 10 minutes. It should be understood that the range may be bound by any suitable combination of the lower limits and upper limits described above.

The force may be applied to achieve any suitable rate of strain. For example, in some embodiments, the force may be applied to produce a rate of strain in the metal alloy of at least about 0.01% per second, at least about 0.1% per second, at least about 1% per second, at least about 10% per second, at least about 100% per second, at least about 1000% per second, at least about 10,000% per second, or higher. In some cases, the force may be applied to achieve a rate of strain in the metal alloy of between about 0.1% per second and about 10,000% per second, or between about 1% per second and about 1000% per second.

While maintaining the metal alloy at an elevated temperature (e.g., above a temperature or within a temperature range), the amount of force applied to the metal alloy may be reduced, in some embodiments. For example, the reduction in the amount of force applied may be such that the metal alloy is no longer strained. During the period of time over which the force applied to the metal alloy is reduced, the metal alloy may be annealed as described above. In some embodiments, the reduction step may comprise reducing the first force by at least about 50%, at least about 75%, at least about 85%, at least about 95%, or at least about 99%. In some embodiments, the reducing step may comprise reducing the applied force to zero. In other embodiments, the reducing step may comprise reducing the applied force to a non-zero value.

After reducing the force applied to the metal alloy, the amount of force may remain reduced over any suitable period of time. For example, in some embodiments, the amount of force applied to the metal alloy may remain reduced for at least about 5 seconds, at least about 30 seconds, at least about 60 seconds, at least about 120 seconds, at least about 300 seconds, or at least about 600 seconds. In some cases, the amount of force applied to the metal alloy may remain reduced for between about 5 and about 600 seconds or between about 10 and about 300 seconds.

In some embodiments, another force may be applied after the step of reducing the applied force. For example, while maintaining a metal alloy above a temperature, a second force (or third force, etc.) may be applied to strain the metal alloy over a period of time subsequent to the period of time over which the first force is applied and subsequently reduced. In some embodiments, the application of multiple forces to strain the metal alloy may result in a cumulative engineering strain (or a cumulative true strain, or a cumulative von Mises strain) of at least about 3%, at least about 5%, at least about 10%, at least about 25%, at least about 50%, at least about 80%, at least about 95%, at least about 99%, or at least about 99.8%. The application of multiple forces to strain the metal alloy may result in a cumulative engineering strain (or a cumulative true strain, or a cumulative von Mises strain) of between about 3% and about 99.8%, or between about 50% and about 95%.

In some embodiments, each step of applying a force may produce a substantially similar strain in the metal alloy. For example, in some embodiments, each period of time over which a force is continuously applied results in an engineering strain (or a true strain, or a von Mises strain) of about 3%, about 5%, about 10%, about 25%, about 50%,

about 80%, about 95%, about 99%, or about 99.8%. In other embodiments, the amount of strain produced by at least one force application step may be substantially different than the others. For example, the application of a first force may result in a first change in engineering strain, while the application of a second force may result in a substantially larger or substantially smaller engineering strain.

Each force application step in a multi-step process may also strain the metal alloy at a similar rate. Alternatively, in other embodiments, one or more force application steps occurs at a substantially higher or substantially lower rate of strain. In addition, in some instances, the amount of time over which the applied force remains reduced may be substantially similar between each force application step of a multi-cycle process. In other instances, the amount of time over which the applied force remains reduced may be substantially longer or substantially shorter between at least two force application steps. For example, in some embodiments, the amount of time over which the force remains reduced may be substantially longer between first and second force application steps than between second and third force application steps.

One or more force application steps in a multi-step process may occur at a substantially different temperature than one or more other force application steps in a multi-step process. For example, in some embodiments, the first force application step may occur at a substantially higher temperature than at least one subsequent force application step. As another example, the first force application step can occur at a substantially lower temperature than at least one subsequent force application step.

Grain boundaries (e.g., special grain boundaries, general grain boundaries) may be characterized using Coincidence Site Lattice (CSL) theory. CSL theory distinguishes special and general grain boundaries according to the crystallographic misorientation between the two neighboring grains. According to CSL theory, sigma represents the inverse of the number density of the coincident lattice points between two misoriented crystals such as those that meet at a grain boundary. For example, a sigma value of 3 means that 1/3 of the lattice points of the two crystal grains meeting at a grain boundary coincide. As used herein, special boundaries are defined under CSL theory as those with sigma values from 1 up to and including 29, while general grain boundaries are defined as those with sigma values greater than 29. Grain boundary analysis is customarily performed by measuring the lengths of grain boundaries within a cross-section of the metal alloy. The fraction of special grain boundaries is calculated by dividing the sum of

the lengths of the special grain boundaries by the sum of the lengths of all the grain boundaries in the cross-section. This analysis may be achieved by using, for example, electron backscatter diffraction (EBSD).

EBSD analysis methods are known to those of ordinary skill in the art, and may be used to examine the crystallographic orientation of crystals in a material, which can be used to determine texture and/or orientation of crystalline or polycrystalline materials. EBSD can be conducted using a Scanning Electron Microscope (SEM) equipped with a backscatter diffraction camera. The diffraction camera can include a phosphor screen and a camera to register the image on the phosphor screen. Alternatively, a CCD detector may be used to register the image. A flat, polished crystalline specimen may be placed into position in the specimen chamber, highly tilted (e.g., about 70° from horizontal) towards the diffraction camera. When electrons impinge on the specimen, they can interact with the atomic lattice planes of the crystalline structures. Many of these interactions satisfy Bragg conditions and undergo backscatter diffraction. The angle of the specimen allows the diffracted electrons to escape the material and be detected either at the phosphor screen or on a CCD detector as a diffraction pattern. Once the diffraction pattern is acquired in this manner, it may be analyzed using methods known to those of ordinary skill in the art, to discern the orientation of the crystal from which the pattern was formed. Grain boundary characteristics, including the sigma number, may also be discerned from EBSD data, by comparing the orientations of two crystal grains that meet at a grain boundary. The methods for calculating the sigma numbers of grain boundaries from such orientation information are also known to those of ordinary skill in the art.

In some embodiments, methods may be used to produce metal alloy articles with a relatively high fraction of special grain boundaries. For example, in some embodiments, metal alloys and articles described herein may have special grain boundary fractions of at least about 55%, at least about 60%, at least about 65%, at least about 70%, or at least about 75%. In some embodiments, metal alloys and articles described herein may have special grain boundary fractions of between about 55% and about 75%, or between about 65% and about 75%.

The methods described herein may be used with a wide variety of metal alloys. The metal alloy can contain, in some cases, at least 3, at least 4, at least 5, or any other number of metal components. In some cases, the largest component of the metal alloy,

by mass, is copper. In some embodiments, the metal alloy can contain at least about 75 wt%, at least about 90 wt%, at least about 95 wt%, at least about 99 wt%, between about 75 wt% and about 99.99 wt%, between about 90 wt% and about 99.99 wt%, between about 95 wt% and about 99.99 wt%, or between 99 wt% and about 99.99 wt% copper. The metal alloy can include a variety of minority components (i.e., components other than the most abundant component, by mass, within the metal alloy). For example, the metal alloy can comprise chromium and/or zirconium as a minority component.

U.S. Patent Application Serial No. 13/019,124, filed February 1, 2011, and entitled "Thermo-Mechanical Process to Enhance the Quality of Grain Boundary Networks in Metal Alloys," is incorporated herein by reference in its entirety for all purposes.

The following example is intended to illustrate certain embodiments of the present invention, but is not to be construed as limiting and does not exemplify the full scope of the invention.

EXAMPLE 1

This example describes a set of experiments in which metal alloys were subject to a thermo-mechanical process to enhance the amount of special grain boundaries. The processing included subjecting the samples to one or more cycles of applied force(s) to strain the samples.

Three types of copper-based alloys were tested. Two copper-chromium (Cu-Cr) alloys were tested. The first Cu-Cr alloy included 0.30 wt% Cr, about 99.7 wt% copper, and small amounts of impurities (Cu-0.30 wt% Cr alloy). The solvus temperature of the Cu-0.30 wt% Cr alloy was 935 °C (1208 K). The second Cu-Cr alloy included 0.13 wt% Cr, about 99.87 wt% copper, and small amounts of impurities (Cu-0.13 wt% Cr alloy). The solvus temperature of the Cu-0.13 wt% Cr alloy was 845 °C (1118 K). A copper-zirconium alloy including 0.06 wt% zirconium, 99.94 wt% copper, and small amounts of impurities (Cu-0.06 wt% Zr alloy) was also tested. The solvus temperature of the Cu-0.06 wt% Zr alloy was 860 °C (1133 K).

To begin, 13 metal alloy samples were cut to form rectangular pieces measuring approximately 9 mm x 9 mm x 10 mm. The types of materials and process parameters for each of the 13 samples are outlined in Tables 1, 2 and 3. The cut samples were preheated in air at their processing temperatures (outlined in Tables 1, 2, and 3) for 30 minutes.

After preheating, one or more cycles of force were applied to deform the samples at their processing temperatures. In this example the deformation was compressive, and the applied force was a uniaxial compression. Tables 1, 2, and 3 include the amounts of engineering strain produced per cycle as a measure of the deformation. In addition, Tables 1, 2, and 3 include the rates of strain for each of the tested samples. For example, Sample 1 (see Table 1) was strained at a rate of 0.017 s^{-1} (i.e., the sample was reduced in height by 1.7%, relative to its height at the start of the cycle, each second) until the engineering strain reached 17% (about 10 s) for the cycle.

After the prescribed time elapsed for applying the force, the force on the material was reduced to zero and the samples were maintained at the processing temperature for an "intermediate time," as indicated in Tables 1, 2, and 3. During the intermediate time, the samples were annealed. In some cases, subsequent cycles of applying and reducing force were used. Tables 1, 2, and 3 include lists of the number of cycles for each of the materials. For each sample tested, the sample was quenched in water after the final cycle.

Each strained sample was cut through its middle. The cut samples were mechanically polished using emery paper. Samples were subsequently polished using a diamond suspension, followed by a colloidal silica suspension polish for at least 30 minutes. Finally, the samples were electropolished to remove surface deformation regions.

Grain orientation data was acquired using electron backscatter diffraction (EBSD, TSL/EDAX Digiview) attached to a Field Emission Scanning Electron Microscope (FE-SEM) (Zeiss Supra55) using OIM™ Data Collection Version 5 (TSL/EDAX) software. The scan conditions were as follows: total scan area of 750 x 750 microns, magnification of x300, and a scan step of 3 microns. The edge regions of the 750 x 750 micron scans were trimmed to 740 x 740 microns by eliminating all data within 5 microns of the scan edge, as these regions frequently contained inaccurate data due to beam control issues during data acquisition.

The data was appropriately cleaned up using the software to eliminate inaccurate data points during data acquisition process (e.g. corresponding to a partially rough surface or contamination particles on the surface).

The cleaned orientation data was analyzed to determine the percentage of special grain boundaries in each sample using OIM™ Data Analysis Version 5 software. Grain

boundaries were defined as boundaries whose misorientation between 2 neighboring points was more than 15 degrees. Each grain boundary was classified as either "special" (sigma between 1 and 29) or "general" (sigma greater than 29). The percentages of "special" grain boundaries were calculated by dividing the total length of the special grain boundaries by the total length of all of the grain boundaries (both special and general), and multiplying by 100%. FIG. 1 includes an image of Sample 3 (see Table 1) of this example, which included 71% special grain boundaries. FIG. 2 includes an image of Sample 4 (see Table 1) of this example, which included 12% special grain boundaries.

Table 1. Experimental results for Cu-0.3 wt% Cr samples tested in Example 1

Sample	Process Temp, T_P (K).	T_P/T_S	Eng. Strain per cycle	Rate of Strain (s^{-1})	Inter-mediate Time (s)	# of Strain Cycles	% of Special Grain Boundaries	Grain Size (μm)
1	1153	0.954	17%	0.017	20	5	55%	32
2	1173	0.971	17%	0.017	20	5	67%	42
3	1193	0.988	17%	0.017	20	5	71%	50
4	1073	0.888	17%	0.017	20	5	12%	50

Table 2. Experimental results for Cu-0.13 wt% Cr samples tested in Example 1

Sample	Process Temp, T_P (K).	T_P/T_S	Eng. Strain per cycle	Rate of Strain (s^{-1})	Inter-mediate Time (s)	# of Strain Cycles	% of Special Grain Boundaries	Grain Size (μm)
5	1023	0.915	17%	0.017	20	5	32%	12
6	1098	0.982	17%	0.017	20	5	67%	26
7	1123	1.004	17%	0.017	20	5	66%	37
8	1148	1.027	17%	0.017	20	5	73%	60
9	1173	1.049	17%	0.017	20	5	63%	58

Table 3. Experimental results for Cu-0.06 wt% Zr samples tested in Example 1

Sample	Process Temp, T_P (K).	T_P/T_S	Eng. Strain per cycle	Rate of Strain (s^{-1})	Inter-mediate Time (s)	# of Strain Cycles	% of Special Grain Boundaries	Grain Size (μm)
10	1123	0.991	17%	0.017	20	5	62%	38
11	1148	1.013	17%	0.017	20	5	61%	22
12	1173	1.035	17%	0.017	20	5	61%	30
13	1123	0.991	17%	0.017	60	5	67%	37

What is claimed is:

CLAIMS

1. A method of processing a metal alloy, comprising:

while maintaining the metal alloy at a temperature expressed in Kelvins of at least about 0.95 times the solvus temperature of the metal alloy expressed in Kelvins:

applying a force to strain the metal alloy over a first period of time; and

reducing the applied force over a second period of time subsequent to the first period of time;

wherein the metal alloy is processed to have a special grain boundary fraction of at least about 55%.

2. A method as in claim 1, wherein the metal is processed to have a special grain boundary fraction of at least about 60%.

3. A method as in claim 1, wherein the temperature expressed in Kelvins is between about 0.95 times and about 1.05 times the solvus temperature of the metal alloy expressed in Kelvins.

4. A method as in claim 1, wherein the metal alloy comprises a face-centered cubic metal with a stacking fault energy of less than about 100 mJ/m^2.

5. A method as in claim 1, wherein the largest component of the metal alloy, by mass, is copper.

6. A method as in claim 1, wherein the metal alloy comprises at least about 75 wt% copper.

7. A method as in claim 1, wherein the metal alloy comprises chromium or zirconium as a minority component.

8. A method as in claim 1, wherein the reducing step comprises reducing the applied force to zero.

9. A method as in claim 1, wherein the reducing step comprises reducing the applied force to a non-zero value.

10. A method as in claim 1, further comprising heating the metal alloy above the temperature prior to maintaining the metal alloy above the temperature.

11. A method as in claim 1, further comprising, while maintaining the metal alloy at a temperature expressed in Kelvins of at least about 0.95 times the solvus temperature of the metal alloy expressed in Kelvins, applying a second force to strain the metal alloy over a third period of time subsequent to the first and second periods of time, and reducing the applied second force over a fourth period of time subsequent to the third period of time.

12. A method as in claim 11, wherein the first force is applied at a first temperature and the second force is applied at a second temperature, and the first and second temperatures are substantially different.

13. A method as in claim 12, wherein the first temperature is higher than the second temperature.

14. A method as in claim 1, wherein the first period of time is at least about 0.01 seconds.

15. A method as in claim 1, wherein the second period of time is at least about 0.01 seconds.

16. A method as in claim 1, wherein the applied force produces an engineering strain of at least about 3%.

17. A method as in claim 1, wherein the applied force produces a von Mises strain of at least about 3%.

18. A method as in claim 1, wherein the applied force produces a cumulative engineering strain of at least about 10%.

19. A method as in claim 1, wherein the applied force produces a rate of strain of at least about 0.01% per second.

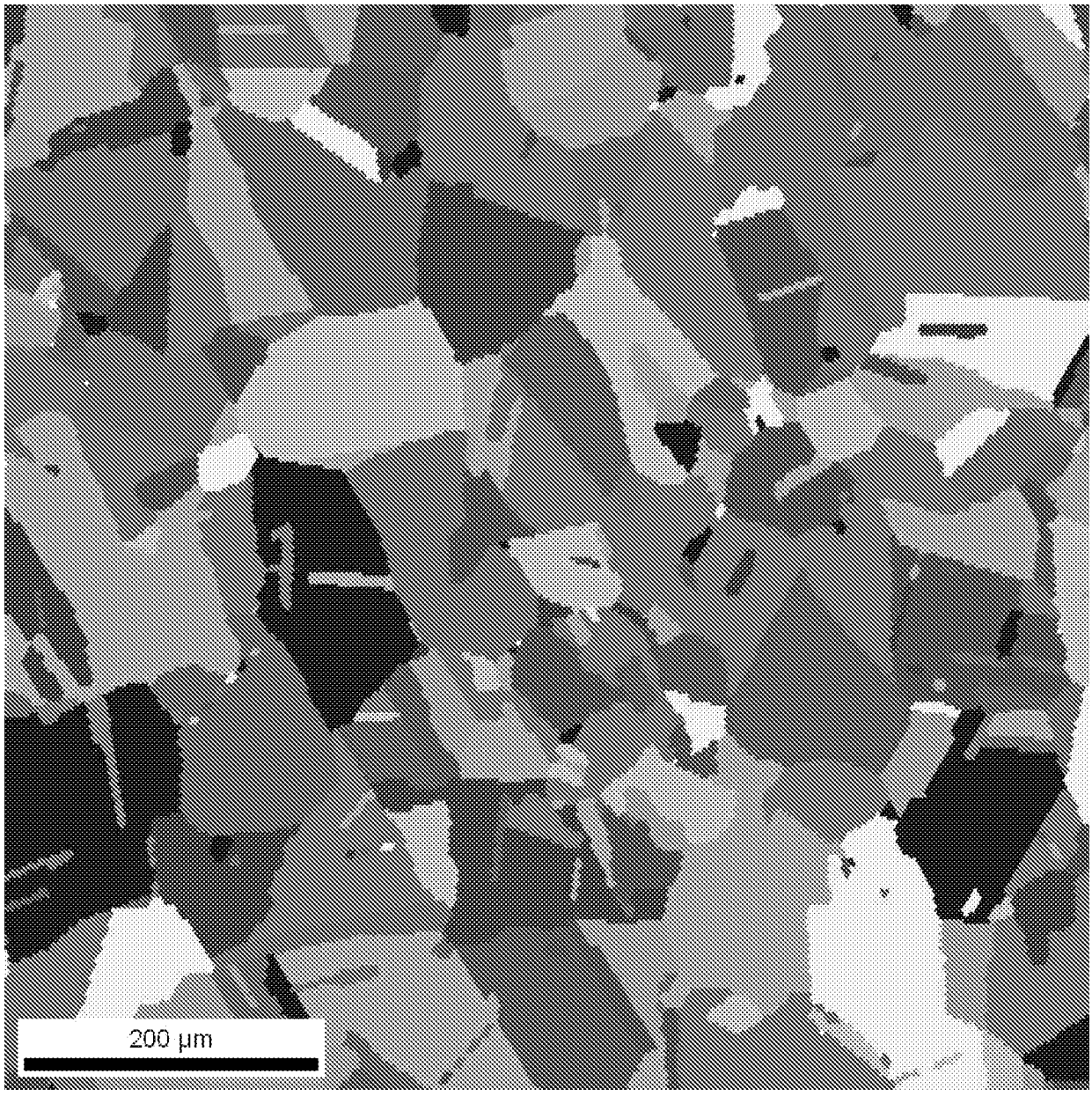


FIG. 1

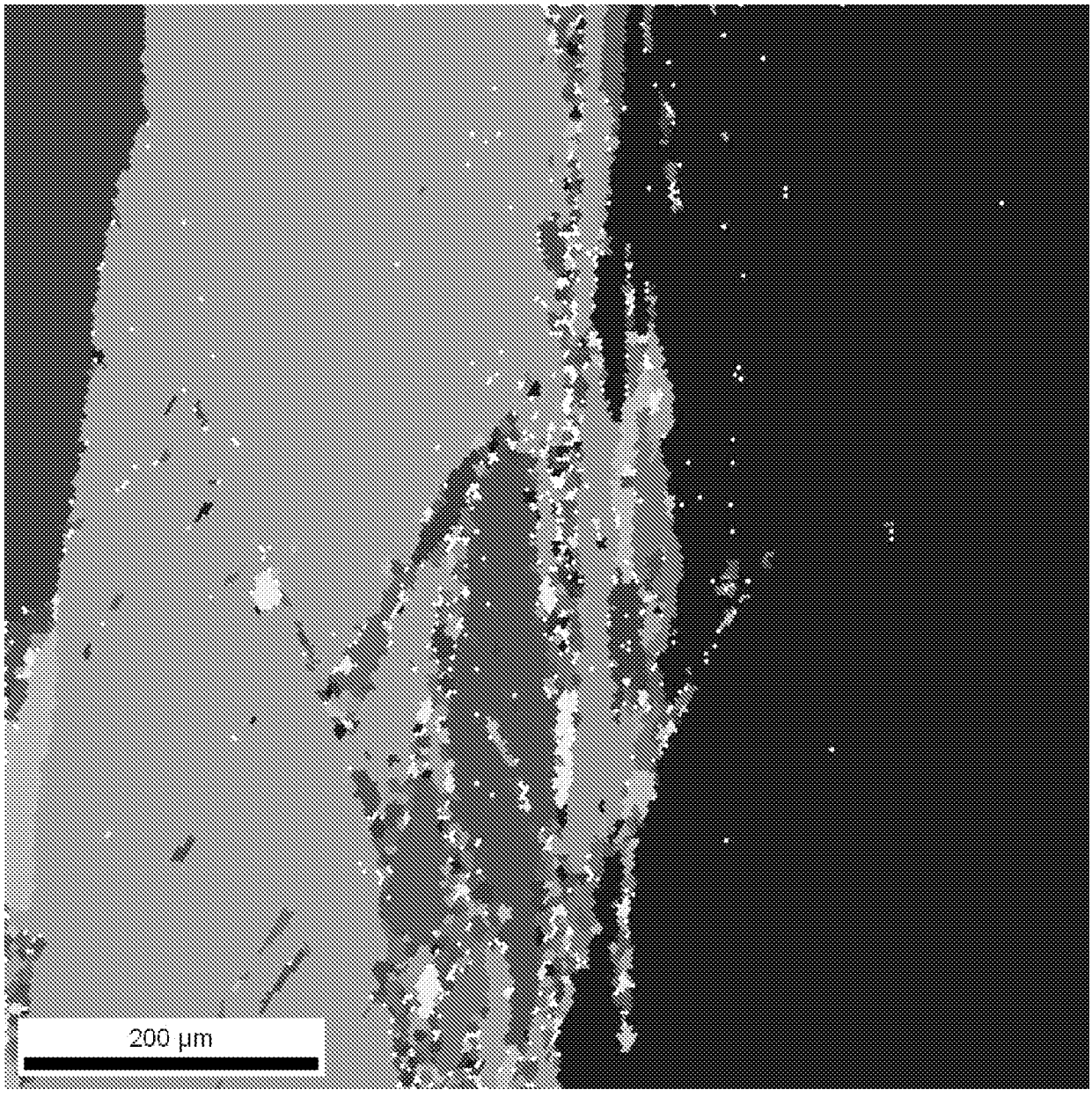


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/023458

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C9/00 C22F1/08
ADD.

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)
C22C C22F

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2012/004868 A1 (MITSUBISHI SHINDO KK [JP]; SAKURAI TAKESHI [JP]; ABE YOSHIO [JP]; SAIT) 12 January 2012 (2012-01-12) abstract Examples; paragraphs [0043] - [0054]	1-19
X,P	EP 2 377 959 A1 (DOWA METALTECH CO LTD [JP]) 19 October 2011 (2011-10-19) paragraph [0035] paragraph [0046] paragraph [0060] paragraph [0065] claim 5 tables 1,3	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
23 April 2012	04/05/2012

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1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/023458

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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