Notice

DESCRIPTION CN119638402A

A method for sintering fine-grained zinc oxide ceramics based on room temperature flash firing.

基于室温闪烧的氧化锌细晶陶瓷烧结方法

[0001]

Technical Field

技术领域

[n0001]

This invention belongs to the field of ceramic sintering technology, specifically relating to a method for sintering fine-grained zinc oxide ceramics based on room temperature flash sintering.

本发明属于陶瓷烧结技术领域，具体涉及一种基于室温闪烧的氧化锌细晶陶瓷烧结方法。

[0003]

Background Technology

背景技术

[n0002]

Currently, ceramic materials, with their excellent mechanical strength, insulation properties, and high temperature resistance, are showing broad application and development prospects and are an indispensable key material in modern society and construction development.

目前，陶瓷材料以其优异的机械强度、绝缘性能、耐高温等特性，展现出广阔的应用和发展前景，是现代社会和建设发展中必不可少的关键材料。

The manufacturing of ceramic materials is still mainly based on traditional sintering.

Traditional sintering processes involve high sintering temperatures and long sintering times, which leads to grain growth and generates huge energy consumption.

陶瓷材料的制造目前仍以传统烧结为主，传统烧结工艺烧结温度高，烧结时间长，造成晶粒生长，同时产生巨大的能耗。

Therefore, it is crucial to find a method for rapid densification of ceramic bodies.

因此，寻求陶瓷坯体快速致密化的方法至关重要。

In order to reduce energy consumption in the ceramic sintering process, various new sintering technologies, such as flash sintering, microwave sintering, and electric discharge plasma sintering, have been proposed and put into practical application.

为了降低陶瓷烧结过程中的能耗，各种新型烧结工艺，如闪烧、微波烧结、放电等离子体烧结等，被提出并投入实际应用。

[n0003]

Flash sintering is a novel ceramic sintering method that involves applying appropriate AC or DC voltage to both ends of a ceramic green body to achieve high densification within a few seconds to a few minutes. Such a short sintering time and relatively low furnace temperature mean that the energy consumption required by flash sintering technology is greatly reduced compared to traditional sintering processes.

其中，闪烧是一种新型的陶瓷烧结方法，即通过陶瓷生坯两端施加适当的交流或直流电压使得陶瓷生坯能够在短短数秒至数分钟内高度致密化；如此短的烧结时间和相对较低的炉温就意味着闪烧技术所需的能耗与传统烧结工艺相比，极大地降低了。

The investigation found that during the process of heating the sample in the furnace before the flash burn occurred, the sample absorbed a limited amount of heat, most of which was dissipated by the furnace space, resulting in a certain amount of energy waste. However, existing flash firing technology cannot get rid of the limitations of heating furnaces. Only a few green body systems with high electrical conductivity can directly apply heat to the sample, achieving room temperature flash firing and reducing energy loss.

调研发现闪烧发生之前炉体加热样品过程中，样品吸收的热量有限，大部分都被炉体空间耗散掉，造成一定的能源浪费。 然而，现有闪烧技术还无法摆脱加热炉的限制，只有少数高电导率的生坯体系将热量直接作用于样品，实现了室温闪烧，减少能量损耗。

[n0004]

To achieve room temperature flash calcination for the preparation of fine-grained ceramics, existing technologies employ methods such as generating a high-temperature electric arc under ultra-high pressure to perform room temperature flash calcination of zinc oxide, or increasing the electrical conductivity of the powder to enable rapid Joule heating of the sample by titanium dioxide powder under room temperature and high pressure conditions to obtain a dense preform. Additionally, water-assisted high-voltage room temperature conduction is used to perform Joule heating of zinc oxide preforms.

为了实现室温闪烧制备细晶陶瓷，现有技术通过加超高压产生高温电弧的方式对氧化锌实行室温闪烧，还有通过提高粉体的电导率，使得二氧化钛粉体在室温高压条件下就可以快速对样品进行焦耳加热，获得致密素胚；另外，也有利用水辅助高电压下室温导通对氧化锌素胚进行焦耳加热。

[n0005]

However, the preparation of fine-grained ceramics by high-voltage flash calcination at room temperature places high demands on high-voltage equipment. At the same time, the high-temperature electric arc generated by high voltage poses a significant safety hazard and can easily cause personal injury.

然而，采用高电压在室温闪烧制备细晶陶瓷对高压设备有较高的要求，同时高电压产生的高温电弧具有较大的安全隐患，容易造成人身伤害。

Using liquid-assisted (water or ethanol) room temperature flash calcination makes it difficult to obtain high-density, high-strength fine-grained ceramics due to the voids left by the evaporation of the liquid.

采用液体辅助(水或者乙醇)室温闪烧，由于液体的挥发遗留空隙，难以获得高致密高强度的细晶陶瓷。

By using intrinsically highly conductive powder for room temperature flash calcination, the ceramic prepared has its intrinsic high insulating properties altered.

采用本征高导电的粉体进行室温闪烧，制备的陶瓷改变了其高绝缘的本征特性。

[0008]

Summary of the Invention

发明内容

[n0006]

Based on the aforementioned shortcomings and deficiencies in the prior art, one of the objectives of this invention is to at least solve one or more of the aforementioned problems in the prior art. In other words, one of the objectives of this invention is to provide a room temperature flash sintering method for zinc oxide fine-grained ceramics that satisfies one or more of the aforementioned requirements.

基于现有技术中存在的上述缺点和不足，本发明的目的之一是至少解决现有技术中存在的上述问题之一或多个，换言之，本发明的目的之一是提供满足前述需求之一或多个的一种基于室温闪烧的氧化锌细晶陶瓷烧结方法。

[n0007]

To achieve the above-mentioned objectives, the present invention adopts the following technical solution:

为了达到上述发明目的，本发明采用以下技术方案：

[n0008]

A method for sintering fine-grained zinc oxide ceramics based on room temperature flash calcination includes the following steps:

一种基于室温闪烧的氧化锌细晶陶瓷烧结方法，包括以下步骤：

[n0009]

(1) The zinc oxide ceramic green body is placed in room temperature air and a layer of black insulating material is sprayed on the surface of the green body; positive and negative electrodes are set at both ends of the ceramic green body, and the positive and negative electrodes are connected to the power supply through wires; the ceramic green body is also wrapped with black heat-insulating material as a sleeve.

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(1)将氧化锌陶瓷生坯置于室温空气中，并在生坯表层喷涂一层黑色绝缘材料；在陶瓷生坯的两端分别设置正负电极，正负电极通过导线连接至电源；陶瓷生坯还采用黑色保温材料作为包套进行包裹处理；

[n0010]

(2) Turn on the power supply and increase the voltage until the ceramic green body generates a microcurrent in the milliampere range. Then keep the voltage constant. Under the Joule heating and heat preservation effect of the microcurrent, the temperature of the ceramic green body continues to rise.

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(2)开启电源，升高电压至陶瓷生坯产生毫安级的微电流，然后保持电压不变，在微电流焦耳热和保温作用下，陶瓷生坯的温度不断上升；

[n0011]

(3) After the temperature of the ceramic green body rises to the target temperature, the voltage is further increased so that the current of the ceramic green body climbs to the target current density value. After maintaining the target time, the power is turned off to obtain zinc oxide fine-grained ceramic.

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(3)待陶瓷生坯的温度上升至目标温度，进一步升高电压，使陶瓷生坯的电流攀升至目标电流密度值，保持目标时长后关闭电源，得到氧化锌细晶陶瓷。

[n0012]

As a preferred embodiment, step (3) specifically includes:

作为优选方案，所述步骤(3)具体包括：

[n0013]

Once the current reaches the target current density value, the power supply switches from voltage control mode to current control mode, maintains the target duration, and then shuts down.

电流达到目标电流密度值后，电源由电压控制模式切换为电流控制模式，并维持目标时长后关闭电源。

[n0014]

As a preferred embodiment, the target temperature is 150–200°C.

作为优选方案，所述目标温度为150～200°C。

[n0015]

As a preferred embodiment, the target current density value is controlled to be 100-1000 mA /mm².

作为优选方案，所述目标电流密度值控制为100～1000mA/mm²。

[n0016]

As a preferred embodiment, the target duration is 30–180 seconds.

作为优选方案，所述目标时长为30～180s。

[n0017]

As a preferred embodiment, in step (2), the electric field strength of the voltage applied to the ceramic green body is adjusted within the range of 50 to 300 V/cm.

作为优选方案，所述步骤(2)中，电压作用于陶瓷生坯的电场强度的调节范围为50～300V/cm。

[n0018]

As a preferred embodiment, in step (1), the black insulating material is one of insulating carbon black, insulating rubber, or black polyurethane.

作为优选方案，所述步骤(1)中，黑色绝缘材料为绝缘炭黑、绝缘橡胶、黑色聚氨酯中的一种。

[n0019]

As a preferred option, in step (1), the black insulation material is one of black glass wool, rock wool, mineral wool, or extruded polystyrene.

作为优选方案，所述步骤(1)中，黑色保温材料为黑色玻璃棉、岩棉、矿棉、挤塑聚苯乙烯中的一种。

[n0020]

As a preferred embodiment, in step (1), the electrode is one of a platinum electrode, a silver electrode, or a copper electrode.

作为优选方案，所述步骤(1)中，电极为铂电极、银电极、铜电极中的一种。

[n0021]

As a preferred embodiment, the ceramic green body is in the shape of a round sheet, a strip, or a dog bone.

作为优选方案，所述陶瓷生坯为圆片状、长条状或狗骨头形状。

[n0022]

As a preferred embodiment, the ceramic green body is prepared by granulation, pressing, debinding, and pre-firing, and the binder used in granulation is polyvinyl alcohol.

作为优选方案，所述陶瓷生坯采用造粒、压片、排胶、预烧制得，造粒采用的粘结剂为聚乙烯醇。

[n0023]

Compared with the prior art, the beneficial effects of this invention are:

本发明与现有技术相比，有益效果是：

[n0024]

Based on the semiconductor properties of zinc oxide, when the voltage is within a certain range during external electric field treatment, a certain amount of microcurrent (mA level) will accumulate. According to Joule's law, the process of continuous microcurrent action is the process of continuous Joule heat generation. In the traditional low-voltage flash burning process of zinc oxide materials, a heating furnace is usually used to provide a certain excitation temperature. In this process, the heat absorbed by the sample is limited, and most of it is dissipated by the furnace space, resulting in a certain amount of energy waste. At the same time, furnace heating makes the experimental setup and process cumbersome.

基于氧化锌的半导体特性，其在外电场处理过程中，当电压处于一定范围时，会有一定的微电流(mA级别)积聚；根据焦耳定律可知，微电流持续作用的过程就是电流持续产生焦耳热的过程；传统低电

压闪烧氧化锌材料的过程中，通常是采用以加热炉提供一定的激发温度，此过程样品吸收的热量有限，大部分都被炉体空间耗散掉，造成一定的能源浪费，同时炉体加热使得实验装置和过程繁琐；

[n0025]

Compared with traditional low-voltage flash zinc oxide, this invention does not require heating the furnace to provide the excitation temperature, reducing energy consumption and avoiding the cumbersome experimental setup and operation process. Compared with existing high-voltage flash technology, this invention uses conventional low-voltage sintering, which effectively ensures personal safety during experimental operations. In addition, no liquid (water or ethanol) is needed as an auxiliary material during the sintering process, avoiding the liquid evaporation and residual voids that would result in non-dense sintering.

本发明与传统低电压闪烧氧化锌相比，不需要加热炉体提供激发温度，减少能耗，避免实验装置和操作过程的繁琐；与现有的高电压闪烧技术相比，本发明采用常规的低电压烧结，有效保障了实验操作过程中人身安全；另外，烧结过程中不需要添加液体(水或者乙醇)作为辅助材料，避免了液体挥发残留空隙，造成的烧结的不致密；

[n0026]

This invention utilizes a method to reduce blackbody radiation by coating the surface of the ceramic green body with a black insulating material and then covering it with a black heat-

insulating material to prevent heat dissipation. Under the continuous action of low voltage and low current, the Joule heat generated by the zinc oxide green body sample is rapidly accumulated by the heat-insulating cover, thus slowly reaching an excitation temperature similar to that of the furnace body, thereby promoting flash firing. It has the advantages of low energy consumption, energy saving, simple equipment, and simple and efficient operation.

本发明利用降低黑体辐射的方法，将陶瓷生坯表层涂覆黑色绝缘材料，并包覆黑色保温材料，避免热量散发；利用氧化锌素胚样品在低电压的持续作用下，低电流产生的焦耳热在保温包套作用下，热量快速积聚，从而缓慢达到同炉体相近的激发温度，从而促进闪烧的发生；具有低能耗节能、设备简单、操作简单高效等优点。

[0030]

Attached Figure Description

附图说明

[n0027]

Figure 1 is a structural diagram of the encapsulated and insulated room temperature flash-burning zinc oxide according to Embodiment 1 of the present invention;

图1是本发明实施例一的包套保温室温闪烧氧化锌的构架图；

[n0028]

Figure 2 is a SEM image of the zinc oxide fine-grained ceramic obtained by room temperature sintering in Example 1 of the present invention;

图2是本发明实施例一的室温烧结得到的氧化锌细晶陶瓷的SEM图；

[n0029]

Figure 3 is the XRD pattern of the zinc oxide fine-grained ceramic obtained by room temperature sintering in Example 1 of the present invention.

图3是本发明实施例一的室温烧结得到的氧化锌细晶陶瓷的XRD图谱。

[0034]

Detailed Implementation

具体实施方式

[n0030]

To more clearly illustrate the embodiments of the present invention, specific implementation methods will be described below with reference to the accompanying drawings.

为了更清楚地说明本发明实施例，下面将对照附图说明本发明的具体实施方式。

Obviously, the accompanying drawings described below are only some embodiments of the present invention. For those skilled in the art, other drawings and other implementation methods can be obtained based on these drawings without creative effort.

显而易见地，下面描述中的附图仅仅是本发明的一些实施例，对于本领域普通技术人员来讲，在不付出创造性劳动的前提下，还可以根据这些附图获得其他的附图，并获得其他的实施方式。

[n0031]

Example 1:

实施例一：

[n0032]

The sintering method for fine-grained zinc oxide ceramics based on room temperature flash firing in this embodiment includes the following steps:

本实施例的基于室温闪烧的氧化锌细晶陶瓷烧结方法，包括以下步骤：

[n0033]

(1) Pressing the embryo;

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(1)压制生胚；

[n0034]

Polyvinyl alcohol (PVA, molecular weight 40000) was added to deionized water to make a 10wt% binder. High-purity nano zinc oxide powder was mechanically mixed with the binder and dried. 0.5g of the dried mixed powder was added to a mold and pressed into a dog bone shape under a pressure of 300MPa. The size of the blank was 20×3×2mm.

将聚乙烯醇(PVA，分子量40000)加入去离子水中制成10wt%的粘结剂，把高纯度纳米氧化锌粉末与该粘结剂进行机械混合并烘干；取0.5g的烘干混合粉体加入模具中，并在300MPa压力下压制成狗骨头形，坯体的尺寸是20×3×2mm。

[n0035]

(2) Degumming treatment;

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(2)排胶处理；

[n0036]

The pressed green body is placed in a muffle furnace and heated to 400°C at a heating rate of 2°C/min. After holding at this temperature for 2 hours, it is cooled with the furnace to obtain a zinc oxide ceramic green body.

将压制成型的生坯放入马弗炉中，以2°C/min的升温速率升温至400°C并保温2小时后随炉冷却，得到氧化锌陶瓷生坯。

[n0037]

(3) Coating electrodes;

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(3)涂覆电极；

[n0038]

Positive and negative platinum electrodes are placed at both ends of the ceramic green body; in order to reduce the contact resistance between the ceramic green body and the platinum electrodes, high-temperature silver paste is applied to both ends of the ceramic green body and baked at 650°C for 10 minutes to cure the silver paste.

在陶瓷生坯两端设置正负铂电极；为了降低陶瓷生坯与铂电极的接触电阻，在陶瓷生坯两端涂上高温银浆，并在650°C下烘烤10分钟进行银浆固化。

[n0039]

(4) Apply a black coating;

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(4)涂覆黑色涂层；

[n0040]

To better preserve heat and reduce heat loss due to microcurrent accumulation, insulating carbon black is sprayed onto the surface of the ceramic green body and baked in an 80°C oven for 30 minutes to form a non-conductive carbon black coating on the surface of the ceramic green body, as shown in Figure 1.

为了更好的保温，减少微电流积聚的热量散失，采用在陶瓷生坯表层喷涂绝缘炭黑，并在80°C烘箱中烘烤30分钟，在陶瓷生坯表层形成不导电炭黑涂层，如图1所示。

[n0041]

(5) Thermal insulation wrapping treatment;

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(5)保温包套包裹处理；

[n0042]

The ceramic green body (i.e., the sample) coated with black is wrapped in 5cm thick black glass wool (referred to as insulation wool). The positive and negative platinum electrodes are connected to the AC power supply with copper wire (i.e., conductor) with a radius of 0.5mm, as shown in Figure 1.

将涂覆黑色涂层的陶瓷生坯(即样品)包裹于5cm厚的黑色玻璃棉(简称保温棉)中，以半径为0.5mm的铜线(即导线)将正负铂电极连接到交流电源上准备进行闪烧实验，如图1所示。

[n0043]

(6) Under room temperature conditions, after the power is turned on, gradually and slowly increase the voltage across the ceramic green body to 400V (the electric field strength is the

ratio of voltage to the length of the ceramic green body, 200V/cm). When a current of 6mA (the current density is the ratio of current to the cross-sectional area of the ceramic green body, 1mA/mm²) appears in the circuit, maintain this electric field strength and current for 5 minutes. At this time, the sample temperature will continue to rise to about 150°C. Next, quickly increase the voltage to 600V (electric field strength 300V/cm). At this time, the current will increase rapidly at a rate of 15mA/s. Finally, the current will reach the preset current density value of 600mA/mm² and enter the stabilization period. The power supply will switch from voltage control mode to current control mode and maintain the sintering for 30s to achieve material densification and realize the sintering of zinc oxide ceramic material.

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(6)室温条件下，接通电源后，逐步缓慢增加陶瓷生坯两端电压至400V(电场强度为电压与陶瓷生坯长度之比，200V/cm)时，待电路中出现6mA(电流密度为电流与陶瓷生坯的截面积之比，1mA/mm²)的电流后，保持此电场强度和电流5分钟，此时样品温度不断升高至150°C左右；接下来迅速提升电压至600V(电场强度300V/cm)，此时电流以15mA/s的速度迅速增加，最终电流达到电流密度预设值600mA/mm²进入稳定期，电源由电压控制模式切换为电流控制模式，保持30s材料烧结致密，实现氧化锌陶瓷材料的烧结。

[n0044]

As shown in Figure 2, the zinc oxide sintered at room temperature in this embodiment has high density and grain size in the range of 0.5-2μm;

如图2所示，本实施例室温烧结的氧化锌具有较高的致密度，晶粒尺寸在0.5-2μm范围内；

[n0045]

As shown in Figure 3, the zinc oxide ceramic after encapsulation and heat preservation flash firing in this embodiment does not produce any impurity phases.

如图3所示，本实施例的包套保温闪烧后的氧化锌陶瓷没有杂质相产生。

[n0046]

Example 2:

实施例二：

[n0047]

The difference between the room temperature flash sintering method for zinc oxide fine-grained ceramics in this embodiment and that in Embodiment 1 is as follows:

本实施例的基于室温闪烧的氧化锌细晶陶瓷烧结方法与实施例一的不同之处在于：

[n0048]

Based on the size of the zinc oxide ceramic green body, the corresponding target temperature is 150-200°C, the target current density is controlled at 100-1000mA/mm², the target holding time is 30-180s, and the adjustment range of the electric field strength applied to the ceramic green body is 50-300V/cm, which can be determined according to the actual application requirements.

根据氧化锌陶瓷生坯的尺寸，相应的目标温度为150～200°C，目标电流密度值控制为100～1000mA/mm²，保持的目标时长为30～180s以及电压作用于陶瓷生坯的电场强度的调节范围为50～300V/cm，可根据实际应用需求进行确定；

[n0049]

Other steps can be found in Example 1.

其它步骤可以参考实施例1。

[n0050]

Example 3:

实施例三：

[n0051]

The difference between the room temperature flash sintering method for zinc oxide fine-grained ceramics in this embodiment and that in Embodiment 1 is as follows:

本实施例的基于室温闪烧的氧化锌细晶陶瓷烧结方法与实施例一的不同之处在于：

[n0052]

Insulating carbon black can also be replaced by insulating rubber or black polyurethane.

绝缘炭黑还可以替换为绝缘橡胶、黑色聚氨酯中的一种；

[n0053]

Black glass wool can also be replaced by one of rock wool, mineral wool, or extruded polystyrene.

黑色玻璃棉还可以替换为岩棉、矿棉、挤塑聚苯乙烯中的一种；

[n0054]

The platinum electrode can also be replaced by either a silver electrode or a copper electrode;

铂电极还可以替换为银电极、铜电极中的一种；

[n0055]

Ceramic green bodies can also be in the form of round pieces or strips;

陶瓷生坯还可以为圆片状或长条状；

[n0056]

To meet the needs of different applications;

满足不同应用的需求；

[n0057]

Other steps can be found in Example 1.

其它步骤可以参考实施例1。

[n0058]

Given that there are numerous embodiments of the present invention, the raw materials and amounts involved can be selected within a limited range according to actual needs, and the experimental data of each embodiment are extensive and numerous, it is not suitable to list and describe them one by one here. However, the content to be verified and the final conclusions obtained in each embodiment are similar.

鉴于本发明方案实施例众多，涉及的原料及用量均可在限制的范围内根据实际需求进行选择，各实施例实验数据庞大众多，不适合于此处逐一列举说明，但是各实施例所需要验证的内容和得到的最终结论均接近。

Therefore, the verification content of each embodiment will not be described one by one here.

故而此处不对各个实施例的验证内容进行逐一说明。

[n0059]

The above description is merely a detailed explanation of preferred embodiments and principles of the present invention. For those skilled in the art, there may be changes in specific implementation methods based on the ideas provided by the present invention, and these changes should also be considered within the scope of protection of the present invention.

以上所述仅是对本发明的优选实施例及原理进行了详细说明，对本领域的普通技术人员而言，依据本发明提供的思想，在具体实施方式上会有改变之处，而这些改变也应视为本发明的保护范围。