METHOD OF MAKING LARGE GRAIN-SIZED SUPERALLOYS

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References Cited

UNITED STATES PATENTS
3,524,744 8/1970 Parikh ................................................................ 75/171

ABSTRACT

A process for making nickel-base superalloys possessing superior high-temperature properties which employs powder metallurgical techniques and includes the steps of densifying the powdered alloy into a blank approaching 100 percent theoretical density, cold working the blank at a controlled temperature, recrystallizing the cold-worked blank for a period of time sufficient to nucleate new grains and thereafter heat treating the recrystallized blank at a controlled temperature for a period of time sufficient to attain the desired magnitude of grain growth.

7 Claims, 4 Drawing Figures

Diagram:

1. Microcast
2. Confining and Density
3. Cold Work
4. Recrystallize
5. Heat Treat
FIG. 2.

FIG. 3.

FIG. 1.

FIG. 4.

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BACKGROUND OF THE INVENTION

Modern superalloys of the general types to which the present invention is applicable contain large amounts of second-phase gamma-prime and complex carbides in a gamma matrix which contribute significantly to their high-temperature properties. The presence of these constituents, however, has made such alloys exceedingly difficult to form subsequent to casting. Additional problems are further introduced as a result of the tendency of such alloys to undergo segregation, which significantly detracts from their high-temperature strength characteristics. The elimination of such segregation is virtually impossible due to the extent of it.

The foregoing problems have been overcome by employing powder metallurgical techniques for making bodies of such superalloys. In accordance with this technique, the superalloy is microcast or atomized to a powder state and then consolidated in a substantially oxygen-free environment to a blank of the desired size and configuration, which is substantially free from segregation. A continuing problem experienced in superalloy components made by such powder metallurgical techniques has been the severe limitation in effecting any appreciable grain growth in the resultant densified component. It is believed that such grain growth restriction is in part attributable to oxides and other relatively insoluble impurities which are present on the surfaces of the powder particles. Various precautions taken to reduce the presence of such insoluble impurities have not been successful since the problem in achieving such grain growth has been encountered even with powderd alloys containing as little as 30 parts per million (p.p.m.) oxygen.

In accordance with the process comprising the present invention, the problem of effecting grain growth in densified powder components has now been overcome providing for a metallurgical structure which is of superior homogeneity and of superior physical properties at elevated temperatures than cast and wrought forms of the same superalloy compositions.

SUMMARY OF THE INVENTION

The benefits of the present invention are achieved by an improved process for making large grain-sized nickel-base superalloys in which the alloy is initially microcast or otherwise subdivided into a powder form of controlled size and is thereafter confined and densified into a body or blank approaching substantially 100 percent theoretical density. The densified body is subjected to cold working at a temperature below the recrystallization temperature of the alloy and thereafter is recrystallized at a temperature between the recrystallization temperature and the solvus of the gamma-prime phase for a period of time sufficient to nucleate new grains. The recrystallized body is thereafter heat treated at a temperature above the solvus of the gamma-prime phase and below the incipient melting temperature of the alloy for a period of time sufficient to effect grain growth and the attainment of the desired ultimate grain size.

The nickel-based superalloys made in accordance with the process comprising the present invention are characterized as being of exceptionally large grain size and possessing superior tensile strength and stress rupture life at elevated temperatures, that is, temperatures in excess of about 1,400°F. In comparison to similar-type alloys heretofore known.

Further advantages and benefits of the present invention will become apparent upon a reading of the description of the preferred embodiments taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow sheet illustrating the sequence of steps in accordance with the preferred practice of the process comprising the present invention;

FIG. 2 is a photomicrograph of a Kalling's etched sample taken at a magnification of 500 times of the grain structure of a superalloy after densification from loose powder to a density corresponding substantially to 100 percent theoretical density;

FIG. 3 is a photomicrograph of the same alloy shown in FIG. 2 at the same magnification after being cold worked and subjected to recrystallization; and

FIG. 4 is a photomicrograph of the grain structure of a Kalling's etched tensile specimen taken at a magnification of 10 times prepared from the alloy shown in FIGS. 2 and 3 after heat treatment to effect grain growth.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now in detail to the drawing, and as diagrammatically shown in FIG. 1, the process comprising the present invention consists of five basic steps which are performed in the same sequence as illustrated in the flow sheet. As shown, a nickel-based superalloy of the desired composition is initially microcast or microcast so as to form a powder of the desired configuration and particle size. The microcast or microfluid solidified and densified, forming a body or blank having a density approaching a 100 percent theoretical density. The resultant blank is thereafter cold worked, that is, subjected to deformation at a temperature below the recrystallization temperature of the alloy, followed by a recrystallization step in which nucleation of new grain occurs. Thereafter, the recrystallized blank is subjected to a heat treatment at a controlled temperature, during which a growth in the grain size is effected and by proper control, can be increased up to almost a single crystal structure.

The provision of the nickel-based alloy in the form of a metallic powder in which each of the powder particles is of substantially the same nominal composition can be achieved by a variety of techniques, of which microcasting, such as achieved by atomization of a melt of the alloy, constitutes the most convenient and preferred technique. The microcasting of the molten alloy can be achieved, for example, by an atomization process employing an atomization nozzle and technique as described in U.S. Pat. No. 3,253,783, which is assigned to the same assignee as the present invention and is incorporated herein by reference.

Due to the deleterious effects of oxygen and oxides of the metals comprising the alloy, the atomization of the superalloy and the collection of the powder particles is achieved under conditions whereby oxygen and oxygen-containing substances, including water, are not permitted to contact the powder particles for any appreciable time to minimize oxidation and/or the alloy equipment. The degree of precaution required to prevent oxidation of the superalloy during the atomization process is dependent to a large extent on the specific alloying constituents present in the alloy. For example, the presence of aluminum and titanium require particular precautions due to their susceptibility to oxidation attack at the high temperatures encountered in conventional microcasting techniques. Under such conditions, it is conventional to effect microcasting in the presence of inert atmospheres such argon or helium, which are substantially moisture free. Commercially available argon containing minimal amounts of conventional impurities has been found particularly satisfactory for providing a nonoxidizing, substantially dry inert atmosphere for microcasting such superalloys. In accordance with conventional practice, the interior of the equipment to be employed is initially evacuated and thereafter back-filled with the substantially dry, nonoxidizing atmosphere prior to initiation of the atomization of the melt. Regardless of the specific technique employed for forming the powder, the oxygen content of the powder as finally densified is preferably controlled to a level of less than about 100 p.p.m.

In accordance with conventional atomization or microcasting procedures, the superalloy is transformed into a metallic powder in which the particles preferably are of a generally
spherical configuration and wherein each powder particle is of substantially the same or similar alloy chemistry. The metallic powder is thereafter recovered and is subjected to a screening operation so as to segregate the powder particles which are suitable for forming the densified body or billet of superalloy. Conventionally, particles of a size less than about 60 mesh United States Standard Sieve Size (250 microns) can be satisfactorily employed down to a particle size as small as about 1 micron. Particularly satisfactory results are obtained when the powder particles range from about 100 mesh (150 microns) to about 10 microns, and wherein the particles are further randomly distributed over the aforementioned range. This provides for optimum packing density of the free-flowing powder, facilitating subsequent densification thereof.

The resultant superalloy powder, having the desired composition and particle size, is thereafter confined and densified at elevated temperatures so as to form a body or billet approaching 100 percent theoretical density. The densification of the metallic powder can be achieved by any one of the variety of techniques well known in the art, including extrusion, hot upsetting, vacuum die pressing, hot isostatic compaction, explosive compaction, etc. The densification process is preferably done at an elevated temperature to facilitate a bond of the powder particles and to facilitate compaction and deformation thereof into a billet approaching substantially 100 percent theoretical density. For most nickel-base superalloys, preheat temperatures ranging from 1,900°F. up to about 2,500°F. can be satisfactorily employed. The specific temperature used within the aforementioned range is dictated by that temperature approaching the solubus or just below the incipient melting point of the powder particles. The aforementioned explosive compaction technique in which the powder is subjected to violent densification is usually done without any appreciable preheat. In the extrusion and hot upsetting compaction techniques, it is conventional to confine the powder within a suitable container which is evacuated and subsequently sealed. Optimum packing of the interior of such containers with the loose powder can be achieved by subjecting the containers to sonic or supersonic frequencies wherein packing densities ranging from about 60 percent to about 70 percent of a theoretical 100 percent density can be attained. It is also contemplated that the loose powder particles can be confined in the cavity of a die, subjected to vacuum and compacted so as to make a preform approaching 85–90 percent theoretical density. Such a preform can also be attained by compacting the powder in vacuum and sintering it at an elevated temperature, forming a self-sustaining body or billet which subsequently can be subjected to further compaction to attain substantially 100 percent density.

Of the foregoing compaction techniques, hot extrusion of the powder while contained within an elongated deformable container has been found convenient and satisfactory for producing the improved superalloy in elongated rod form. Such containers may comprise any metal having sufficient ductility to enable their deformation by extrusion at elevated temperatures without rupture of the sidewalls, thereby maintaining the sealed integrity of the powder particles therein. Typical of such ductile metals which are compatible with the superalloy powder and which can be satisfactorily employed for the practice of the present invention are various of the so-called conventional stainless steels such as AISI-type 304 or an AISI 1010 mild steel.

At the completion of the compaction or densification operation, the resultant densified billet is allowed to cool and is thereafter cold worked by subjecting it to a mechanical deformation, such as by passing it between a pair of rolls or by subjecting it to a further extrusion operation. The cold working of the densified billet can be achieved in one or more successive passes to impart the desired degree of cold work to the billet, which is dictated by that amount necessary to provide for a substantially complete recrystallization of the alloy at the specific temperature used during the following recrystallization step. For most nickel-base superalloys, it has been found that the magnitude of cold working expressed in terms of percentage reduction of the cross-sectional area of the densified body or billet during such cold working can range from only several percent up to about 50 percent or more. The maximum degree of cold working imparted to the densified billet is dictated by practical considerations, including equipment limitations and time. Usually, 50 percent reductions in cross-sectional area in one pass have been found satisfactory and cross-sectional area reductions or the equivalent cold working in a range of about 30 percent to about 50 percent at moderate temperatures ranging from about 1,000°F. to about 1,700°F. constitutes a preferred practice.

During the cold-working step, the densified blank or billet is preferably heated to facilitate deformation thereof and as previously indicated, can be heated to moderate temperatures which approach but are below the recrystallization temperature of the specific alloy. For most nickel-based superalloys of the type to which the process comprising the present invention is applicable, the recrystallization temperature generally is in the range of from about 1,700°F. to about 2,100°F. In view of this, it is preferred to heat the densified billet to a temperature of from about 1,000°F. to about 1,700°F. during such cold reduction.

For the purpose of the present invention, the terminology "recrystallization temperature," as employed in the specification and subjoined claims, is defined as that temperature above which a nucleation and growth of new strain-free grains occurs accompanied by consumption of the cold-worked matrix as a result of the growth of such grains.

The resultant densified and cold-worked billet is thereafter subjected to recrystallization at a temperature above the minimum recrystallization temperature but below the gamma-prime solvus temperature. The gamma-prime solvus temperature. The gamma-prime solvus temperature, as herein used, is defined as the temperature at or above which the gamma-prime phase dissolves in the gamma phase matrix. The gamma-prime phase in turn is defined as a variety of intermetallic compounds which are generally expressed by the formula Nib(X,Y, Z), in which X, Y and Z represent, for example, aluminum, titanium, cobalt, etc., and wherein "a" and "b" are integers. These intermetallic compounds at temperatures below the gamma-prime solvus temperature are dispersed throughout the gamma matrix and act as a strengthening agent.

In accordance with the preceding definitions, recrystallization of the cold-worked and densified billet is achieved at a temperature generally ranging from about 1,700°F. up to about 2,100°F. for a period of time sufficient to effect a nucleation of new strain-free grains in the cold-worked billet. Recrystallization is continued for a period of time sufficient to effect substantially full recrystallization of the billet, which, for most nickel-based superalloys which are cold worked in an amount ranging from about 10 percent to about 50 percent in terms of reduction of cross-sectional area or the equivalent thereof at recrystallization temperatures of from 1,700°F. up to about 2,100°F., requires about 2 to about 12 hours. It will be noted that the recrystallization of a cold-worked billet can be performed at any time after the cold working and similarly, the heat-treating step can be performed at any time after the recrystallization step. The absence of any criticality in time with respect to the performance of the several process steps provides further advantages in connection with the versatility and processing flexibility afforded.

At the completion of the recrystallization step, the densified, cold-worked and recrystallized billet is subjected to a heat treatment in which grain growth occurs. The heat-treating operation is carried out by heating the recrystallized billet to a temperature above the gamma-prime solution or solvus temperature and below the incipient melting point of the gamma matrix. The incipient melting point of the gamma matrix for nickel-based superalloys of the general type to which the process is applicable conventionally ranges from about 2,200°F. up to about 2,500°F. The duration of heat treatment can be varied so as to provide the desired degree of
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grain growth. Normally, heat-treating periods of from about 30 to about 60 hours at heat-treatment temperatures ranging from about 2,100°F to about 2,400°F for nickel-based superalloys of the general type evaluated have been found satisfactory to produce a resultant microstructure in which the grain size is approximately one-eighth inch in diameter. It is feasible, by continuing the heat treatment of the billet over prolonged periods of time, to effect further increases in grain size until ultimately a billet of a single grain crystal is attained.

It will be apparent from the foregoing that it is now feasible, employing powder metallurgical practices, to form billets and components composed of nickel-based superalloys which are of a relatively large grain structure and possess superior high-temperature physical properties in comparison to the same or similar superalloys in a cast and/or wrought form. The benefits of the process comprising the present invention are achieved with any one of a variety of well-known superalloys which are nickel based, that is, in which the major alloying constituent is nickel. Typical of the various nickel-based alloys which are presently known and which can be processed in accordance with the present invention are the compositions as set forth in Table 1. It will be understood that the enumerated superalloy compositions are provided for illustrative purposes and are not intended as being restrictive of other suitable nickel-based alloy compositions that can be satisfactorily processed to achieve the benefits of the present invention.

Following the recrystallization step, the billet was subjected to heat treatment at a temperature of 2,150°F for a period of about 72 hours. The heat treatment temperature employed is above the gamma-prime solvus temperature but below the incipient melting temperature of this alloy. The large grain structure attained as a result of the heat treatment step is clearly evident in the photomicrograph shown in FIG. 4 of the drawings which comprises a Kalling’s etched micrograph of a tensile specimen prepared from the billet and photographed at a magnification of 10 times.

In comparison, a control specimen prepared from the same powder and subjected to the same compaction by extrusion followed by recrystallization and heat treatment, but omitting the cold-working step, did not evidence any appreciable grain growth characteristics and possessed high temperature physical properties substantially inferior to that of the specimen as evidenced by the microstructure shown in FIG. 4. Comparative round and elevated temperature tests of the tensile properties of the alloy prepared in accordance with the process comprising the present invention and the same alloy in a cast-and-wrought condition revealed the alloy made in accordance with the process comprising the present invention to be at least as good, and in most cases, superior to that of the prior art structure.

### TABLE 1—NOMINAL COMPOSITIONS OF SOME NICKEL-BASE SUPERALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
<th>W</th>
<th>Co</th>
<th>Nb</th>
<th>Zr</th>
<th>Other</th>
<th>Ni</th>
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<tr>
<td>Nimonic 75...</td>
<td>0.12</td>
<td>20</td>
<td>0.5</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nimonic 60A...</td>
<td>0.08</td>
<td>20</td>
<td>1.6</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nimonic 69...</td>
<td>0.10</td>
<td>20</td>
<td>1.6</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nimonic 68...</td>
<td>0.12</td>
<td>20</td>
<td>2.0</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nimonic 60...</td>
<td>0.09</td>
<td>11</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Waspaloy...</td>
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<td>1.3</td>
<td>3.0</td>
<td>4.4</td>
<td>13.3</td>
<td>0.008</td>
<td>0.06</td>
<td></td>
<td></td>
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<tr>
<td>Udimet 700...</td>
<td>0.15</td>
<td>15</td>
<td>4.3</td>
<td>3.5</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Rene 41...</td>
<td>0.09</td>
<td>19</td>
<td>1.5</td>
<td>2.1</td>
<td>10.6</td>
<td>11.0</td>
<td>0.005</td>
<td></td>
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<tr>
<td>IN-100 (cast)...</td>
<td>0.18</td>
<td>10</td>
<td>5.5</td>
<td>5.0</td>
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<td>18.0</td>
<td>0.015</td>
<td>0.05</td>
<td>50</td>
<td></td>
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<tr>
<td>MA-RM-250 (cast)...</td>
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<td>9.0</td>
<td>9.0</td>
<td>2.0</td>
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<td>0.008</td>
<td>5.0 Fe (max)...</td>
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</tr>
</tbody>
</table>

* (1) Ti-6Al-4V.

In order to further illustrate the process comprising the present invention, the following typical examples are provided. It will be understood that the examples are furnished for illustrative purposes and are not intended to be limiting the scope of the invention as herein described and defined in the subjoined claims.

### EXAMPLE I

A nickel-based superalloy corresponding to the nominal composition of Udimet 700, as set forth in Table 1, was microcast into spherical powder particles and were screened providing a randomly sized powder ranging from 10 microns up to 60 microns in size. The free-floating powder was confined in an elongated cylindrical container composed of a mild steel and compacted therein by subjecting the container to supersonic vibrations. The container was subsequently evacuated and sealed by welding and thereafter was extruded to a fully dense rod, while heated to a temperature of 1,950°F.

The microstructure of the resultant densified billet is illustrated in FIG. 2. The resultant extruded rod thereafter was preheated to 1,700°F, which is approximately 200°F below its recrystallization temperature. At this preheat temperature, the billet was cold worked by passing it through a pair of rolls, effecting approximately a 50 percent reduction in cross-sectional area in one pass. The resultant cold-worked billet was subsequently recrystallized for a period of 2.5 hours at a temperature of 2,100°F, which is a temperature above the recrystallization temperature but below the gamma-prime solvus temperature for this alloy. The resultant recrystallized billet is illustrated in FIG. 6. In addition, stress rupture properties, a property particularly important in alloys subjected to high temperature stress applications, were measured at a temperature of 1,850°F and at a stress of 20,000 psi for the alloy comprising the present invention and identical alloy compositions of the cast-and-wrought type heretofore known. The alloy processed in accordance with the present invention had a stress rupture life to failure of 196 hours, whereas conventional cast-and-wrought U-700 alloy of the same composition had a life of only 10 hours under these same conditions.

While it will be apparent that the description of the preferred embodiments of the present invention is well calculated to provide the advantages and benefits of the process comprising the present invention, it will be appreciated that the process is susceptible to variation, modification and change without departing from the spirit of the invention.

What is claimed is:

1. The method of forming a dense mass of a nickel-based superalloy which comprises the steps of compacting and densifying a powder of said superalloy into a billet, cold working said billet by effecting deformation thereof at a temperature below the recrystallization temperature of the alloy, recrystallizing the cold-worked said billet by heating it to a temperature above its recrystallization temperature and below the gamma-prime solvus temperature for a period of time sufficient to effect nucleation of new grains, and thereafter heat treating the recrystallized said billet at a temperature above the gamma-prime solvus temperature and below the incipient melting point of the gamma matrix for a period of time sufficient to effect growth of the grain to the desired size.
2. The method as defined in claim 1, wherein said powder is of a particle size ranging from about 60 mesh to about 1 micron and contains less than about 100 p.p.m. oxygen.

3. The method as defined in claim 1, wherein said billet formed by said confining and densifying is substantially of a 100 percent theoretical density.

4. The process as defined in claim 1, wherein said cold working is performed so as to provide a degree of cold working to said billet equivalent to that resulting from a reduction in its cross-sectional area of from several percent up to about 50 percent.

5. The method as defined in claim 1, wherein said cold working is performed on said billet which is preheated to a temperature ranging from about 1,000°F. to about 1,700°F. in a manner to impart a working thereof equivalent to that resulting from about a 30 percent to about a 50 percent reduction in its cross-sectional area.

6. The method as defined in claim 1, wherein said recrystallizing the cold-worked said billet is accomplished for a period of time ranging from about 2 hours up to about 12 hours at a temperature of about 1,700°F. to about 2,100°F.

7. The method as defined in claim 1, wherein the recrystallization temperature of said superalloy ranges from about 1,700°F. to about 2,100°F.