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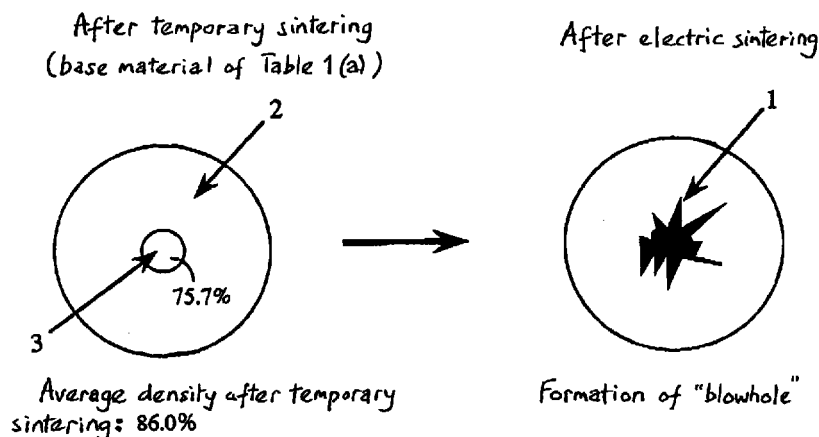
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(54) **MoSi₂-based heating element and method for manufacturing the same**

(57) There is provided an MoSi₂-based heating element having improved durability, and a method for inhibiting the formation of defects during the processes for manufacturing such an MoSi₂-based heating element. The MoSi₂-based heating element is a heating element containing 70% or more MoSi₂ in which the difference between the average density of the entire heating ele-

ment and the density of the central portion corresponding to one fifth of the diameter of the heating element (true density ratio) is 5% or less, preferably 3% or less. In the process of temporary sintering, sintering is performed in a temperature pattern of an adequately adjusted temperature raising rate.

Fig.2



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Description

TECHNICAL FIELD

[0001] The present invention relates to a heating element containing 70% or more MoSi_2 (molybdenum silicide), and to a method for manufacturing such a heating element. More specifically, the present invention relates to a heating element wherein the difference between the average density of the entire part of the heating element and the material for the heating element (base material) and the density of the central portion of the heating element corresponding to one fifth of the diameter of the heating element (true density ratio) is small, and the entire base material is uniformly sintered, and a method for manufacturing such a heating element. (The above difference will hereinafter be referred to as "difference of density".) The heating element of the present invention includes a heating element and the component of the material of the heating element consisting totally of MoSi_2 . The terms "heating element" and "material of the heating element" are herein used in this sense. The term "central portion" used hereafter means the central portion of the heating element corresponding to one fifth of the diameter of the heating element.

BACKGROUND ART

[0002] In the manufacture of a heating element comprising MoSi_2 as the main component, the material (MoSi_2) powder adjusted to have a specific particle diameter is first mixed with forming additives such as a clayey mineral (bentonite etc.), water, and an organic solvent, then the mixture is extruded into a desired shape, such as a rod.

[0003] Next, water or the organic binder, which is not required after extrusion is removed from the extruded article by drying or degreasing. The true density ratio of the article at this time is normally 50-70%.

[0004] In order to prevent this extruded article from oxidation, the article is subjected to temporarily sintering in a neutral or reductive atmosphere (also known as primary sintering) to raise the true density ratio of said article to 70-95%.

[0005] An electric current is passed in the temporarily sintered body thus obtained in an oxidizing atmosphere (including the air) for the resistance heating (electric sintering) of the temporarily sintered body. By this electric sintering, an oxide film is normally formed on the surface of the sintered body, and the true density ratio is raised to 90-100%, and finally, the member for constituting the heating element is produced. Thereafter, the heating part consisting of the above material is normally electrically welded to a terminal part for the practical use.

[0006] In prior art techniques, the relationship between the difference in density between the inner part and the outer part of the heating element normally of a rod-shape and the properties of the heating element has not been clarified, and the method for obtaining the uniform density of the sintered body in the above sequent process of temporary sintering and electric sintering has not been also clarified. The present inventors repeated experiments and obtained the following findings.

[0007] Although the effect (difference of density) is small if the diameter of the rod-shaped heating element is 9 mm or less, sintering is not uniformly performed and difference of density increases if the diameter of the heating element exceeds 9 mm, and the extremely significant problem described below arises if the diameter exceeds 15 mm. Although the diameter of a heating element as large as 24 mm is available, difference of density tends to increase as the diameter increases.

[0008] Even if the base material having difference of density due to temporary sintering is further sintered by the electric sintering process, the difference of density does not decrease, resulting in remaining difference of density in the final product of the heating element.

[0009] The heating element having difference of density between the central portion and the peripheral portion of the temporarily sintered body (primarily sintered body) will have problems of formation of a porous portion known as "blowhole" during electric sintering, or formation of cracks due to strain caused by difference in thermal expansion of the material. Also when the base materials of the same diameter are welded, since there is difference in hardness between the central portion and the peripheral portion, the problem of cracking at the welded portion arises. Also, since the resistance to oxidation at low temperatures is insufficient at the central portion of a lower density, it is easily oxidized once oxygen is mixed, becomes powdery, causing damage when the material is used in the grip part of the heating element.

[0010] It is an object of the present invention is to solve the above problems and to provide a durable heating element comprising MoSi_2 as a main component having small difference of density between the central portion and the peripheral portion of the heating element, and a method for manufacturing such a heating element. It is another object of the present invention to minimize the problem of forming a porous portion known as "blowhole" in the central portion, or forming cracks due to difference in thermal expansion of the materials of the heating element, in a series of manufacturing processes of temporary sintering and electric sintering of the materials to form the heating element. It is a further object of the present invention is to inhibit the formation of cracks when the heating element is welded, and to

prevent the damage of the heating element due to oxidation of the central portion at low temperatures.

DISCLOSURE OF THE INVENTION

5 **[0011]** The present inventors conducted repeated experiments for solving the above problems, and found that the durability of a heating element during using could be improved by controlling the density of the material for the heating element. The present inventors also found a controlling method.

[0012] According to a first aspect of the present invention, there is provided an MoSi₂-based heating element containing 70% or more MoSi₂ characterized in that the difference between the average density of the entire heating element and the density at the central portion corresponding to one fifth of the diameter of the heating element (true density ratio) is 5% or less.

[0013] According to a second aspect of the present invention, there is provided the heating element according to the first aspect characterized in that said difference between the average density of the entire heating element and the density at the central portion of the heating element (true density ratio) is 3% or less.

15 **[0014]** According to a third aspect of the present invention, there is provided a method for manufacturing an MoSi₂-based heating element characterized in that the difference between the average density of the entire heating element and the density at the central portion corresponding to one fifth of the diameter of the heating element (true density ratio) is 5% or less, comprising the steps of slowly raising the temperature of a heating element material containing MoSi₂ to a range between 1350°C and 1650°C in 5 to 15 hours, temporarily sintering the material until the difference between the average density of the entire heating element material and the density at the central portion corresponding to one fifth of the diameter of the heating element material (true density ratio) becomes 5% or less, and supplying electric power for sintering the material.

20 **[0015]** According to a fourth aspect of the present invention, there is provided the method for manufacturing the MoSi₂-based heating element according to the third aspect, characterized in that said difference between the average density of the entire heating element and the density at the central portion of the heating element (true density ratio) after temporary sintering and electric sintering of the material is 3% or less.

BRIEF DESCRIPTION OF THE DRAWINGS

30 **[0016]**

FIG. 1 shows graphs of temperature raising patterns on the temporary sintering of Examples and Comparative Examples;

FIG. 2 is an illustrative diagram showing the formation of "blowhole," a defect when temporarily sintered body having a low density is sintered by supplying electric power;

35 FIG. 3 is an illustrative diagram showing the formation of "crack," a defect when temporarily sintered body having a high density is sintered by supplying electric power;

FIG. 4 is an illustrative diagram showing the formation of "crack," a defect when two rod-shaped sintered bodies are welded by supplying electric power; and

40 FIG. 5 is a graph showing heating temperature cycles (200°C to 480°C) in the low-temperature oxidation resistance test of a sintered heating element.

Description of Symbols

45 **[0017]**

- 1 Blowhole
- 2, 5 Peripheral portions
- 3, 6 Central portions
- 50 4, 7 Cracks
- 8, 9 Two rods to be electrically welded
- 10 End surface

BEST MODE FOR CARRYING OUT THE INVENTION

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[0018] The material of the heating element comprising MoSi₂ as a main component is heated to 1400-1650°C for temporary sintering (primary sintering). The reason why difference of density occurs between the central portion and the peripheral portion of the temporarily sintered body in this process is that sintering of the peripheral portion of the

material of the heating element, where heat is easily transferred, begins earlier than the central portion.

[0019] If only the peripheral portion is early sintered in the temporary sintering process, a doughnut-shaped hard layer is shaped in the cross-section of the temporarily sintered body, causing a bridging phenomenon to occur and making it difficult to transmit sintering into the central portion. As a result, the density of the central portion of the base material is not as high as that of the peripheral portion, and difference of density occurs.

[0020] As described above, the difference of density of the base material having difference of density due to temporary sintering does not decrease even if sintering is further promoted by the electric sintering (resistance sintering) which is different in the heating system.

[0021] In order to solve this problem, sintering must be performed so as not to produce bridging during temporary sintering.

[0022] Generally in the sintering of powder, densification proceeds accompanying shrinkage in the order of the formation of a neck (shrinkage: small) → the growth of the neck (shrinkage: large) → the outward diffusion of pores.

[0023] In the sintered body of larger diameter, however, difference between temperatures occurs between the peripheral portion (in the vicinity of the surface) and the central portion because of the effect of heat transfer, resulting in change in the rate of shrinkage.

[0024] For example, when the formation of a neck begins in the central portion of the temporarily sintered body, the growth of the neck is already proceeding in the peripheral portion. Therefore, in conventional temporary sintering at a simple temperature pattern (constant-rate temperature raising, maintaining at a constant temperature, etc.), this tendency is stronger in sintered bodies of larger diameters, and bridging is easily produced.

[0025] In order to minimize this phenomenon, only a minimum required energy was supplied depending on the progress of sintering so that the movement of undesirable substances (the significant shrinkage of only the peripheral portion, etc.) did not occur. That is, after the material for the heating element containing 70% or more MoSi_2 was heated to a temperature between 1000 and 1300°C in a relatively short time, the temperature was gradually raised at least to the range between 1350 and 1650°C in 5 to 15 hours to temporarily sinter the material of the heating element so that the difference of density (true density ratio) between the central portion and the peripheral portion of the cross-section of the material decreased to 5% or less.

[0026] As a result, it is considered that sintering proceeds uniformly throughout the base material, and uniform shrinkage occurs in the direction toward the center.

[0027] Thus, the present inventors sintered the material in the temperature pattern in which the temperature raising rate was adequately adjusted in temporary sintering, and obtained a sintered body having an extremely small difference of density between the central portion and the peripheral portion of said temporarily sintered body even if the temporarily sintered body had a large diameter.

[0028] That is, a temporarily sintered body having a difference of density between the central portion and the peripheral portion (true density ratio) of said temporarily sintered body of 5% or less, furthermore, having a difference of density (true density ratio) of 3% or less was obtained.

[0029] The central portion means a central portion corresponding to one fifth of the diameter of the heating element as described above. For measuring the density of this central portion, the central portion is fixed and the peripheral portion is shaved with a lathe, and the average density when the central portion has the size of one fifth of the original size (1.8 mm in diameter if the original diameter is 9 mm) is made the density of the central portion (true density). The measurement of density is performed according to the ordinary Archimedean method.

[0030] It was found that the temporarily sintered body thus obtained is electrically sintered at about 1700°C, the density of the entire sintered body increased uniformly, and a heating element having excellent durability was obtained.

[0031] No blowholes or cracks occurred in the heating element thus obtained during the manufacturing process, and even when the rod-shaped heating element was welded, no cracks occurred due to difference of density between the central portion and the peripheral portion. The problem that the heating body was damaged from the inside, when the inside was selectively oxidized (in particular when a blowhole was produced) and became powdery, was eliminated.

[Examples and Comparative Examples]

[0032] A material for a heating element containing 70% or more MoSi_2 was extruded and degreased into a rod-shaped article having a diameter of 11 mm. The extruded article was temporarily sintered in temperature raising patterns shown in FIG. 1a to d. FIG. 1a and b are the temperature raising patterns for Comparative Examples 1 and 2, respectively; and FIG. 1c and d are the temperature raising patterns for Examples 1 and 2, respectively. The average density and the density of the central portion, and the difference of density between the average density and the density of the central portion are shown in Table 1. Here, a to d of FIG. 1 correspond to a to d of Table 1, respectively.

[0033] In Comparative Examples 1 and 2, sintered in simple temperature raising patterns shown in the temperature raising patterns of a and b in Table 1, difference of density of 5.7% to 10.3% occurred between the average density and the central portion of the temporarily sintered bodies.

[0034] Whereas in the temperature raising patterns of c and d in Examples 1 and 2 of the present invention, in which only a minimum required energy is supplied as required depending on the progress of sintering, temporarily sintered bodies having difference of density as small as 0.3% to 2.8% were obtained.

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[Table 1]

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Temperature pattern	(a)	(b)	(c)	(d)
Average density of entire base material (%)	86.0	93.5	91.2	91.5
Density at the central portion (%)	75.7	87.8	88.4	91.2
Difference between average density and the density at the central portion (%)	10.3	5.7	2.8	0.3

[0035] The density is shown in the true density ratio.

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(Test 1)

[0036] Next, the occurrence of defects when temporarily sintered bodies of a low sintering density was electrically sintered was checked.

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[0037] Using a temporarily sintered body of a true density ratio of 88% uniformly sintered (Example 3), and a temporarily sintered body of Comparative Example 1 sintered in temperature raising pattern a having difference of density between the central portion and the peripheral portion, electric sintering was performed at 1700°C for 2 minutes.

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[0038] Example 3, which was uniformly sintered in temporary sintering, was uniformly sintered also in electric sintering, and its true density ratio reached 99%. On the other hand, in the temporarily sintered body of Comparative Example 1, substances in the central portion having a lower density were attracted to the peripheral portion during electric sintering, and a blowhole 1 was formed in the central portion as FIG. 2 shows.

[0039] Numeral 2 represents the cross-section of the peripheral portion, and numeral 3 represents the cross-section of the central portion of the temporarily sintered rod-shaped body. As Table 1 shows obviously, the average density of the temporarily sintered body shown in FIG. 2 is 86.0% and the density of the central portion 3 is 75.7%.

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(Test 2)

[0040] Next, the occurrence of defects when temporarily sintered bodies of a high sintering density was electrically sintered was checked.

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[0041] Using a temporarily sintered body of a true density ratio of 92% uniformly sintered (Example 4), and a temporarily sintered body sintered in temperature raising pattern b of Comparative Example 2 having difference of density between the central portion and the peripheral portion, electric sintering was performed at 1700°C for 2 minutes.

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[0042] Although Example 4, which was uniformly sintered in temporary sintering, was intact even after electric sintering, a crack 4 was formed during temperature lowering in the temporarily sintered body of Comparative Example 2, which had difference of density, due to difference in thermal expansion between the central portion and the peripheral portion. Numeral 5 represents the cross-section of the peripheral portion, and numeral 6 represents the cross-section of the central portion of the temporarily sintered rod-shaped body.

[0043] As Table 1 shows obviously, the average density of the temporarily sintered body shown in FIG. 3 is 93.5% and the density of the central portion 6 is 87.8%.

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(Test 3)

[0044] Next, the occurrence of defects when electric welding was performed was checked.

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[0045] Two temporarily sintered bodies of Example 1, which are c of Table 1 having a relatively small difference of density (average temporarily sintered density of 91.2%, the density at the central portion of 88.4%, difference of density of 2.8%) were electrically sintered. In electric sintering, no above-described "blowhole" or crack was formed.

[0046] In order to manufacture a long heating element using the two rods 8 and 9, as FIG. 4 shows, both ends 10 were contacted with each other, and an electric current was passed and a pressure was applied for electric welding.

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[0047] Although the welding surfaces are compressed and deformed in electric welding, a crack 7 as FIG. 4 shows was formed due to difference in hardness between the central portion and the peripheral portion in the rod-shaped temporarily sintered body having difference of density.

[0048] On the other hand, when welding was performed using a sintered body after electric sintering having an extremely small difference of density (equivalent to Example 2 having a difference of density of 0.3% or below), welding

could be performed without cracks on the welded surfaces.

[0049] As seen from this, when subjected to strong deformation, a relatively small difference of density between the peripheral portion and the central portion of 2.8% is insufficient, and a difference of density of 2.0% or less, preferably 1.0% or less is desired.

(Test 4)

[0050] A low temperature oxidation resistance test was performed using an entirely uniformly sintered electrically sintered body of a diameter of 18 mm having a true density ratio of 95.0% (Example 5) and an electrically sintered body having an average density of 95.2% and the density of the central portion of 83.0% after electric sintering (Comparative Example 3).

[0051] Each of the base materials was cut into a length of 100 mm, and was subjected to repeated temperature cycles shown in FIG. 5 (200°C-480°C) in the air. In this temperature range, since the base materials excelled in oxidation resistance, and formed no SiO₂ films, Mo and Si were simultaneously oxidized, and powder was formed.

[0052] After 100 cycles, the base material having difference of density (Comparative Example 3) was considerably oxidized because its central portion has a low density and a large area contacting with oxygen, and became powdery and had no trace of its original form.

[0053] On the other hand, in the high-density base material having no difference of density, the inside was not oxidized and remained intact even though the surface layer became powdery slightly.

[0054] Therefore, if the base materials are assumed to be used as heating elements by supplying electric power, a conventional base material having difference of density between the central portion and the peripheral portion is damaged; however, the base material of the present invention is not damaged and excels in durability.

INDUSTRIAL APPLICABILITY

[0055] By temporary sintering in a temperature pattern of the present invention in which the temperature raising rate is adequately adjusted, sintering proceeds uniformly throughout the base material, and uniform shrinkage occurs in the direction toward the center, to form a sintered body having an extremely small difference of density between the central portion and the peripheral portion even in a temporarily sintered body of a large diameter. That is, the difference between the density of the central portion and the average density (true density ratio) of a temporarily sintered body can be made 5% or less, and further, 3% or less.

[0056] By final sintering of this temporarily sintered body by electric sintering at 1700°C, the density of the entire sintered body is uniformly increased, and a heating element product having an excellent durability can be obtained.

[0057] In the heating element product thus obtained, no blowholes or crack are formed in a series of the manufacturing process, and no crack are formed during welding rod-shaped heating elements due to difference of density between the central portion and the peripheral portion. Furthermore, the heating element of the present invention has advantages of having no problems in which the inside of the heating element (in particular as in the case where a blow-hole is formed) is selectively oxidized during the use, becomes powdery, and is damaged from the inside.

Claims

1. An MoSi₂-based heating element containing 70% or more MoSi₂, characterized in that the difference between an average density of the entire heating element and a density of the central portion corresponding to one fifth of the diameter of the heating element (true density ratio) is 5% or less.
2. The heating element according to Claim 1, characterized in that said difference between the average density of the entire heating element and the density of the central portion of the heating element (the true density ratio) is 3% or less.
3. A method for manufacturing an MoSi₂-based heating element characterized in that the difference between an average density of the entire heating element and a density of the central portion corresponding to one fifth of the diameter of the heating element (true density ratio) is 5% or less, characterized by comprising the steps of:

slowly raising the temperature of a heating element material containing MoSi₂ to a range between 1350°C and 1650°C in 5 to 15 hours;

temporarily sintering the material until the difference between the average density of the entire heating element material and the density at the central portion corresponding to one fifth of the diameter of the heating element material (true density ratio) becomes 5% or less; and

supplying electric power for sintering the material.

4. The method for manufacturing the MoSi₂-based heating element according to Claim 3, characterized in that said difference between the average density of the entire heating element and the density at the central portion of the heating element (true density ratio) after electric sintering of the material is 3% or less.

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Fig.1

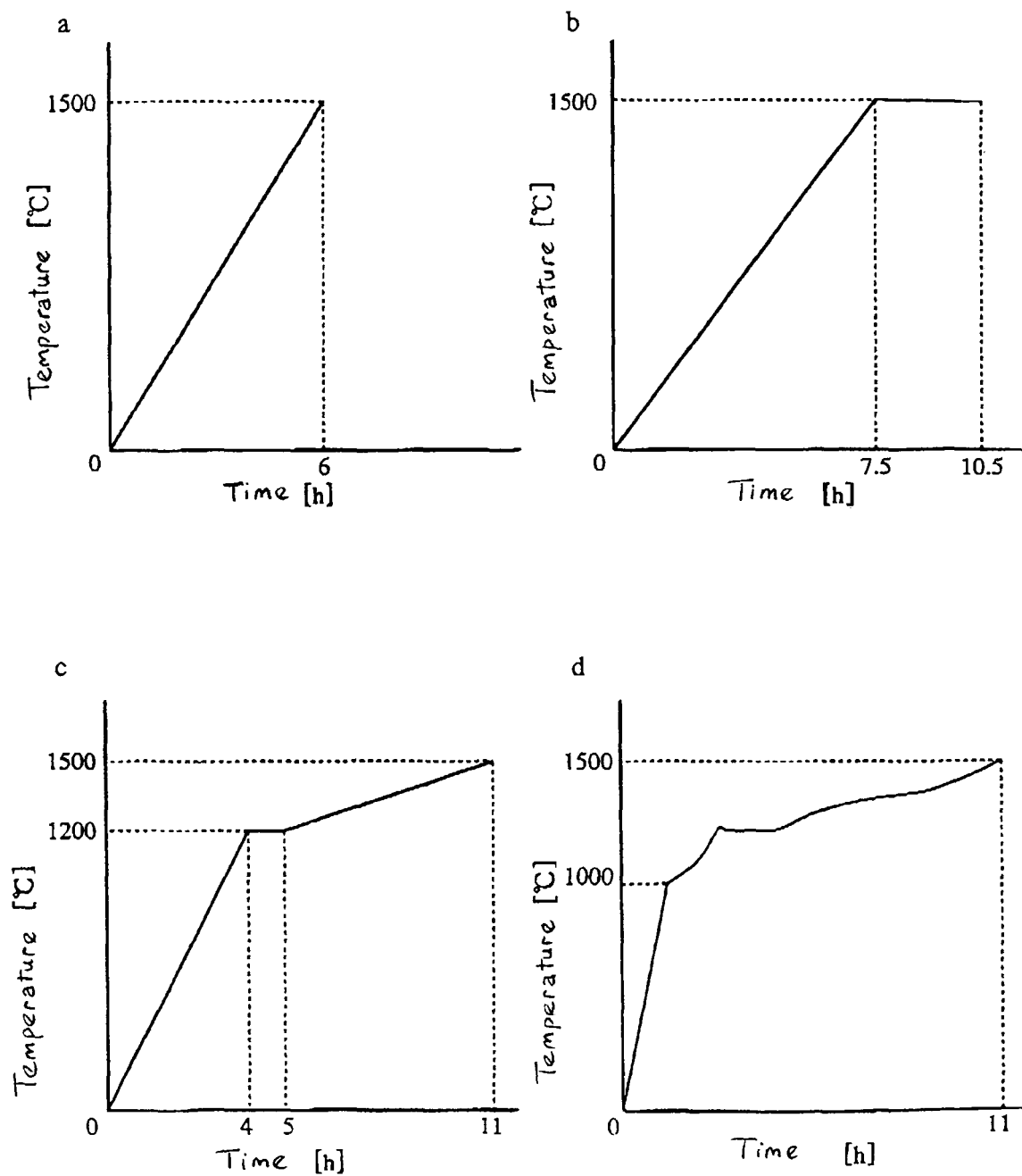


Fig. 2

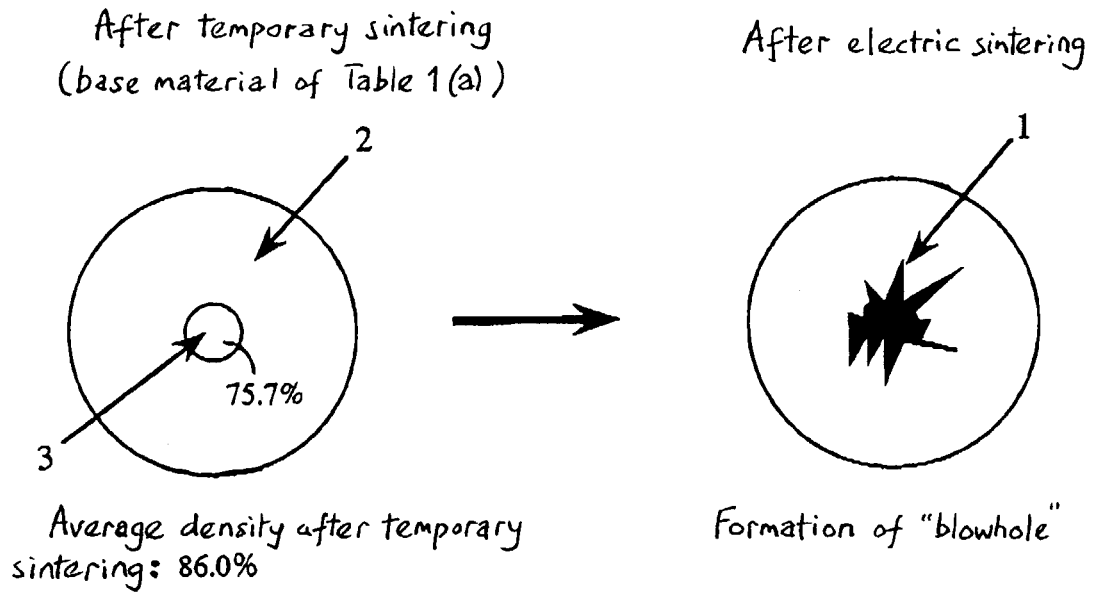


Fig. 3

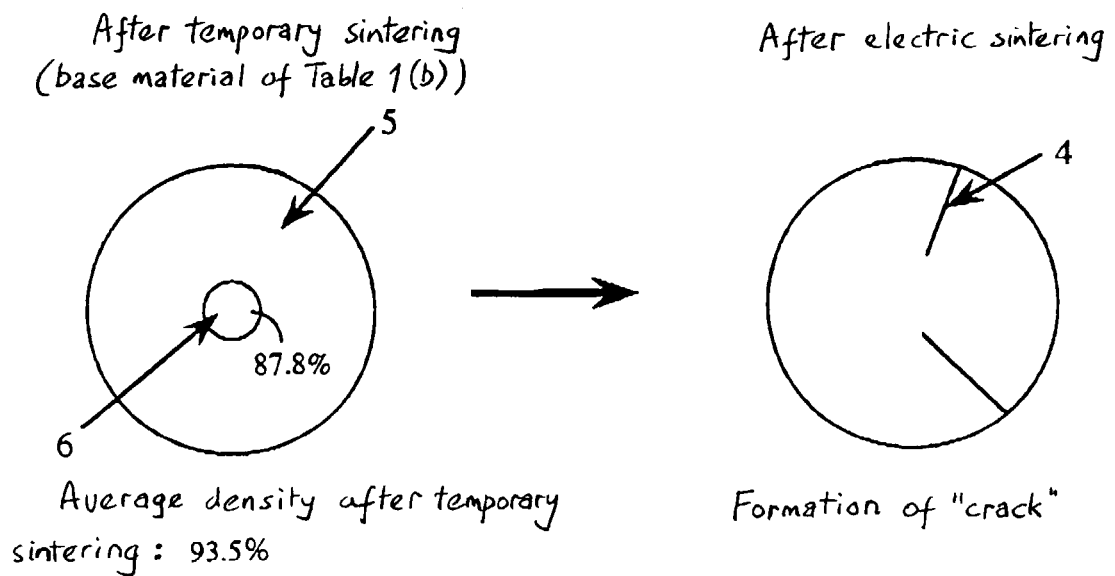
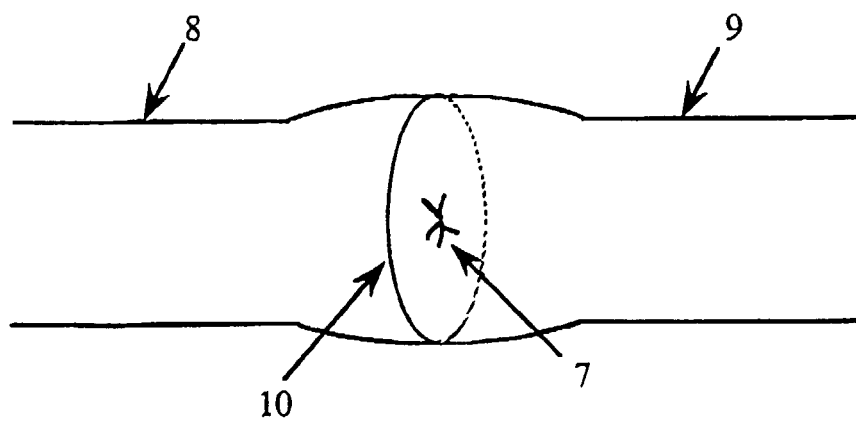


Fig. 4



Formation of "crack"

Fig. 5

