



METHODS OF FORMING ARTICLES FROM ALLOYS OF TIN AND/OR TITANIUM



G00002

Field of the Invention

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The present invention relates to methods for the production of articles, particularly shaped articles, from alloys which contain Sn and/or Ti. In particular, the invention provides, in various aspects, methods which include semi-solid metal powder forming, solid state metal powder diffusion and metal powder preform forming followed by hot pressing.

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Background to the Invention

Titanium is the fourth most abundant structural metal in the crust of the earth after aluminum, iron and magnesium. Due to their superior strength to weight ratios, excellent corrosion and erosion resistance and high heat transfer efficiency, titanium and its alloys have proven to be some of the most appropriate material choices for a wide variety of critical applications in the aerospace, marine and automotive industries. With improvements in titanium and titanium alloy production, the cost for titanium and its alloys in some regions of the world has been dramatically reduced. The cost of Ti powders is equivalent to the cost of the stainless steel powders which are commonly used in the powder metallurgy (PM) and powder injection molding (PIM) industries world wide. As such, the use of titanium and its alloys has rapidly expanded to include applications in the pharmaceutical and chemical areas as well as in nuclear power plants, food, and medical prostheses. Commercial applications are also seen in sporting equipment, fashion and apparel, such as golf clubs, bicycle frames, watch cases, jewellery, eyeglasses and pens.

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Generally, casting is the most widely used technology to produce products of titanium and its alloys. However, titanium, particularly in the liquid state, has a very high chemical activity. It reacts strongly with oxygen, nitrogen, hydrogen, water and carbon monoxide/dioxide and also reacts with almost all the refractory crucible materials at high temperatures. Therefore, melting and casting must be carried out in special crucibles under

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a very high vacuum. After casting, expensive post-machining is often required to achieve the desired final dimensions. In addition, for high performance applications, hot isotropic pressing (HIP) of the castings is normally required in order to completely eliminate casting porosity. All of these barriers result in a very high fabrication cost, which limits the
5 widespread application of titanium alloys to a great extent.

Powder metallurgy has been evaluated as another means of producing articles of titanium alloys. However, this process generally involves complicated HIP compaction methods which makes it difficult for general applications.

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Semi-solid metal forming (SSMF) is a newly developed process for forming alloys under semi-solid state conditions, rather than in the liquid state such as in casting or solid state such as in sintering (conventional PM and PIM). The process relies on the thixotropic behavior of the semi-solid slurries containing non-dendritic solid particles which are able
15 to flow like viscous liquids when a shear force is applied. This peculiar flow behavior has led to the development of some novel forming processes, such as so called thixo-casting and thixo-molding, for fabrication of near-net shaped components with high performance. Mass production is being carried out in the United States of America and Europe with a growing trend. Due to the process characteristics, the current applications are only limited
20 to certain Al and Mg alloys.

The principle of semi-solid processing has also been applied to the fabrication of metallic slurries based on pre-blending and compaction of powders with different melting points in a process termed as COMPASS (consolidation of mixed powders as synthetic slurry).

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Recently, Yasue, et al in the National Industrial Research Institute of NaGaya (NIRIN), Japan, successfully formed a Ti-6 wt.% Al alloy via semi-solid metal powder forming methods. The process showed the feasibility in processing the above alloys at a temperature around 700 °C (die set temperature). However, the relatively high process
30 temperature (die set temperature) required makes this process unattractive to commercial producers.

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The principle of the solid state diffusion process is to press the alloy powder below the melting points of the powder for a predetermined pressure and time. The microstructures produced in this method are similar to those produced by semi-solid forming processes, but
5 using a relatively long process time. There has been little discussion in the public literature related to this forming method which can be used for producing prototyping components.

Objectives

10 The invention advantageously provides a semi-solid metal powder forming technology for fabricating net-shaped and miniature titanium alloy components with low cost and high dimensional accuracy. As such, industry may advantageously benefit in being able to produce titanium alloy components cost effectively with enhanced productivity.

15 Summary of the Invention

According to a first aspect of the present invention there is provided a method of forming an article from a tin-containing alloy, the method comprising the steps of:

- (a) injecting elemental metal powders of metal constituents of the alloy into a
20 preheated die at a temperature of above about 240°C;
 - (b) applying a predetermined pressure to the elemental powders for a predetermined time period to produce a green part; and
 - (c) alloying the green part at a predetermined temperature for a predetermined time period to form the article;
- 25 wherein the elemental metal powders include Sn powder in an amount of at least 2 wt% based on the total weight of the elemental metal powders.

In this aspect, the elemental metal powders may include at least Ti and Sn powders, optionally with other metal powders. In one embodiment the elemental metal powders
30 include at least Ti, Sn and Al powders.

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According to this aspect, the elemental metal powders include Sn powder in an amount of at least 2 wt% based on the total weight of the elemental metal powders. Preferably, the elemental metal powders include Sn powder in an amount of from 2-12 wt% based on the total weight of the elemental metal powders.

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In this aspect, the alloy include any alloy of Sn, but is preferably directed to alloys of Sn with Al and/or Ti. As such, the invention of this aspect may be considered to be a semi-solid metal powder forming process for Sn containing alloys given the temperature of injecting step (a) of 240°C.

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Preferably, in this aspect, the pressurising step (b) includes applying a pressure of from 1000 to 2800 psi for a time period of from 0.5 to 3 minutes. Further, it is preferred that alloying step (c) includes alloying the green part at a temperature of from 1250 to 1350°C for a time period of from 30 to 150 minutes.

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According to a second aspect of the invention there is provided a method of forming an article from a titanium-containing alloy, the method comprising the steps of:

(a) injecting elemental metal powders of metal constituents of the alloy into a preheated die at a predetermined temperature, the temperature being determined based on the constituents of the alloy;

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(b) applying a predetermined pressure to the elemental powders for a predetermined time period to produce a green part; and

(c) alloying the green part at a predetermined temperature for a predetermined time period to form the article;

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wherein the predetermined temperature of injecting step (a) is greater than about 100°C if the elemental metal powders include Sn powder, and is greater than about 350°C if the elemental metal powders include Al powder.

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In one embodiment, according to this aspect, the elemental metal powders include Ti and Al powders and the predetermined temperature of injecting step (a) is between 450 and 550°C. In this embodiment, it is preferred that the predetermined pressure in the

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pressurizing step (b) is from 2000 to 3000 psi and the predetermined time period in step (b) is from 120 to 480 minutes. This embodiment may therefore be considered a solid state diffusion process for Ti-Al alloys.

5 According to a third aspect the invention provides a method of forming an article from an alloy, the method comprising the steps of:

(a) introducing elemental metal powders of metal constituents of the alloy into a die and applying a pressure of from 2000 to 3000 psi for a time period of from 1 to 5 minutes to form a preform;

10 (b) applying a predetermined pressure and temperature to the preform for a predetermined time period to produce a green part; and

(c) alloying the green part at a predetermined temperature for a predetermined time period to form the article.

15 In this regard, this aspect of the invention includes a process which involves an initial step of forming a preform followed by, generally, a semi-solid state metal powder forming process or a solid state metal powder diffusion process. For example, pressurizing step (b) and alloying step (c) may include either of the processes described for the first and second aspects of the invention.

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Detailed Description of Preferred Embodiments

Embodiments of the various aspects of the invention will now be described in detail, in some instances with reference to the accompanying drawings in which:

25 Figure 1 illustrates graphically a Ti-Al binary phase diagram.

Figure 2 illustrates graphically a Ti-Sn binary phase diagram.

Figure 3 illustrates a Ti-6Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1350 °C v 1hr.

Figure 4 illustrates a Ti-6Sn elemental blended alloy formed by semi-solid forming
30 followed by alloying treatment at 1400 °C v 1hr.

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Figure 5 illustrates Ti-6Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1450 °C v 1hr.

Figure 6 illustrates Ti-9Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1350 °C v 1hr.

5 Figure 7 illustrates Ti-9Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1400 °C 2.5hr (spherical Ti powders).

Figure 8 illustrates a Ti-12Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1400 °C v 1hr.

10 Figure 9 illustrates Tii-5Al-2.5Sn elemental blended alloy formed by semi-solid forming followed by alloying treatment at 1350 °C v 1hr.

Figure 10 illustrates Ti-8Al fabricated by semi-solid state diffusion followed by alloying treatment 1350 °C for 1 hr. (predominated alpha-Ti structure).

Figure 11 XRD analysis results for Ti-9Sn elemental blended alloy formed by semi-solid metal powder forming process prior to alloying.

15 Figure 12 XRD analysis results for Ti-9Sn elemental blended alloy formed by semi-solid metal powder forming process followed by alloying at a temperature of 1350 °C.

Figure 13 XRD analysis results for Ti-5Al-2.5Sn elemental blended alloy formed by semi-solid state metal powder forming process followed by alloying at a temperature of 1450°C.

Figure 14 XRD analysis results for Ti-8Al elemental blended alloy formed by solid state diffusion process followed by alloying at a temperature of 1250 °C.

25 Raw Materials - Metal Powders

The elemental metal powders used in each of the aspects of the invention are Ti, Al and Sn. Many other elemental metal powders may be added, but for simplicity and clarification, only the above elemental metal powders have been the subject of experimental analysis.

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Metal Alloys and Their Blending

The above metal powders were carefully weighed and mixed using an experimental blender. The duration of the mixing was approximately 4 hours minimum. Various
5 mixtures of the elemental metal powders were formed as indicated below.

Ti-Al alloys

10 Ti-6Al
Ti-8Al
Ti-20Al

Ti-Sn Alloys

15 Ti-6Sn
Ti-9Sn
Ti-12Sn

Ti-Al-Sn Alloys

20 Ti-5Al-2.5Sn
Ti-6Al-5Sn
Ti-6Al-8Sn

25 It is impossible to conduct experiments in respect of all possible combinations of Ti, Al and/or Sn alloys. However, the first aspect of the invention provides advantages using semi-solid metal forming techniques with the incorporation of elemental Sn powder. In principle, any alloys containing more than 2% elemental Sn powder can be formed in this method. Other identified commercial and semi-commercial grades of Ti alloys, which can
30 be processed in this way are given below by way of example only:

Ti-6Al-2Sn-4Zr-2Mo

Ti-5Al-2.5Sn-ELI (**clarification required**)

Ti-2.25Al-11 Sn-5Zr-1Mo

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Ti-5Al-5Sn-2Zr-2Mo

Ti-6Al-2V-2Sn

Ti-6Al-2Sn-4Zr-6Mo

Ti-5Al-2Sn-2Zr-4Mo-4Cr

5 Ti-6Al-2Sn-2Zr-2Mo-2Cr

Ti-1 1.5Mo-6Zr-4.5Sn

Ti-1 5V-3Al-3Cr-3Sn

Ti-5Al-2.5Sn

Ti-5Al-6Sn-2Zr-1Mo-2.5Si

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The Die Set Design

Two die sets have been designed: one a Ti-watch case which is used to verify the formability of the materials using the newly developed metal powder semi-solid forming technology of the first aspect of the invention, and the other a tensile bar which is used to verify the mechanical properties.

The die set used for the tensile bars was very similar to a conventional PM die set design, but was combined with heating facilities generally adopted in conventional PIM, plastic injection molding or die casting die set designs.

This die set used for the watchcase components was similar to a conventional PM die set design, but a full profile ejector was applied. In order to minimize friction and possible damage to the component, an upper part for accommodating the extra powders was designed so as to be movable such that the parts formed could be easily ejected without damage.

Semi-solid metal powder forming according to the first aspect of the invention was carried out using a hot plate press and a hydraulic press specifically designed and installed for this project.

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The die set on the hot plate press could be heated to a maximum temperature of 600 °C. A maximum pressure of 3000psi could be applied to the die set and held at a predetermined temperature for up to at least 10 hours. All of the Ti watchcase samples were produced with this press using the designed watchcase die set. Initially, tensile bars were also
5 produced using this small hot plate press. When the fusibilities were shown on this machine, a tensile bar die set for large press and semi-auto operation was then designed.

As stated above, a hydraulic press was used to produce the required tensile bars for tensile property verification after initial testing on the small hot plate press. The die set was heated
10 up to 280°C and held for about 1- 5 minutes. Most of the tensile bars were produced using this machine as it is very fast and easy to operate (semi-auto) whereas the small press was manual and very slow.

Forming Methods

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The present invention considers a number of different forming methods. These, which include powder metallurgy, solid state metal powder diffusion, semi-solid metal powder forming and metal powder forming followed by hot pressing, will be dealt with in turn below.

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Powder Metallurgy

For the tensile bars, predetermined metal powder constituents of the alloy were poured into the cavity of the die set and pressed under a pressure of 2500 to 2800psi for about 3 to 5
25 minutes. Tensile bars were successfully produced.

For watchcase components, predetermined metal powder constituents of the alloy were poured into the cavity of the die set and pressed under a pressure of 2500 to 2800psi for about 3 to 10 minutes. It was found that it was very difficult to produce complete
30 watchcase components using this method. The watchcases produced exhibited defects such as cracks.

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From this, it can be seen that conventional powder metallurgy processing can only be used to produce some simple shaped tensile bars and is not appropriate for the production of more complex shaped components like watchcases without the use of binders.

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Solid State Metal Powder Diffusion Process

For tensile bars, solid state diffusion processing was used to produce articles of Ti-6Al, Ti-8Al and Ti-20Al elementally mixed metal powder alloys. The powders were poured into the preheated die at 450 to 600°C and held for about 3 to 6 hours at a pressure of 2500 to 3500 psi. It was found that once the temperature was over 550°C the die set became jammed and various surface defects, such as scratches and distortion occurred. At temperatures lower than 500°C, the die set exhibited no obvious problems.

15 For the watchcase components, solid state diffusion processing was used to produce articles of Ti-6Al, Ti-8Al and Ti-20Al elementally mixed metal powder alloys. these were produced under the same parameters as used for the tensile bars. Some watchcases have been successfully produced in this way.

20 For Ti-Sn alloys, die set temperatures of greater than 100°C at applied pressure of from 2500 to 3000 psi for periods of from 1 to 8 hours have successfully produced both tensile bar and watchcase samples.

Semi-Solid Metal Powder Forming Process

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For tensile bars, a group of Ti alloys containing 2 to 12 % elemental Sn metal powder was processed using a semi-solid metal powder forming process. The Sn-containing Ti alloys were put into the die set cavity which was preheated to 250 to 300°C and held under a pressure of 1000 to 2500psi for about 1 to 3 minutes. Tensile bars were successfully produced in this way.

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For watchcase components, the group of Sn-containing Ti alloys were put into the watchcase die cavity which was preheated temperature of 250 to 300°C and held under a pressure of 2500 to 2800psi for about 1 to 3 minutes. Watchcase samples were successfully produced in this way.

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Metal powder preform forming followed by hot pressing

In this process, the metal powder alloys were firstly formed into a simple shape, similar to the final geometry of the components to be made, by conventional PM process. The
10 preforms were then processed using either a semi-solid forming or solid state diffusion process. This process is advantageously tidy and surface finish can be further improved.

The preforms were then processed using either a semi-solid forming or solid state diffusion process. For more complicated geometry components, a simple shape can be formed first
15 and then followed by progressive forming (several die set together) using either semi-solid or solid state diffusion process.

Comparison of the forming methods

20 Conventional powder metallurgy can be used to produce simple tensile bars, but is not easily employed to produce sound watchcase samples. Solid state diffusion processes can be used to produce articles of almost all Sn containing alloys including Ti-xSn-x, but with a long holding/processing time. This time may be from 30 minutes to 8 hours in order to achieve reasonably high compacted density. However, the semi-solid metal powder
25 forming process makes it possible to form alloys of Ti-Sn, Ti-Sn-x, Ti-Sn-x-x etc. at relatively low temperature and very short cycling time. Table 1 attached summarizes the characteristics of the above three processes.

Alloy Treatment/Sintering
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The above-formed tensile bars and watchcases were sintered at a temperature of from 1200 to 1450°C under vacuum and Argon. The holding time was about 1 to 3 hours. The

sintering profiles are shown in Table 2.

Property Evaluation

5 Density

Density was measured using a pycnometer. The elemental powder density is given in Table 3, the densities of the elemental alloy mixture, green parts and sintered parts are given in Table 4 and the dimensional characteristics are shown in Table 5.

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As can be seen from Table 4, the green part density is very close to the sintered density, the sintered density being about 98% of the theoretical density, assuming the mixed powder density is the theoretical density. It is also noted that for some alloys containing Al elemental powder, the sintered density is lower than the green part density. This may be due to the relaxation of the Al powder during sintering. It is also confirmed that for Ti-20%Al, the sintered density is much lower than the green part density and the size of the sintered components are much larger than those of the green parts.

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Shrinkage Factor

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From Table 5, it can be concluded that:

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- The sintering temperature does not affect the shrinkage once the temperature is over 1300°C.
- For semi-solid metal powder forming, the shrinkage factor is in the range of 0.4 to 2.1 % for Ti-Sn alloys and 0.25 to 0.7% for Ti-Al-Sn alloys.
- The shrinkage in both the length and width directions are isotropic for semi-solid forming, but anisotropic for the dimensions of the component made by PM.

30 Mechanical testing

Mechanical testing was carried out using an Instron tensile machine. The parameters used were: speed: 3 mm/min. Max. 10 tons and the tensile results are given in Table 6.

Microstructure and phase diagram

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As shown from Ti-Al binary phase diagram illustrated in Figure 1, for Al compositions containing 8 wt.% Al or less, the final composition will be alpha-Ti provided equilibrium conditions are met. In practice, there may be a small quantity of beta or delta phase Ti existing as the equilibrium conditions may not be reached or phase transformation may be incomplete.

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The binary phase diagram for Ti-Sn is given in Figure 2. As can be seen in the diagram, the final phase will be alpha-Ti, where the original composition contains less than 20 wt.% Sn, under equilibrium conditions. Again, in practice there may be some beta and other compounds present due to the sintering conditions applied.

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Microstructure

The selective microstructures for Ti-6Sn, Ti-9Sn and Ti-12Sn are given in Figures 3 to 5, Figures 6 to 7 and Figure 8 respectively. As can be seen, the microstructures mainly consist of the alpha-Ti phase with some minor compounds, which are identified by the subsequent XRD analysis. The basic microstructures following sintering at temperatures in the range of 1300 to 1450°C are similar. Based on the microstructure, there are still voids present at a level of 1 to 2% which may be eliminated by optimizing the process parameters.

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The selective microstructure for Ti-5Al-2.5Sn is shown in Figure 9. It can be seen that the microstructures are uniform and predominated by α -Ti and minor compounds identified by the subsequent XRD analysis.

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The selective microstructures for Ti-8Al are given in Figure 10. It can be seen that the grain size is very similar to the original particle size, which indicates that no abnormal

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grain size growth has taken place. The percentage voids for this alloy formed by semi-solid state processing followed by sintering is relative large compared to the other alloys outlined above. The reason is that this process is very similar to the conventional PM process but only the processing temperature is increased from room to a temperature which
5 is below the melting point of Al.

XRD Analysis

The XRD analysis of selective compositions is given in Figures 11 to 14. As can seen from
10 the Figure 11, there are some indications of oxidation during forming which was conducted at open atmosphere. However, after alloying or sintering, no oxides were found in the samples. It is also indicated that there are some compounds present in the microstructures as indicated in Figures 12 to 14, which is probably due to insufficient holding time for the phase transformation to take place completely. It should be pointed
15 out that the sintering step has not yet been optimized for this process.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit
20 and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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CLAIMS:

1. A method of forming an article from a tin-containing alloy, the method comprising the steps of:
 - 5 (a) injecting elemental metal powders of metal constituents of the alloy into a preheated die at a temperature of above about 240°C;
 - (b) applying a predetermined pressure to the elemental powders for a predetermined time period to produce a green part; and
 - (c) alloying the green part at a predetermined temperature for a
10 predetermined time period to form said article;wherein said elemental metal powders include Sn powder in an amount of at least 2 wt% based on the total weight of the elemental metal powders.
2. A method according to claim 1, wherein said elemental metal powders include at
15 least Ti and Sn powders.
3. A method according to claim 1, wherein said elemental metal powders include at least Ti, Sn and Al powders.
- 20 4. A method according to claim 1, wherein said elemental metal powders include Sn powder in an amount of from 2-12 wt% based on the total weight of the elemental metal powders.
5. A method according to claim 1, wherein pressurising step (b) includes applying a
25 pressure of from 1000 to 2800 psi for a time period of from 0.5 to 3 minutes.
6. A method according to claim 1, wherein alloying step (c) includes alloying the green part at a temperature of from 1250 to 1350°C for a time period of from 30 to 150 minutes.

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7. A method of forming an article from a titanium-containing alloy, the method comprising the steps of:
- (a) injecting elemental metal powders of metal constituents of the alloy into a preheated die at a predetermined temperature, the temperature being determined based on the constituents of the alloy;
 - (b) applying a predetermined pressure to the elemental powders for a predetermined time period to produce a green part; and
 - (c) alloying the green part at a predetermined temperature for a predetermined time period to form said article;
- wherein said predetermined temperature of injecting step (a) is greater than about 100°C if said elemental metal powders include Sn powder, and is greater than about 350°C if said elemental metal powders include Al powder.
8. A method according to claim 7, wherein said elemental metal powders include Ti and Al powders and said predetermined temperature of injecting step (a) is between 450 and 550°C.
9. A method according to claim 8, wherein the predetermined pressure in the pressurising step (b) is from 2000 to 3000 psi and the predetermined time period in step (b) is from 120 to 480 minutes.
10. A method of forming an article from an alloy, the method comprising the steps of:
- (a) introducing elemental metal powders of metal constituents of the alloy into a die and applying a pressure of from 2000 to 3000 psi for a time period of from 1 to 5 minutes to form a preform;
 - (b) applying a predetermined pressure and temperature to the preform for a predetermined time period to produce a green part; and
 - (c) alloying the green part at a predetermined temperature for a predetermined time period to form said article.
11. An article formed by a method according to any one of the preceding claims.