



(11)

EP 4 818 345 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.10.2026 Bulletin 2026/41

(21) Application number: **24897434.7**

(22) Date of filing: **21.11.2024**

(51) International Patent Classification (IPC):
C22C 27/04 ^(2006.01) **C22C 1/04** ^(2023.01)
B22F 1/00 ^(2022.01) **B22F 3/15** ^(2006.01)
B22F 3/24 ^(2006.01) **C22F 1/00** ^(2006.01)
C22F 1/18 ^(2006.01)

(52) Cooperative Patent Classification (CPC):
C22C 1/04; C22C 27/04; B22F 1/00; B22F 3/15;
B22F 3/24; C22F 1/00; C22F 1/18

(86) International application number:
PCT/JP2024/041266

(87) International publication number:
WO 2025/115748 (05.06.2025 Gazette 2025/23)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **01.12.2023 JP 2023203732**

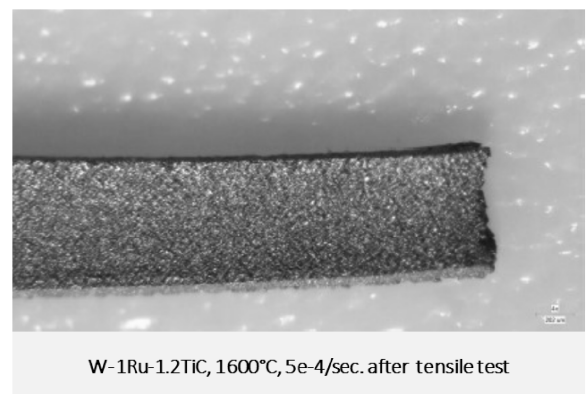
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(54) **SUPERPLASTIC ALLOY**

(57) To provide a superplastic alloy comprising a transition metal carbide and a dissimilar metal element that has superplasticity. A superplastic alloy containing tungsten, 1 or 2 or more dissimilar metal elements solid-solutionized and grain-boundary segregated in the tungsten matrix phase, and 1 or 2 or more transition metal carbides finely precipitated at grain boundaries and/or within grains, wherein the superplastic alloy contains 0.1 to 20% by weight of the dissimilar metal element and 0.2 to 5.0% by weight of the transition metal carbide relative to tungsten.



W-1Ru-1.2TiC, 1600°C, 5e-4/sec. after tensile test

Figure 1

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a superplastic alloy containing at least tungsten.

BACKGROUND ART

10 **[0002]** Normally, when a test piece of metallic materials is subjected to tension tests, it deforms plastically and the central part of the test piece locally constricts to form a neck, and finally undergoes ductile fracture in a cup-and-cone shape. The total elongation of the test piece is, for example, around 30 to 40% for mild steel, and about 50 to 60% even for soft metals like aluminum and copper, never exceeding 100%.

15 **[0003]** However, when a solid metallic material containing an alloy is deformed in a high-temperature range at a constant, relatively low strain rate, for example in tension, it may elongate by several hundred to several thousand percent or more. Such a phenomenon is called superplasticity (also referred to as superplastic deformation or superplastic phenomenon). There are mainly two types of superplasticity: transformation superplasticity caused primarily by phase transformation of the material, and fine-grained superplasticity occurring in polycrystalline materials with a grain size of several micrometers or less. In fine-grained superplasticity, the strain rate sensitivity index (m value) of flow stress, which corresponds to the slope of a log-log plot of flow stress and strain rate, is high, and generally, an m value of 0.3 or more and
20 an elongation to failure of 200% or more are considered the criteria for the manifestation of superplastic behavior. When the superplastic phenomenon manifests, the flow stress also decreases, and plastic forming methods utilizing this phenomenon have been put to practical use for high-strength, hard-to-process materials such as nickel-based super-alloys.

25 **[0004]** As metallic materials exhibiting superplasticity, aluminum alloys and titanium alloys used in integral molding technologies for structures in the automotive and aerospace industries are mainstream, and other examples include magnesium alloys, cobalt alloys, stainless steel alloys, and super heat-resistant alloys. For example, as an aluminum alloy having superplasticity, JP H06-240395 (Patent Document 1) discloses an aluminum alloy for superplastic forming. The aluminum alloy described in Patent Document 1 contains 4.0 to 7.0% magnesium, more than 1.5% and 2.5% or less manganese, and 0.00005 to 0.01% beryllium, with iron as an impurity restricted to less than 0.2%, and the balance
30 consisting of aluminum and other unavoidable impurities (see claim 1, etc., of Patent Document 1). It possesses good superplastic characteristics while simultaneously exhibiting significantly superior corrosion resistance and weldability compared to conventional aluminum alloy sheets for superplastic forming, thus fully satisfying the performance required for various building materials, other containers, and various structural materials.

35 **[0005]** Furthermore, regarding titanium alloys, Non-Patent Document 1 discloses an example of evaluating cooperative grain boundary sliding, which plays an important role in superplasticity, using a Ti-4.5Al-3V-2Fe-2Mo alloy (SP-700 alloy). Non-Patent Document 1 describes that an elongation of 1200% or more was obtained, particularly under conditions of a temperature of 750°C and a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$.

40 **[0006]** However, since the aluminum alloy described in Patent Document 1 is derived from a light metal, it has a low melting point and is not suitable for products requiring heat resistance. In addition, although the titanium alloy described in Non-Patent Document 1 has superior strength compared to aluminum alloys, it is difficult to use at high temperatures of 1000°C or higher. As one means for use at high temperatures of 1000°C or higher, an alloy based on refractory metals (transition metals) is conceivable.

45 **[0007]** Among refractory metals (transition metals), tungsten, for example, has many superior properties such as a high melting point, a low thermal expansion coefficient, high thermal conductivity, discharge resistance characteristics, and chemical stability at high temperatures. Furthermore, when tungsten is made into an alloy, focusing on the melting point, the tungsten alloy has a high melting point of 3000°C or higher compared to the melting points of the aforementioned titanium alloys at 1500 to 1600°C and nickel-based alloys (e.g., Inconel (registered trademark)) at 1300 to 1400°C. However, the scope of industrial application of tungsten has been limited due to its brittleness and poor workability.

50 **[0008]** For tungsten, which is a brittle material, techniques are known in which elements such as rhenium are solid-solutionized to improve mechanical properties, or elements such as rhenium are added for the purpose of increasing electrical resistivity at room temperature. However, while tungsten materials including tungsten alloys have the advantage of being usable at high temperatures as described above, there have been concerns regarding low electrical resistivity, a small number of dissimilar metals capable of greatly enhancing electrical resistivity through solid solution, and embrittlement such as low-temperature embrittlement, recrystallization embrittlement (increase in ductile-to-brittle transition temperature (DBTT) due to recrystallization at high temperatures), or irradiation embrittlement due to high-energy particle irradiation (e.g., neutron beams). As a technology for improving such embrittlement, for example, WO 2013/018714 A1 (Patent Document 2) discloses an alloy in which a carbide of a Group III to VI transition metal element is solid-solution segregated and finely precipitated at the grain boundaries of tungsten.
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[0009] The technology disclosed in Patent Document 2 provides an alloy having high strength and high toughness with improved embrittlement, and a method for producing the same, by processing a mixed powder of a transition metal carbide and tungsten using a mechanical alloying (MA) method and a hot isostatic pressing (HIP) method, and further applying a Grain boundary Sliding based Microstructural Modification (GSMM) method to control the microstructure.

[0010] Patent Document 2 contains descriptions such as "Practically, grain boundary sliding treatment and superplastic deformation aiming at grain boundary strengthening to solve brittleness are performed," and "W-TiC (tungsten-titanium carbide) exhibits large superplastic deformation (160% or more at 1600°C) by grain boundary sliding treatment" (see [0044] to [0046] of Patent Document 2). However, in reality, as a result of the grain boundary sliding treatment, the grain size increases by about one order of magnitude, and the superplastic elongation is rather significantly reduced in the W-TiC subjected to the treatment. Normally, a small grain size is required for fine-grained superplasticity to occur. However, there is no description regarding grain size in the relevant scope of Patent Document 2, and consequently, there is no disclosure or suggestive description regarding the elongation of superplastic deformation of the material after the grain boundary sliding treatment.

[0011] Furthermore, the applicant's group has disclosed a tungsten alloy having high electrical resistivity and a method for producing the same in JP 2023-45532 (Patent Document 3). First, Patent Document 3 describes that by solid-solutionizing 0.1 to 19% by weight of a dissimilar metal (particularly ruthenium) in tungsten, the electrical resistivity at room temperature increased by a factor of 4 or more, and the electrical resistivity at higher temperatures (> 1000°C) increased by a factor of 2 or more. Moreover, Patent Document 3 describes that not only a dissimilar metal like ruthenium but also the constituent elements (transition metal and carbon) of a transition metal carbide are further solid-solutionized in tungsten.

[0012] However, since the object of Patent Document 3 is to increase electrical resistivity, while tests showing an increase in electrical resistivity were conducted on the tungsten-transition metal (particularly ruthenium) alloy, no tests were conducted to determine whether it exhibits a superplastic phenomenon. Therefore, it was unclear whether it had a superplastic phenomenon. In addition, regarding tungsten-transition metal-transition metal carbide, Patent Document 3 simply mentions it, and tests showing an increase in electrical resistivity or tests determining the presence of a superplastic phenomenon like the tungsten-transition metal (particularly ruthenium) alloy were not conducted; thus, from Cited Document 3, it was unclear whether it possessed a superplastic phenomenon.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0013]

Patent Document 1: JP H06-240395

Patent Document 2: WO 2013/018714 A1

Patent Document 3: JP 2023-45532

NON-PATENT DOCUMENTS

[0014] Non-Patent Document 1: Eiichi Sato, "Clarification of Microstructural Guidelines for Reducing Superplastic Forming Temperature of Titanium Alloy Sheets," Amada Foundation Supported Research Report, Vol. 29, pp. 130-133 (2016).

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0015] Therefore, the object of the present invention is to provide a superplastic alloy comprising tungsten, a transition metal, and a transition metal carbide, which exhibits superplastic deformation.

Means for Solving the Problems

[0016] The object of the present invention is effectively achieved by providing a superplastic alloy containing tungsten, and 0.1 to 20% by weight of a dissimilar metal element and 0.2 to 5.0% by weight of a transition metal carbide relative to the tungsten, wherein one or more dissimilar metal elements are solid-solutionized and grain-boundary segregated in the tungsten matrix phase, and one or more transition metal carbides are finely precipitated at the grain boundaries or within the grains.

[0017] Furthermore, the object of the present invention is even more effectively achieved when the superplastic alloy

has a total elongation of 50 to 1000%, or when the dissimilar metal element is selected from ruthenium, osmium, iridium, rhodium, hafnium, and zirconium, or when the transition metal carbide is selected from carbides of transition metal elements belonging to the 4th, 5th, or 6th period and the Group 4 to Group 6 elements.

Effects of the Invention

[0018] In the present invention, regarding tungsten, which conventionally has poor formability and is restricted in its product shape, a superplastic alloy exhibiting superplastic deformation can be realized by adding a small amount of a transition metal element (such as ruthenium) that imparts a fairly large lattice strain to cause solid solution and grain boundary segregation, and by providing high-density grain boundaries in a thermally stable state within the alloy.

BRIEF DESCRIPTION OF DRAWINGS

[0019]

[FIG. 1] is an image showing the surface of W-1Ru-1.2TiC.

[FIG. 2] is an image showing the surface of pure tungsten (comparative example).

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, modes for carrying out the present invention will be described.

[0021] The superplastic alloy according to the present invention contains tungsten as a main component, and 0.1 to 20% by weight of a dissimilar metal element, and 0.2 to 5.0% by weight (corresponding to 0.6 to 14 mol%) of a transition metal carbide relative to the tungsten. The total elongation of the superplastic alloy is 50% to 1000%, the strain rate is $5.0 \times 10^{-1} \text{ s}^{-1}$ or less, and it exhibits superplastic deformation at 1000 to 2000°C. The peak stress is 800 MPa or less. Also, the grain size of the superplastic alloy is 20 μm or less, preferably 0.1 to 10 μm .

[0022] Here, regarding superplasticity, as described in the background art section, if the strain rate sensitivity index (m value) is 0.3 or more and the total elongation is 50% or more, it exhibits superplasticity and can be industrially applied to many things. That is, if the m value is less than 0.3, the total elongation is small and difficult to fully elongate, and it will not have the so-called "superplasticity". On the other hand, if the total elongation is more than 1000% (even if it elongates too much), industrial importance is not high, and rather it becomes difficult to process.

[0023] Regarding the strain rate, if it is higher than $5.0 \times 10^{-1} \text{ s}^{-1}$, plastic deformation due to dislocation slip rather than deformation due to grain boundary sliding becomes dominant, and superplasticity is not exhibited.

[0024] Regarding the temperature, if it is less than 1000°C, the total elongation is small, and superplasticity is not exhibited. Also, if it is higher than 2000°C, even if it exhibits superplasticity, processing becomes difficult due to equipment constraints.

[0025] If the peak stress is greater than 800 MPa, even if it exhibits superplasticity, processing becomes difficult due to equipment constraints.

[0026] In this specification, the "dissimilar metal element" refers to a transition metal element of the 4th period of the periodic table and Group 3 to Group 10 elements of the 4th period, and transition metal elements of the 5th and 6th periods of the periodic table and Group 3 to Group 5 elements, and Group 7 to Group 10 elements of the 6th period (that is, excluding molybdenum and tungsten). Metals from atomic number 21 scandium to atomic number 28 nickel in the 4th period, atomic number 39 yttrium to atomic number 46 palladium in the 5th period, and lanthanoids, atomic number 72 hafnium to atomic number 78 platinum in the 6th period can be used (molybdenum is atomic number 42, and tungsten is atomic number 74).

[0027] As for the dissimilar metal element, it can be selected from the above elements, but considering the improvement of superplasticity and various brittleness of tungsten and molybdenum, Group 4, 5, 7, 8, and 9 elements of the 5th or 6th period such as ruthenium (Ru), osmium (Os), tantalum (Ta), niobium (Nb), iridium (Ir), rhodium (Rh), hafnium (Hf), and zirconium (Zr) are desirable. Furthermore, ruthenium (Ru), osmium (Os), iridium (Ir), rhodium (Rh), hafnium (Hf), and zirconium (Zr) are desirable. The reason for this is that these dissimilar metal elements have atomic radii and electronegativities significantly different from tungsten, and when solid-solutionized in tungsten, they impart a large lattice strain, which is considered to result in easy segregation at grain boundaries. In addition, when these dissimilar metal elements form an alloy with tungsten, it is thought that by using a forced solid solution/ultra-fine grain introduction method such as MA (mechanical alloying), segregation of the dissimilar metal elements at the high-density grain boundaries introduced by MA is induced during sintering (grain boundary segregation), affecting superplastic deformation, its control, or the improvement of various types of embrittlement.

[0028] In the superplastic alloy according to the present invention, if it is a ternary superplastic alloy such as W-A-B (where W is tungsten, A is the aforementioned dissimilar metal element, and B is a transition metal carbide), A is preferably

0.1 to 20% by weight relative to tungsten. If it is less than 0.1% by weight, the total elongation increases compared to pure tungsten, that is, it exhibits superplasticity, but it does not reach the elongation of 50 to 1000% mentioned earlier. If it is more than 20% by weight, it will exceed the maximum solid solubility limit, and on the contrary, the elongation will not differ from that of pure tungsten, and there is a risk of promoting other embrittlement (low-temperature embrittlement, recrystallization embrittlement). The maximum solid solubility limit (in the equilibrium phase diagram) relative to tungsten is, for example, 19% by weight for osmium, 14% by weight for ruthenium, 10.3% by weight for iridium, 7% by weight for rhodium, 1.8% by weight for zirconium, and 9% by weight for hafnium. As described above, the solid solubility of dissimilar metal elements in the temperature range of 1000 to 2000°C is lower than the maximum solid solubility limit and decreases with falling temperatures; conversely, the degree of grain boundary segregation of dissimilar metal elements (necessary for promoting grain boundary sliding) increases as the temperature falls.

[0029] The transition metal carbide denoted as B contained in the superplastic alloy according to the present invention will be described.

[0030] The transition metal carbide (B) in the W-A-B ternary superplastic alloy is selected from carbides of transition metal elements belonging to the 4th period, 5th period, or 6th period, and any of Group 4 elements to Group 6 elements.

The reason for selecting such carbides is that these carbides have extremely high melting points and exist thermally stably even at high temperatures, as a result of which high-density grain boundaries introduced by, for example, mechanical alloying (hereinafter referred to as "MA") are pinned by the carbides, allowing fine crystal grains necessary for superplastic manifestation to be maintained without coarsening even at high temperatures, and furthermore, the transition metal carbides precipitated at grain boundaries or within grains often satisfy the Kurdjumov-Sachs orientation relationship (K-S relationship) showing good atomic matching with the tungsten matrix, and especially the solid solution segregation and precipitation of transition metal carbides at the grain boundaries (which are inherently weak and brittle) functions to significantly strengthen the grain boundaries, thereby improving superplastic deformation, recrystallization embrittlement, etc., in addition to achieving the desired superplasticity.

[0031] The transition metal carbide is preferably 0.2 to 5.0% by weight (0.6 to 14 mol%) relative to tungsten. If it is less than 0.2% by weight, the grain boundary pinning effect by the carbide is insufficient, causing crystal grains to coarsen during sintering or heating after sintering, and superplasticity is not exhibited. If it is more than 5.0% by weight, the carbides distributed within the grains coarsen, leading to fracture (cracking) within the carbides, and on the contrary, the elongation rate related to superplasticity will not differ from that of pure tungsten, with the risk of promoting other embrittlement (low-temperature embrittlement, recrystallization embrittlement).

[0032] Further, in the superplastic alloy according to the present invention, a quaternary system of tungsten-molybdenum-dissimilar metal element-transition metal carbide may be used, for example. At this time, since tungsten and molybdenum belong to the same group (Group 6A) and show almost the same properties, they form a complete solid solution with each other and can be varied in any proportion.

[0033] The superplastic alloy according to the present invention has been described above. Next, a method for producing the superplastic alloy according to the present invention will be described taking a ternary superplastic alloy mainly comprising tungsten-dissimilar metal element-transition metal carbide as an example.

[0034] Next, the method for producing the superplastic alloy according to the present invention, that is, a method for solid-solutionizing and grain-boundary segregating a dissimilar metal element in tungsten and finely precipitating a transition metal carbide at grain boundaries and within grains, will be described. First, it is necessary to solid-solutionize the dissimilar metal element and the transition metal carbide, which are starting material powders, into the matrix metal of tungsten (note that solid solution of a transition metal carbide refers to decomposing the transition metal carbide into its constituent elements, the transition metal element and carbon, and solid-solutionizing those constituent elements into the matrix metal). The reason for solid-solutionizing the transition metal carbide, unlike the solid solution of the dissimilar metal element, is that both are solid-solutionized and then finely precipitated at grain boundaries or within grains to be utilized as fine precipitates. Therefore, solid solution is required at a stage before sintering (referred to as the first solid solution step). Consequently, it is necessary to adopt a method different from known methods such as arc melting for solid solution. To solid-solutionize a transition metal carbide or the like in tungsten, for example, a mechanical alloying (MA) method is desirable. The mechanical alloying method is generally a method of performing alloying and ultra-refinement of crystal grains (introduction of high-density crystal grain boundaries) by repeatedly causing severe plastic deformation of folding and rolling between powders using, for example, collision energy of balls in a ball mill in an atmosphere of inert gas or hydrogen gas and/or in a vacuum atmosphere. In the present invention, a vacuum condition containing no oxygen or nitrogen, which are impurities promoting embrittlement, is preferable. However, in MA under a vacuum, compared to MA under a gas atmosphere, the heat generated by MA is accumulated inside the container. Therefore, significant adhesion of powder to many balls and the inner wall of the container occurs, which may make it difficult to recover the mechanically alloyed (valuable) powder. Therefore, during MA execution, cold air (0°C or below) is continuously sent to forcefully cool the inside of the container. If an inert gas is used, the inert gas itself becomes an impurity, nano-sized bubbles (Ar bubbles, etc.) are formed and remain at a considerably high density in the sintered body, and these nanobubbles grow and connect during high-temperature deformation to accelerate the fracture of the sintered body, leading to difficulties in successfully

controlling the superplastic deformation of the alloy itself or potentially hindering improvements in other forms of embrittlement. Although the mechanical alloying (MA) method is preferable in this first solid solution step, other methods may be used. As another method, for example, the transition metal carbide is not solid-solutionized in the matrix metal, and therefore, in order to maintain fine crystal grains at high temperatures as thermally stable fine dispersed particles (due to the grain boundary pinning effect of the dispersed particles) rather than as fine precipitates, a method is also possible in which tungsten, a dissimilar metal element, and a transition metal carbide are each pulverized by a ball mill or the like and mixed; such a method also results in phenomena similar to the MA method.

[0035] On the other hand, for a dissimilar metal element, heating for a time sufficient for mutual diffusion required for solid solution allows the amount of dissimilar metal element shown in the equilibrium phase diagram to be solid-solutionized; thus, solid solution by heating after sintering, or solid solution during sintering is effective. However, heating must be performed within a range where the grain boundary pinning effect of the transition metal carbide functions effectively and the grain size does not coarsen. Moreover, when the atomic radius or electronegativity of the dissimilar metal element is significantly different from that of tungsten, the solid solubility limit (shown in the equilibrium phase diagram) of the dissimilar metal element is restricted, so that only a limited solid solubility is obtained with solid solution methods based on heating during or after sintering. Even in such a case, using MA makes it possible to achieve solid solubility exceeding the solid solubility limit (forced solid solution). However, if heated over a long period during or after sintering until a thermal equilibrium state is reached, the amount of the dissimilar metal element exceeding the solid solubility limit at that temperature will precipitate within grains or at grain boundaries; therefore, short-time heating and rapid cooling are required to secure a solid solubility exceeding the solid solubility limit. Furthermore, even when it is difficult to promote solid solution by heating as mentioned above, achieving solid solution before sintering using MA is effective.

[0036] In the solid solution step (first solid solution step) of solid-solutionizing the dissimilar metal element and the transition metal carbide in tungsten, first, the solid solution temperature in the solid solution step before sintering is preferably -20 to 100°C . If it is less than -20°C , there is a risk of damage to the container or balls used for MA (low-temperature embrittlement), and if it exceeds 100°C , condensation of the MA-treated powder onto the balls or inner wall of the container becomes significant. In addition, when solid-solutionizing, a vacuum condition of 10^{-8} to 100 Pa, or a pure hydrogen atmosphere (atmospheric pressure = 1.013×10^5 Pa), or an inert gas atmosphere (atmospheric pressure), or a mixed gas atmosphere of hydrogen and an inert gas (atmospheric pressure) is preferred. Maintaining an ultra-high vacuum of less than 10^{-8} Pa is difficult, while if it exceeds 100 Pa, oxidation and nitridation of the powder cannot be ignored. Next, the solid solution temperature during or after sintering (referred to as the second solid solution step) is preferably 1200°C to the temperature indicating the maximum solid solubility limit (about 3000°C) in the equilibrium phase diagram. If it is less than 1200°C , the solid solubility is insufficient, and if it exceeds the temperature indicating the maximum solid solubility limit, i.e., 3000°C , the solid solubility does not increase even if the temperature is further raised. In this specification, the "temperature indicating the maximum solid solubility limit (in the equilibrium phase diagram)" is the temperature indicating the solid solubility limit when the maximum amount of a dissimilar metal element is solid-solutionized in tungsten, which is, for example, 2945°C for osmium, 2300°C for ruthenium, 2545°C for iridium, 2240°C for rhodium, 2210°C for zirconium, and 2512°C for hafnium, all of which are below 3000°C .

[0037] Next, the powder of the superplastic alloy in which the dissimilar metal element and the transition metal carbide are solid-solutionized is sintered. Regarding the sintering method, from the perspective of merely sintering, normal pressure sintering methods or the aforementioned hot isostatic pressing (HIP) method may be used. On the other hand, for example, a spark plasma sintering method using a plasma sintering apparatus (Ed-Pas method, pulse energization method, pulse energization pressure sintering method, plasma activated sintering method, energization heating sintering method, etc.) allows sintering (to obtain a high-density sintered body) at a considerably low heating temperature in a short time (about 10 minutes) that does not reach a thermal equilibrium state at that temperature, and cooling over a wide range of cooling times is possible from rapid cooling capable of suppressing precipitation. Therefore, in the spark plasma sintering method, it is possible to perform sintering and solid solution simultaneously, and even for an alloy powder of a dissimilar metal element forcibly solid-solutionized by MA or the like, a high-density sintered body can be obtained while substantially maintaining its high solid solubility (before precipitation occurs). In any case, regarding sintering, the above-mentioned methods may be appropriately adopted in consideration of usage conditions and the like.

[0038] In the sintering step, the sintering temperature is preferably 1200 to 2000°C . MA-treated and clean alloy powder has extremely high sinterability, and sintering proceeds rapidly around 1200°C , but if it is lower than 1200°C , sintering is insufficient, and if it is higher than 2000°C , grain coarsening occurs, and the fine crystal grains or fine precipitation (nanostructure) necessary for improving embrittlement cannot be obtained. The cooling time is preferably 1 to 60 minutes down to 2000 to 600°C . A cooling time of less than 1 minute is difficult to achieve with the production method of the present invention. On the other hand, a cooling time of 60 minutes or more is inefficient. Also, when sintering, a vacuum condition of 10^{-8} to 10^{-2} Pa is preferable. Maintaining an ultra-high vacuum of less than 10^{-8} Pa is difficult, while if it exceeds 10^{-2} Pa, oxidation of the superplastic alloy may become a problem.

[0039] Although embodiments of the present invention have been described above, the present invention is not limited to these embodiments, and it goes without saying that various modes can be adopted within the scope of the matters

described in the specification, claims, and/or drawings of the present application.

EXAMPLES

[0040] Examples relating to the above-described embodiments will be explained. Note that this example is merely an example, and is not limited to what is described below, and it goes without saying that various modes can be adopted within the scope of the matters described in the specification, claims, and/or drawings of the present application.

[Production Example]

[0041] Production of Superplastic Alloy for High-Temperature Tensile Deformation Behavior Test First, as samples for testing the high-temperature tensile deformation behavior of the ternary superplastic alloy of the present invention, a total of 3 types (excluding pure tungsten) were produced: Commercial pure tungsten (ITER grade) as a comparative reference example; Tungsten-1.2 wt% titanium carbide containing only a transition metal carbide (hereinafter "W-1.2TiC"); Tungsten-1 wt% ruthenium containing only the dissimilar metal element ruthenium (hereinafter "W-1Ru"); and Tungsten-1 wt% ruthenium-1.2 wt% titanium carbide containing both a transition metal carbide and ruthenium (hereinafter "W-1Ru-1.2TiC"). The production conditions are shown in Table 1 below. Among the three types of alloys produced, the average grain sizes of the transition metal carbide-containing W-1.2TiC and W-1Ru-1.2TiC having a grain boundary pinning effect were 1.2 μm and 2.5 μm , respectively, even after heating at 1650°C for about 5 hours by GSMM, both being relatively fine. On the other hand, W-1Ru not containing a transition metal carbide had an average grain size of 8.3 μm as a result of heating at 1800°C for 2 hours under vacuum. Here, the reason for using ITER grade pure tungsten as a comparative example is as follows. Generally, crystal grains need to be fine to exhibit superplasticity, but tungsten alloys are used accompanied by severe plastic working such as hot rolling. Therefore, the structure becomes stretched and enlarged, and the manifestation of superplasticity cannot be expected. Here, as available tungsten with a fine micro-structure, ITER grade tungsten used in the International Thermonuclear Experimental Reactor (ITER) under construction in Europe is well known. Therefore, this material was adopted as a material relating to the comparative example.

Table 1: Treatment conditions for each sample

Samples	MA (r.p.m./h)	Sintering		High toughening treatment	Vacuum zero-load heat treatment
		<HIP> temp.(°C)/time(h)/pressure(MPa)	<Ed-Pas> temp.(°C)/time(h)/pressure(MPa)		
Pure Tungsten (ITER grade) Comparative	-	-	-	-	-
W-1.2TiC	360/96	1350°C/3h/196MPa	None	Done(HP)	
W-1.2TiC-1Ru	360/84	None	1600/30/40	Done(HP)	
W-1Ru	360/90	None	1600/30/41	None	1800°C/2h
Notes: MA indicates mechanical alloying. HIP indicates a hot isostatic pressing process. Ed-Pas indicates an electric discharge plasma activated sintering. GSMN indicates a grain boundary sliding based microstructural modification.					

[0042] In Table 1, "MA" indicates mechanical alloying, and "GSMM" indicates Grain boundary Sliding based Micro-structural Modification for strengthening weak random grain boundaries. Note that the pure tungsten of the comparative example is obtained by sintering high-purity powder at a high temperature in a hydrogen stream for a long time, followed by hot rolling treatment and stress relief treatment, and treatments such as mechanical alloying, GSMM treatment, and vacuum zero-load heat treatment were not performed.

[Example 1] High-Temperature Tensile Deformation Behavior Test Part 1

[0043] As Example 1, a high-temperature tensile deformation behavior test was conducted on a total of four types of samples: the three samples W-1.2TiC, W-1Ru, and W-1Ru-1.2TiC produced in the above production example, and pure tungsten of the comparative example. The dimensions of the miniaturized test pieces used are 16 mm in total length, 4 mm in width at the grip portion, and 0.5 mm in thickness (gauge portion: width 1.2 mm, thickness 0.5 mm, length 5 mm). To prevent oxidation of the test piece during the test, Ta foil (thickness 20 μm) was applied to both sides of the test piece. For the tensile test fixture, a compression load type fixture made of high-strength isotropic graphite, onto which the tensile test piece could be mounted with one touch, was used.

[0044] In the high-temperature tensile test, the initial strain rate was fixed at $5.0 \times 10^{-4} \text{ s}^{-1}$, and the flow stress (the stress at which the work-hardening rate first becomes almost zero, which roughly coincides with the peak stress) and the total elongation of each sample were calculated under vacuum (2 to $5 \times 10^{-2} \text{ Pa}$) at temperatures of 1400°C , 1600°C , and 1800°C , respectively. The results are shown in Table 2 below. Note that in Table 2, the samples of W-1.2 wt% TiC, W-1 wt% Ru, and W-1 wt% Ru-1.2 wt% TiC were denoted as "W-1.2TiC", "W-1Ru", and "W-1Ru-1.2TiC", respectively.

Table2: Results of tensile test at high temperature for each sample

		Peak stress (MPa)			Total elongation (%)		
Samples	Temp. (°C/K)	1400(1673K)	1600(1873K)	1800(2073K)	1400(1673K)	1600(1873K)	1800(2073K)
Pure Tungsten (Comparative)			95	66.7		53	34.9
W-1Ru			160.4	80		1.4	4
W-1.2TiC		538	265	82	24.9	65	105
W-1.2TiC-1Ru		364	120	50	50	293	345
Notes: The strain rate was kept constant at $5 \times 10^{-4} \text{ s}^{-1}$. It is possible that W-1Ru has fractured prior to reaching the peak stress. W-1.2TiC, W-1.2TiC-1Ru did not fracture at 1800°C since the limits of displacement attainable by the fixture were exceeded.							

[0045] In Table 2, regarding W-1Ru, it was predicted from the test results at temperatures of 1600°C and 1800°C that the test piece would exhibit brittle-fracture before reaching the peak stress at 1400°C, so the high-temperature tensile test at 1400°C was not performed. Also, regarding W-1.2TiC and W-1Ru-1.2TiC, at 1800°C, the movable range of the fixture was exceeded and no fracture was observed. That is, as stated in the background art (page 2, third paragraph), it was predicted that an elongation of 100% or more could not be expected in the test temperature range for the GSMM-treated W-1.2TiC, and because a tensile test fixture with a short stroke (about 5 mm: corresponding to about 100% total elongation) was used, it could not be elongated to fracture. On the other hand, for W-1Ru-1.2TiC, a test fixture with a long stroke (about 18 mm: corresponding to about 360% total elongation) was used, but since fracture was not observed even after reaching a total elongation of about 350% at 1800°C, the test was stopped.

[0046] As a result, regarding the peak stress, it monotonically decreased as the temperature increased in all samples. Moreover, the flow stress of W-1Ru-1.2TiC was considerably lower than that of W-1.2TiC over the entire test temperature range. On the other hand, regarding the total elongation, while some decreased (pure tungsten) or showed only a slight increase (W-1Ru) as the temperature increased, for the samples containing titanium carbide (W-1.2TiC and W-1Ru-1.2TiC), an increase in the total elongation was observed as the temperature increased. And, in W-1Ru-1.2TiC, a remarkable increase in total elongation was observed, demonstrating clear superplasticity (giant elongation) at 1800°C and 1600°C. The deformation mechanism of this superplasticity is thought to be grain boundary sliding based on the observation results of the test piece surface after fracture (see Example 3) and the observation results of the stress drop behavior during test piece fracture (brittle fracture). Furthermore, the reason why W-1Ru-1.2TiC had a lower flow stress and larger total elongation compared to W-1.2TiC seems to be that grain boundary sliding was promoted by the grain boundary segregation of Ru. On the other hand, the total elongation of W-1Ru was significantly small, much smaller even than that of pure tungsten. This significant ductility decrease (high-temperature embrittlement) of W-1Ru is thought to have occurred because grain boundary sliding was promoted by the grain boundary segregation of Ru, and the relaxation adjustment mechanism (accommodation) for the stress concentration generated at irregular/discontinuous portions such as grain boundary triple points and grain boundary ledges accompanying grain boundary sliding could not function effectively due to the large grain size, leading to grain boundary fracture due to the generation, growth, and connection of cavities. Note that the solid solution of Ru within the grains creates an atmosphere of solute elements (Ru) around moving dislocations, preventing dislocation slip (solute atmosphere drag resistance), which is thought to result in relatively easy grain boundary sliding.

[Example 2] High-Temperature Tensile Deformation Behavior Test Part 2

[0047] Next, further high-temperature tensile tests were conducted for each test piece when the tensile test temperature was fixed at 1600°C and 1350°C, temperatures at which the total elongation of the test piece did not exceed the movable range of the fixture in Example 1 above. 1350°C is equal to the temperature of the HIP treatment.

[0048] In Example 2, as test pieces, a total of 5 test pieces were prepared: 4 test pieces of the alloys W-1 wt% Ru-1.2 wt% TiC treated with Ed-Pas (spark plasma processing) under conditions of 1530°C, 40 MPa, for 0.5 hours (hereinafter referred to as "W-1Ru-1.2TiC(a)"), W-1 wt% Ru-1.2 wt% TiC treated with GSMM at 1650°C for about 5 hours (hereinafter referred to as "W-1Ru-1.2TiC(b)"), W-1.2 wt% TiC treated with HIP under conditions of 1350°C, 196 MPa, for 3 hours (hereinafter referred to as "W-1.2TiC(a)"), and W-1.2 wt% TiC treated with GSMM at 1650°C for about 5 hours (hereinafter referred to as "W-1.2TiC(b)"), and 1 test piece of pure tungsten (ITER grade) as a comparative example. Among these, W-1.2TiC(a) has basically the same composition as the tungsten alloy that exhibited superplasticity described in Patent Document 2. As for pure tungsten, it was not subjected to treatments like the other test pieces after purchase.

[0049] First, the total elongation, flow stress (peak stress), and strain rate sensitivity index (m value) of each test piece at a temperature of 1600°C at two types of initial strain rates of $5.0 \times 10^{-4} \text{ s}^{-1}$ and $5.0 \times 10^{-3} \text{ s}^{-1}$ were determined. Next, for W-1.2TiC and W-1Ru-1.2TiC, the total elongation and flow stress at a temperature of 1350°C and an initial strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$ were determined for W-1.2TiC(a) and W-1Ru-1.2TiC(a), which have a very small grain size and are expected to show the largest elongation. Furthermore, for W-1Ru-1.2TiC(a), the total elongation and flow stress at a temperature of 1600°C and a high initial strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ were determined. These results are shown in Table 3 below along with the grain sizes of the test pieces.

Table 3: Grain size and results of high temperature tensile test for four kinds of tungsten alloys (examples) and pure tungsten (comparative example)

Material	Grain size (μm)	Total elongation (%)			1350°C (0.44 Tm)	Flow stress (MPa)			m	
		1600°C (0.5 Tm)				1600°C (0.5 Tm)				1350°C (0.44 Tm)
		5 × 10 ⁴ s ⁻¹	5 × 10 ⁻³ s ⁻¹	1 × 10 ⁻² s ⁻¹		5 × 10 ⁻⁴ s ⁻¹	5 × 10 ⁻³ s ⁻¹	1 × 10 ⁻² s ⁻¹		1.5 × 10 ⁻⁴ s ⁻¹
W-1.2TiC-1Ru (a) (EdPas: 1500°C/40MPa/5h)	~0.4	-	> 305.9	> 347.6	>323.9	24.6	84.6	98.9	61.4	0.53
W-1.2TiC-1Ru (b) (GSMM: 1600°C/5h)	1~2	-	132.2		-	52.4	202.3		-	0.62
	2.5	292.9	-		-	120.0	-		-	-
W-1.2TiC (a) (HIP: 1350°C/196MPa/3h)	~0.2	-	97.2		127.2	80.3	229.7		210.3	0.50
W-1.2TiC (b) (GSMM: 1650°C/5h)	~1	-	30.7		-	153.1	323.6		-	0.50
	1.2	65.3	-		-	262	-		-	-
Pure tungsten (Comparative Example)	~10	-	54.4		-	84.3	98.0		-	0.15
		53	-		-	95.1	-		-	-

Notes: The m value (strain rate sensitivity index) indicates the slope of a double-logarithmic plot of flow stress against plastic strain rate, determined via the least squares method.
The stress exponent "n" is given by the reciprocal of the m value (i.e., n = 1/m).

[0050] Regarding the grain size, while it was about 10 μm for the pure tungsten of the comparative example, the grain size for the four alloy test pieces was at most 2.5 μm , approximately 0.2 to 2.5 μm .

[0051] Regarding the total elongation (elongation rate) at a tensile temperature of 1600°C, W-1Ru-1.2TiC, which is the ternary superplastic alloy according to the present invention, showed an elongation rate of around 300% compared to the comparative example or the W-1.2TiC system. In particular, W-1Ru-1.2TiC(a) did not break even after the total elongation reached 347% at a fairly fast strain rate of $1 \times 10^{-2} \text{ s}^{-1}$. Generally, superplasticity that manifests at a temperature below the homologous temperature of 0.5 T_m (T_m : melting point (K)) and at an initial strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ or more is called low-temperature high-speed superplasticity. Since 1600°C corresponds to 0.5 T_m of tungsten, it can be seen that W-1Ru-1.2TiC(a) exhibited low-temperature high-speed superplasticity. In addition, this alloy did not fracture even after the total elongation reached 320% at a lower temperature of 1350°C (0.44 T_m) and a normal strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$.

[0052] Regarding the flow stress (peak stress) at a temperature of 1600°C, the result was W-1.2TiC > comparative example > W-1Ru-1.2TiC at both strain rates of $5.0 \times 10^{-4} \text{ s}^{-1}$ and $5.0 \times 10^{-3} \text{ s}^{-1}$. W-1Ru-1.2TiC(a), which showed the largest elongation among W-1Ru-1.2TiC, had particularly low flow stress, which was 1/2 to 1/5 that of W-1Ru-1.2TiC(b). Also, even at a low temperature of 1350°C (0.44 T_m), the flow stress of W-1Ru-1.2TiC(a) was as low as 64.5 MPa, which was about 1/4 that of W-1.2TiC(a) though the grain size of W-1Ru-1.2TiC(a) is larger than that of W-1.2TiC(a).

[0053] As for the m value, almost the same as the total elongation, it was W-1Ru-1.2TiC > W-1.2TiC > comparative example in descending order. One of the characteristics of superplastic manifestation is that the m value is as large as $m > 0.3$, and in these test results as well, the m value of the tungsten alloy exhibiting superplasticity or considered to exhibit superplasticity showed 0.5 to 0.6. Note that, generally, a proportional relationship is not necessarily recognized between total elongation and the m value.

[0054] From the above test results, it was found that at least the ternary superplastic alloy according to the present invention exhibits superplasticity, and among them, W-1Ru-1.2TiC(a) with fine grains showed particularly large elongation and low flow stress, and was found to manifest low-temperature high-speed superplasticity. Depending on the selection of additive elements/transition metal carbides and the compounding ratio, there is a possibility of exerting further beneficial effects.

[Example 3] Confirmation of Surface After High-Temperature Tensile Test

[0055] Next, as Example 3, the surface of the test piece after the high-temperature tensile test according to Example 1 was confirmed. FIG. 1 is an image showing the surface of the test piece of W-1Ru-1.2TiC when the tensile test was performed at a temperature of 1600°C and a strain rate of $5.0 \times 10^{-4} \text{ s}^{-1}$, and FIG. 2 is an image showing the surface of the test piece of pure tungsten (comparative example) when the tensile test was performed at a temperature of 1800°C and a strain rate of $2.0 \times 10^{-3} \text{ s}^{-1}$.

[0056] In FIG. 1, the gauge portion has elongated uniformly and broken without forming a neck, and "slip lines" indicating the traces of numerous dislocation slips cannot be observed, and cavities formed by grain boundary sliding are visible near the fractured portion. Therefore, in W-1Ru-1.2TiC, it seems that giant elongation is caused by grain boundary sliding, which is the deformation mechanism of fine-grained superplasticity.

[0057] In FIG. 2, a neck is formed and broken, and "slip lines" for each crystal grain are observed. Therefore, the main deformation of pure tungsten is not grain boundary sliding but dislocation slip, which seems to correspond well with the results of pure tungsten in Table 3 (that is, the total elongation is small and the m value is 0.15 (<0.3), meaning the high-temperature deformation of pure tungsten is not superplastic deformation).

INDUSTRIAL APPLICABILITY

[0058] The superplastic (tungsten-containing) alloy of the present invention solves the poor workability associated with conventional tungsten and is applicable to various industries. In fact, aluminum alloys and titanium alloys are adopted as near-net-shape aerospace materials. The heat resistance temperature of conventional superplastic alloys is around 1000°C, and the impact of a superplastic tungsten alloy having a heat resistance performance exceeding 2000°C can be said to be innovative. Moreover, this technology is expected to be easily adaptable to molybdenum, which is in the same 6A group. The W-1Ru-1.2TiC(a) shown in the example is considered to exhibit superplasticity around 1200°C (0.4 T_m) where grain boundary diffusion required for grain boundary sliding is considered to occur.

[0059] Since the deformation resistance is remarkably small and it shows a large elongation, it excels in formability. Ultra-high temperature heaters, reflectors, etc., can be manufactured in free shapes. It can also be adopted for ultra-high temperature HIP cans.

[0060] Because the grain size is small, a smooth surface, which is a characteristic of grain boundary sliding, can be obtained even after massive plastic deformation. This is an important property for reflecting mirrors and the like, and even if additively manufactured tungsten can be realized in the future, it can maintain an advantage.

[0061] Various forming technologies for utilizing superplasticity in industry, such as "vacuum/blow forming", "hot press

forming", "deep drawing forming", "bulging", "dieless drawing", and "extrusion processing", can be applied. In addition, the combined use of Super Plastic Forming and Diffusion Bonding can be applied to the manufacture of composite materials. The technology of applying post-MA powder directly to the bonding interface and bonding is also highly feasible.

[0062] By using the superplastic alloy of the present invention, the interface is activated due to massive plastic deformation, which promotes diffusion bonding and facilitates bonding to other metals. It also easily conforms to fine unevenness. Therefore, it can be used for manufacturing composite materials. By bonding it to the surface of graphite material, high-temperature materials with little outgassing can be manufactured. Composite materials that can be called lightweight tungsten can be manufactured. Although it has high toughness, if coated on tantalum which is active at high temperatures, a tantalum composite material that is not active at ultra-high temperatures can be manufactured. If it can be bonded directly to heat-resistant ceramics, an ultra-heat-resistant ceramic metal composite material can be realized. Tungsten itself cannot be manufactured as large materials, and bonding by HIP etc. is difficult, but superplastic tungsten can be used as a bonding material for bonding tungsten together.

[0063] At present, W-1Ru-1.2TiC with a grain size of 2 to 5 μm after the grain boundary sliding treatment is used, but since the grain size before the grain boundary sliding treatment is 100 to 200 nm, if the as-sintered material (that is, W-1Ru-1.2TiC(a)) is utilized, it can also be applied to the field of microelectronics.

Claims

1. A superplastic alloy comprising tungsten, 1 or 2 or more dissimilar metal elements solid-solutionized and grain-boundary segregated in the tungsten matrix phase, and 1 or 2 or more transition metal carbides finely precipitated at grain boundaries and/or within grains, wherein the superplastic alloy contains 0.1 to 20% by weight of the dissimilar metal element and 0.2 to 5.0% by weight of the transition metal carbide relative to tungsten.
2. The superplastic alloy according to claim 1, wherein the superplastic alloy has a total elongation of 50 to 1000%.
3. The superplastic alloy according to claim 1 or 2, wherein the dissimilar metal element is selected from the group consisting of ruthenium, osmium, iridium, rhodium, hafnium, and zirconium.
4. The superplastic alloy according to claim 1, wherein the transition metal carbide is selected from a carbide of any transition metal element belonging to any of Group 4 elements to Group 6 elements in any of the 4th period, 5th period, or 6th period.

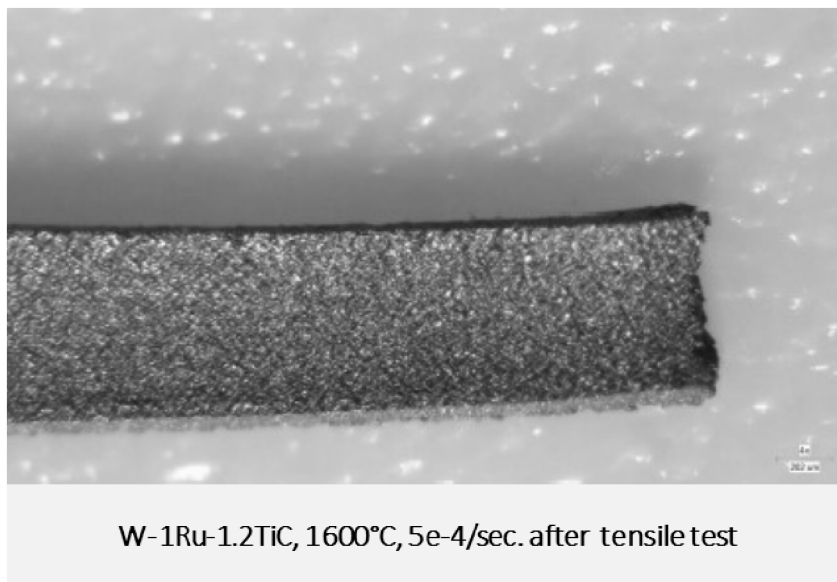


Figure 1

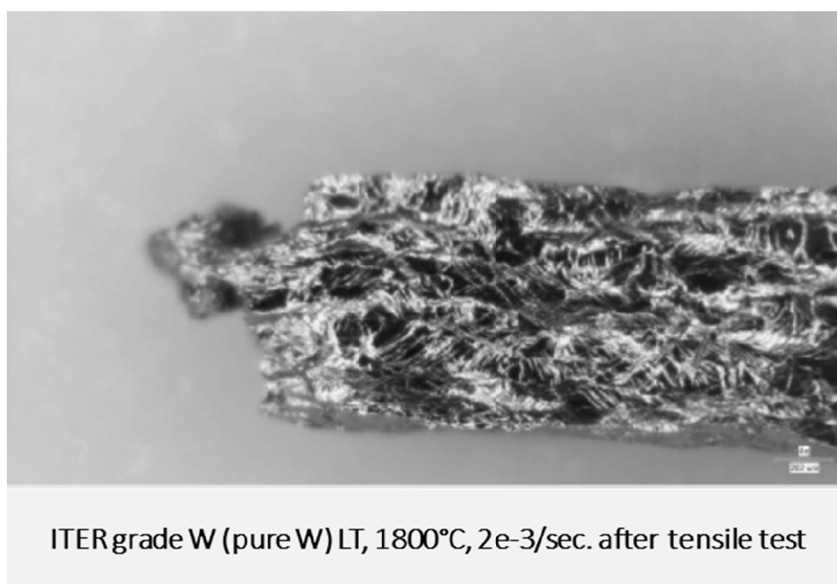


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/041266

A. CLASSIFICATION OF SUBJECT MATTER

C22C 27/04(2006.01)i; **C22C 1/04**(2023.01)i; **B22F 1/00**(2022.01)n; **B22F 3/15**(2006.01)n; **B22F 3/24**(2006.01)n;
C22F 1/00(2006.01)n; **C22F 1/18**(2006.01)n

FI: **C22C27/04** 101; **C22C27/04** 102; **C22C1/04** D; **C22F1/18** B; **C22F1/18** C; **C22F1/00** 628; **C22F1/00** 630K; **C22F1/00** 687; **C22F1/00** 691B; **B22F3/24** C; **B22F1/00** P; **B22F3/15** M

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)

C22C27/04; **C22C1/04**; **B22F1/00**; **B22F3/15**; **B22F3/24**; **C22F1/00**; **C22F1/18**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2025
 Registered utility model specifications of Japan 1996-2025
 Published registered utility model applications of Japan 1994-2025

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/018714 A1 (TOHOKU UNIVERSITY) 07 February 2013 (2013-02-07) claims, paragraphs [0001], [0018]-[0021], [0026], examples	1-4
Y	JP 2023-045532 A (KINZOKU GIKEN KK) 03 April 2023 (2023-04-03) claims, paragraphs [0028]-[0031], examples	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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“&” document member of the same patent family

Date of the actual completion of the international search

05 February 2025

Date of mailing of the international search report

18 February 2025

Name and mailing address of the ISA/JP

Japan Patent Office (ISA/JP)
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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/041266

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WO 2013/018714 A1	07 February 2013	US 2014/0147327 A1 claims, paragraphs [0001], [0038]-[0041], [0045], embodiments EP 2737966 A1	
JP 2023-045532 A	03 April 2023	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

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