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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
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Señor
SUPERINTENDENTE DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E. S. D.

Re: PI.-**SEB S.A.**-Solicitud de Patente de Invención para **"RECUBRIMIENTO CERÁMICO CON PROPIEDADES MEJORADAS DE RESISTENCIA AL RAYADO Y CONDUCCIÓN TÉRMICA"**.-Expediente número **13-258.452**.-

Yo, **ALICIA LLOREDA RICAURTE**, mayor, vecina de esta ciudad, identificada con la cédula de ciudadanía número 39.690.713 de Usaquén, abogada titulada e inscrita, obrando como Representante Legal en Bogotá para todos los asuntos relativos a la propiedad industrial de la sociedad **LANDERS & CÍA. S.A.S.**, organizada y existente de conformidad con las leyes de Colombia y domiciliada en Medellín, Antioquia, Colombia, dentro del término legal y en el ejercicio de lo dispuesto por el Artículo 42 de la Decisión 486 de 2000 de la Comisión de la Comunidad Andina, por medio del presente escrito procedo a **Complementar la Oposición** presentada el 04 de Agosto de 2015, en los siguientes términos:

1. **SOLICITUD DE PATENTE DE INVENCIÓN CONTRA LA CUAL SE PRESENTA OPOSICIÓN.**

La solicitud de Patente de Invención contra la cual se presenta Oposición corresponde a aquella contenida en el Expediente número **13-258.452** y cuyo solicitante es **SEB S.A.** Dicha solicitud de Patente de Invención fue radicada ante esa Superintendencia el 31 de Octubre de 2013, apareció publicada en la Gaceta de Propiedad Industrial No. 726 de 08 de Mayo de 2015, y el término para presentar Oposiciones fundamentadas vence el 05 de Noviembre de 2015.

2. **PRETENSIONES.**

(i) Que se declare la falta de novedad y/o nivel inventivc del objeto reivindicado en la solicitud de Patente de Invención que obra en el Expediente No. **13-258.452** y que se refiere a un "**RECUBRIMIENTO CERÁMICO CON PROPIEDADES MEJORADAS DE RESISTENCIA AL RAYADO Y CONDUCCIÓN TÉRMICA**", con fundamento en la existencia de los siguientes documentos del arte previo: US 6372,290 (D1) →" *Method of making a temperature and scratch resistant anti-sticking coating* ", EP 0810301 (D2) → "*Ceramic heat insulating layer and process for forming same* " y EP 2141138 (D3) → " *Method of repairing a thermal barrier coating and repaired coating formed thereby*", que divulgan un método para realizar un recubrimiento resistente ante la temperatura y al rayado, una capa de cerámica de aislamiento térmico, el proceso para la formación de la misma y un método de reparación de un recubrimiento de barrera termal y además el recubrimiento reparado y formado de este mismo, en donde estas invenciones presentan características técnicas similares a las de la solicitud de Patente de Invención Colombiana CO 13-258.452.

(ii) Que con fundamento en dicha declaración, se niegue el privilegio de patente de invención para el objeto reivindicado en dicha solicitud de Patente que obra en el Expediente No. **13-258.452**.

3. **LEGÍTIMO INTERÉS.**

Mi representada, la sociedad **LANDERS & CÍA. S.A.S.**, es una empresa ubicada en la ciudad de Medellín, Antioquia, Colombia, dedicada al diseño, fabricación y comercialización de productos para la preparación, cocción y consumo de alimentos, por lo que la concesión de la solicitud de patente colombiana CO 13-258.452 impediría que empresas como **LANDERS & CÍA. S.A.S.** fabriquen recubrimientos cerámicos con propiedades mejoradas de resistencia al rayado y conducción térmica que son plenamente conocidos en el estado de la técnica y que son utilizados en el sector desde hace varios años.

4. **FUNDAMENTOS DE LA OPOSICIÓN.**

Según la definición de la reivindicación 1 de la solicitud de patente colombiana CO 13-258.452, esta se encuentra dirigida a proteger un recubrimiento cerámico, destinado a ser aplicado sobre un soporte metálico y que está en la forma de al menos una película continua que tiene un espesor entre 2 y 100 µm, donde dicho recubrimiento comprende una matriz que incluye al menos un polialcóxido metálico y en la que se dispersan partículas de las que, el diámetro oscila entre 0,01 y 50µm, además porque dichas partículas son de un material que tiene una conductividad térmica igual o superior a $10W^{-1}.K^{-1}$ y una densidad aparente de a lo sumo 3,9 g/cm^3.

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Ahora bien, es pertinente mencionar que la reivindicación 21 de la solicitud de patente colombiana CO 13-258.452 se basa en un método para la fabricación de un recubrimiento cerámico sobre al menos una superficie de un artículo de metal, donde dicho método comprende las siguientes etapas:

(i) Posiblemente, un tratamiento de superficie de dicha superficie con el fin de mejorar la adherencia de la capa de sol-gel aplicada en la etapa (iv);

(ii) La preparación de una composición sol-gel con:

- Por lo menos un precursor de sol-gel seleccionado de entre los alcóxidos metálicos,
- Al menos partículas que tienen un diámetro que oscila entre 0,01 y 50 µm y que están de un material que tiene una conductividad térmica igual o superior a 10 $W^{-1}.K^{-1}$ y una densidad aparente de máximo 3,9 g/cm^3, y preferiblemente una dureza Mohs igual a o mayor que 9, y
- Posiblemente (a) al menos un aceite de silicona, reactivo o no, y/o (b) al menos un agente relleno estructurante y/o (c) al menos un pigmento.

(iii) La hidrólisis de dicho precursor de sol-gel mediante la introducción de agua y un catalizador, ácido o base, seguido de una reacción de condensación parcial para la obtención de una composición sol-gel;

(iv) La aplicación sobre dicha superficie de al menos una capa de dicha composición sol-gel SG obtenida siguiendo la etapa iii);

(v) Posiblemente secado de dicha capa a una temperatura comprendida entre 40 y 90°C; y

(vi) Curar dicho artículo recubierto siguiente la etapa (iv) o (v) a una temperatura comprendida entre 150°C y 400°C.

De igual manera es importante resaltar que a lo largo del capítulo reivindicatorio, se reivindican una serie de modalidades preferidas, en donde caracterizan a la matriz del recubrimiento cerámico porque comprende aceite de silicona reactivo o no reactivo, polialcoxilato metálico, óxidos metálicos, sílica entre otros elementos que son necesarios para formar dicho recubrimiento cerámico.

Ahora, de acuerdo a la descripción de la solicitud de patente en cuestión, la presente invención incorpora materiales de relleno con una baja densidad aparente y una alta conductividad térmica. Además de lo anterior, la patente de SEB S.A. menciona el desarrollo de un proceso sol-gel con el fin de obtener un recubrimiento cerámico en el que hay partículas de densidad aparente baja, a la vez de caracterizarse por tener buenas propiedades de conductividad térmica. Por lo tanto la patente de invención colombiana CO-

13-258.452 se refiere a un recubrimiento cerámico, destinado a ser aplicado sobre un soporte de metal y estar en forma de una película continua, donde dicho recubrimiento comprende una matriz que incluye al menos un polialcóxido metálico y en la que se dispersan partículas de diámetros entre 0.01 y 50 µm, asegurando propiedades mejoradas de resistencia al rayado y conducción térmica.

Con base en todo lo anterior y, a partir de la atenta lectura de las divulgaciones adicionales realizadas en la solicitud de patente colombiana CO 13-258.452, atentamente me permito presentar ante ese Despacho una serie de consideraciones técnicas que, basadas en la comparación con la información de documentos del arte previo, demuestran **el incumplimiento de los requisitos de patentabilidad de Novedad y de Nivel Inventivo** establecido en los Artículos 14, 16 y 18 de la Decisión Andina 486 de 2000:

4.1. En primer lugar, y después de una detallada revisión y comparación de los documentos **US 6372,290 (D1)** y **EP 0810301 (D2)**, me permito señalar que la información divulgada en los mismos resuelve, de manera similar, el mismo problema técnico al que la invención de SEB S.A. intenta dar solución. Efectivamente, tanto los documentos D1 y D2 como la patente colombiana CO 13-258.452, comparten el objetivo de proporcionar como producto final un recubrimiento con ciertas propiedades mejoradas que hacen que la superficie donde son aplicados sean resistentes térmicamente, además de presentar resistencia a abrasiones. De igual manera es pertinente resaltar que el método descrito por la invención Colombiana, objeto de estudio comprende etapas que ya son conocidas por las invenciones del estado del arte.

De manera general, tales recubrimientos y métodos de producción junto con la invención de SEB S.A. hacen uso de etapas concretas para la fabricación de recubrimientos cerámicos que posteriormente serán aplicados a superficies metálicas. Así entonces, me permito resaltar que dichos recubrimientos se caracterizan por tener propiedades similares. En consecuencia, me permito manifestar que **dicho recubrimiento cerámico con propiedades mejoradas de resistencia al rayado y conducción térmica es plenamente conocido en el estado de la técnica anterior.**

4.2. En referencia al documento **US 6372,290 (D1),** se considera que particularmente dicho documento corresponde al **arte previo más cercano** a la invencion ya que revela una sustancia portadora de una estructura molecular inorgánica y un revestimiento superficial producido por la aplicación de un tratamiento de sustancias y de calor **con características técnicas estructurales y funcionales similares** al recubrimiento cerámico con propiedades mejoradas de resistencia al rayado y conducción térmica de SEB S.A. Además de esto, me permito manifestar que este documento de igual manera revela un método de producción, así como los usos adecuados para el revestimiento de la superficie.

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Con referencia a lo anterior, me permito mencionar que el objeto de la invención descrita en D1, se centra en proporcionar una superficie metálica, materiales portadores cerámicos y vítreos con propiedades antiadherentes contra el agua y/o aceite a base de materiales orgánicos o emulsiones de agua/aceite. Dichos materiales se caracterizan por ser sustancialmente más resistentes a la temperatura y al rayado que los recubrimientos convencionales de Politetrafluoroetileno (PTFE) o silicona ya conocidos por el estado del arte.

Con base en lo anterior, me permito mencionar que dicha anterioridad establece que las excelentes propiedades antiadherentes de PTFE y los sistemas de superficie de silicona que evitan que los alimentos se quemen, son particularmente notables en los moldes y utensilios para hornear y cocinar. Sin embargo, dado que estos recubrimientos son relativamente gruesos, sus temperaturas máximas útiles son por debajo de 250°C- 300°C. En conexión con lo anterior, este recubrimiento debido a su grosor, sufrirá daños significativos cuando se use de forma frecuente, perdiendo sus características principales en las áreas que ha sido dañada.

Por lo tanto una desventaja de la superficie de revestimiento conocida en el estado del arte, es aquella en donde es necesario aplicar agentes de unión a una superficie resistente al rayado y a la temperatura antes de la aplicación del recubrimiento orgánico. Entonces, mientras dicho recubrimiento no se adhiera a una superficie específica, la propiedad de resistencia a altas temperaturas y resistencia al rayado resultante se perderá en la superficie del material de soporte, en donde la superficie de este modo, se daña mecánicamente, y la propiedad antiadherente de la superficie se deteriorará.

Así entonces y con el fin de dar solución a las anteriores desventajas, el documento D1 se centra en un material de soporte y un revestimiento superficial, en la que el revestimiento superficial, en sus capas moleculares superiores consta de un compuesto de moléculas inorgánicas del material de soporte y moléculas orgánicas de una sustancia aplicada. De igual manera, esta invención propone un nuevo método de producción de una superficie antiadherente sobre una superficie portadora mediante la aplicación de una sustancia orgánica que contiene silicona, seguidamente de un tratamiento térmico para la reticulación de las moléculas de la superficie y de la sustancia mediante la eliminación por evaporación de cualquier exceso de sustancia, donde se da la formación de una nueva red de moléculas.

Así entonces, la superficie resistente al rayado y a altas temperaturas, particularmente presenta resistencia incluso contra temperaturas en exceso de 300°C. Por otro lado, es pertinente mencionar que la sustancia orgánica que forma la capa con las redes de silicona, se aplica a esta superficie, en donde la capa molecular superior de la superficie del sustrato y los grupos moleculares de unión reactivos reaccionan químicamente con las moléculas de la sustancia orgánica y forman un intervalo de transición con respecto a la superficie

orgánica sin generar la formación de una capa orgánica pura. Dentro de este intervalo de transición, los grupos moleculares que reaccionan son sustituidos por átomos o moléculas hidrófobas, oleofóbicos o grupos de moléculas.

Ahora bien, la sustancia orgánica aquí mencionada contiene silicona, la cual a su vez contiene polidimetilsiloxanos o polidimetilsiloxanos con extremos especiales, tales como fenilo, vinilo, silanol, amino, epoxi, o carbinol terminales. Además de esto, los líquidos de silicona son sustancialmente **no reactivos o modificables por grupos reactivos,** que adicionalmente contienen componentes adicionales tales como resinas de silicona, disolventes orgánicos, agua, emulsionantes, compuestos de limpieza, aceleradores de reticulación, sistemas de encapsulación y similares.

En conexión con lo anterior, es evidente que el recubrimiento divulgado por esta anterioridad contiene silicona al igual que el recubrimiento cerámico de SEB S.A. en conde el recubrimiento cerámico de SEB S.A. **contiene aceite de silicona,** el cual representa 0.01 a 2% en peso de dicho recubrimiento además de **caracterizar dicho componente químico por presentar una viscosidad dinámica a 20°C de 0.02 a 0.05 Pa.s. y por ser reactivo o no reactivo.** Entonces, es claro que existen similitudes estructurales y funcionales tanto en la invención de SEB S.A. como en la evidenciada por el documento D1.

Adicionalmente, me permito mencionar que el método definido en el documento D1 se basa principalmente en (a) **aplicar a una superficie un recubrimiento** de una sustancia orgánica que comprende redes de silicona (b) **tratar mediante calor el material portador** (e cual puede ser cerámico) con el recubrimiento de sustancia orgánica. De igual manera, el método descrito en la reivindicación 21 de la invención de SEB S.A , comprende dentro de sus etapas **aplicar sobre una superficie la composición que pretende reclamar** para posteriormente **curar el artículo recubierto a temperaturas entre 150°C Y 400°C.**

Así entonces, me permito resaltar que el objetivo de mejorar propiedades como la conductividad térmica y a resistencia a altas temperaturas y al rayado de ciertos materiales, al igual que un método que comprende etapas similares que conllevan a dicha mejora ya es totalmente conocido en el estado del arte. Por lo anterior, la invención de SEB S.A, al presentar las mismas características esenciales de la invención divulgada en e documento D1 ***no es considerada novedosa.***

4.3. Ahora bien, respecto al documento **EP 0810301 (D2)**, me permito señalar que éste documento de igual manera desvirtúa la novedad de la solicitud de SEB S.A., ya que divulga una capa de aislamiento térmico cerámica formada sobre un material a base de hierro con o sin una capa de unión interpuesta entre ellos. Dicha capa, comprende partículas de agregado de mineral nefelina, un aglutinante compuesto por partículas de sílice y un polímero de metaloxano, en donde el aglutinante llena espacios entre las

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partículas de agregado y une químicamente a las partículas de agregado entre sí con el material de base o a la capa de unión.

Teniendo en cuenta lo anterior, me permito resaltar que tanto el recubrimiento de la invención de SEB S.A., como la capa del documento D2 presentan características idénticas como:

- Su recubrimiento es cerámico.
- Dicho recubrimiento cerámico está destinado a ser aplicado sobre un soporte metálico.
- La matriz del recubrimiento contiene sílice.
- Uno de los pasos fundamentales del método para la elaboración de dicho recubrimiento o capa es calentar el material métalico que tiene la suspensión aplicada.
- Ambas invenciones presentan resistencia a daños mecánicos.

Por lo tanto, es evidente que la esencia de la invención es exactamente la misma, por lo que me permito resaltar que es plenamente conocido para una persona versada en la materia la existencia de distintos recubrimientos cerámicos con características idénticas a las de la invención de SEB S.A.

Así entonces, me permito resaltar que el objetivo de mejorar propiedades como la conductividad térmica, la resistencia al calor y al rayado de ciertos materiales, al igual que un método que comprende etapas similares que conllevan a dicha mejora ya es totalmente conocido en el estado del arte. Por lo anterior, de igual la manera la invención de SEB S.A, al presentar las mismas características esenciales de la invención divulgada en el documento D2 ***no es considerada novedosa.***

De esta forma, es de gran importancia aclarar que una invención novedosa es aquella que no ha sido conocida previamente en el ámbito mundial. En otras palabras una invención se considera nueva cuando no está comprendida en el estado de la técnica antes de la presentación de la solicitud de patente.[1]

Consecuentemente, es importante resaltar que tanto el documento D1 como el documento D2, permiten evidenciar la existencia de métodos y recubrimientos que ayudan a mejorar las propiedades químicas, físicas y mecánicas de artículos específicos que se basan en el mismo principio del recubrimiento cerámico de SEB S.A. Así entonces, me permito manifestar que de ninguna manera la invención de SEB S.A. es novedosa y merece el privilegio de patente, ya que previamente en el estado del arte existían enseñanzas con características fundamentales y similares a la aquí estudiada.

[1] http://api.sic.gov.co/WEB/assets/pdf/Guia_patentes.pdf

Entonces, conociendo que el estado de la técnica describe recubrimientos con propiedades mejoradas y métodos para fabricarlos, se considera que para la persona del oficio normalmente versada en la materia, la invención de SEB S.A. **carece de novedad.**

4.4. Por otro lado, me permito manifestar que de igual manera tras una atenta revisión de los documentos **D2** y **D3,** es evidente que la información divulgada en los mismos resuelve, de manera similar, el mismo problema técnico al que la invención de SEB S.A. intenta dar solución.

Efectivamente, tanto los documentos D2 y D3 como los documentos **WO2010043826**, **EP 2412846** y **EP 2206801**, comparten el objetivo de proporcionar artículos con recubrimientos de sustancias químicas que permitan obtener propiedades mejoradas de resistencia al rayaco y conducción térmica. De manera general, tales invenciones junto con la de SEB S.A. hacen uso de métodos para la fabricación de recubrimientos con características puntuales que son resistentes mecánicamente a las agresiones de uso, resistentes al calor y además permiten una óptima conducción térmica.

4.5. En referencia al documento D2, se considera que particularmente dicho documento corresponde al arte previo más cercano a la invención ya que provee una capa de aislamiento térmico cerámica formada sobre una material de base a base de hierro con o sin una capa de unión interpuesta entre ellos. Ésta capa de aislamiento térmico comprende particularmente partículas de agregado del mineral nefelina, un aglutinante compuesto por partículas de sílice y un polímero de metaloxano, en donde el aglutinante llena los espacios entre las partículas de agregado y une químicamente a las partículas de agregado entre sí con el material de base o a la capa de unión.

Por otro lado, me permito resaltar que la capa de aislamiento térmico de cerámica puede comprender alternativamente: partículas de agregado de sienita, un aglutinante compuesto por partículas de sílice y un polímero de metaloxano, en donde esta vez el aglutinante interviene entre las partículas de agregado para dejar vacíos y unir químicamente a las partículas de agregado entre sí con el material de base o a la capa de unión. De igual manera, esta anterioridad divulga un proceso de formación de la capa aislante de calor de cerámica que comprende las siguientes etapas: (a) mezclar las partículas de agregado de nefelina, un aglutinante de un alcóxido, un organosilicasol, y un medio de dispersión para formar una suspensión, (b) la aplicación de la suspensión, ya sea en la superficie de un material de base a base de hierro, o en cualquier capa de unión formada sobre la superficie y (c) **calentar** el material a base de hierro que tiene la suspensión aplicada.

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Con esta descripción, es posible observar que tanto la anterioridad D2 como la invención de SEB S.A. **implementan un recubrimiento o capa cerámica sobre un material metálico,** en donde dicho recubrimiento o capa están compuestos por al menos **un alcóxido, silica, óxidos inorgánicos**, entre otros componentes.

Continuando con las similitudes, es pertinente resaltar que ambos métodos se ven en la necesidad de aplicar la suspensión o recubrimiento en un material metálico para posteriormente calentar dicho elemento. Ahora bien, la principal diferencia entre la capa divulgada en el documento D2 y el recubrimiento cerámico de SEB S.A. consiste esencialmente en la matriz de componentes utilizada en donde la capa cerámica de aislamiento térmico de D2 comprende específicamente el mineral nefelina.

Ahora, es importante mencionar que, a pesar de que el documento D2 es el estado de la técnica más cercano a la invención del SEB S.A., el documento D3 de igual manera revela características técnicas esenciales acerca del método para formar un recubrimiento con propiedades térmicas mejoradas.

4.6. Con relación al documento **EP 2141138 (D3)**, me permito resaltar que éste divulga una composición de revestimiento y método de reparación adecuado para la reparación de revestimientos de barrera térmica (TBC, por sus siglas en inglés), y en particular TBCs basados en composiciones de alúmina-sílice. El método incluye la **preparación de una composición de recubrimiento que contiene partículas sólidas de cerámica**, partículas cerámicas huecas, y **un aglutinante precursor de sílice, en donde se aplica la composición de revestimiento sobre una superficie de un artículo** expuesto por una abertura, por ejemplo, la espalación del TBC, para posteriormente hacerlo reaccionar con el aglomerante y así producir un recubrimiento de reparación que cubre el área de la superficie del artículo. El revestimiento de reparación resultante contiene partículas de cerámica sólidas y partículas cerámicas huecas en una matriz de sílice formada por la descomposición térmica del aglutinante.

De lo anterior, es claro que el método descrito en esta anterioridad al igual que el mencionado previamente por el documento D1, en donde es fundamental (a) **aplicar a una superficie un recubrimiento** de una sustancia orgánica que comprende redes de silicona (b) **tratar mediante calor el material portador** (el cual puede ser cerámico) con el recubrimiento de la sustancia orgánica, define etapas similares al método de fabricación de un recubrimiento cerámico sobre un artículo de metal definido por SEB S.A.

Teniendo en cuenta lo anterior y de acuerdo a la descripción de la invención de SEB S.A., *"(...) los recubrimientos de sol-gel impartidos por estos documentos no permiten resolver el problema técnico de la presente invención, que consiste en mejorar conjuntamente y eficazmente la resistencia mecánica de un recubrimiento de sol-gel de bajo espesor y su homogeneidad térmica durante el uso."*. Sin embargo, en la descripción

no se menciona un efecto técnico sorprendente atribuido a la matriz de recubrimiento ni se demuestra que los revestimientos o capas del estado del arte previo que incluyen el mismo principio de mejoramiento de propiedades químicas y mecánicas de artículos, como por ejemplo los de cocción culinarios, sean ineficientes en cuanto a su función y manejo.

Con base en esto y en las diferencias previamente descritas, me permito manifestar que la persona normalmente versada en la materia, a partir de las enseñanzas del documento D2, puede modificar la capa de aislamiento térmico cerámica formada sobre una material metálico, teniendo en cuenta el método de los documentos D1 y D3, además del proceso de síntesis sol-gel plenamente conocido en el estado del arte, en donde a partir de una solución a base de un precursor en fase líquida, el recubrimiento es convertido en un sólido a través de un conjunto de reacciones químicas a baja temperatura.

Frente a lo anterior, es importante señalar que la persona versada en la materia podría idear un recubrimiento cerámico, a partir de la combinación de elementos y etapas esenciales de métodos de fabricación del mismo ya conocidos en el estado del arte, tal y como pretende la invención de SEB S.A.

Entonces, me permito manifestar que la persona del oficio normalmente versada en la materia, conociendo que el estado de la técnica describe utensilios culinarios con revestimientos cerámicos con propiedades químicas, físicas y mecánicas mejoradas, podría combinar las enseñanzas de los documentos D1, D2 y D3 y así lograr obtener un producto que reúna esencialmente las mismas características técnicas de la invención de SEB S.A. En este sentido, dicho revestimiento cerámico con propiedades mejoradas de resistencia al rayado y conducción térmica se considera obvio porque la esencia tanto del producto como del método descrito en la invención de SEB S.A. no presenta características nuevas a las ya conocidas.

Consecuentemente, **me permito declarar que la invención reclamada en la patente colombiana 13-258.452 de SEB S.A. carece de Nivel Inventivo en vista de las enseñanzas de los documentos D1, D2 y D3.**

4.7. Por otro lado, es relevante mencionar que documentos como **EP2412846**, **WO2010043826,** y **EP2206801** de igual manera divulgan invenciones similares a la aquí estudiada, **incluso en donde el recubrimiento también es sintetizado por el proceso sol-gel**. Concretamente, el documento EP 2412846 define que artículos como una sartén están provistos de un revestimiento de sol-gel que cubre una de las caras del mismo, en donde dicho revestimiento **tiene forma de una película continua hecha de un material que incluye una matriz formada por polialcoxilato metálico** y 5% en peso de óxido metálico dispersado en la matriz con respecto al peso total del recubrimiento, en donde este revestimiento comprende un pigmento termocrómico y termoestable que hace que el artículo sea resistente a altas temperaturas.

LLOREDA CAMACHO &CO
Calle 72 No. 5-83 Piso 5, Bogotá, D.C. Tel: 6069700 Fax 6069701

Por su parte el documento WO2010043826 divulga un elemento de cocción que comprende **un recubrimiento vítreo con propiedades mejoradas de resistencia al impacto y obtenido mediante la síntesis sol-gel, cuya matriz contiene al menos un polialcoxilato metálico**, un óxido metálico en forma de agregado coloidal con un tamaño inferior a una micra o 400 nm finamente dispersado en la matriz. Dicho óxido metálico puede ser de sílice, alúmina, óxido de cerio, óxido de zinc, óxido de vanadio y óxido de circonio, preferiblemente sílice coloidal y alúmina.

De igual manera, me permito resaltar que el documento EP 2206801 se refiere a un compuesto para utensilios de cocina en la preparación de alimentos, que **comprende un elemento de soporte de material metálico, cuya superficie exterior se encuentra cubierta por una capa protectora vítrea.**

Además de lo anterior, es de gran importancia hacer énfasis en que empresas como Whitford, DuPont™ y Weilburger Coatings, comercializan en el mercado de distintos países, una serie de recubrimientos adheridos a superficies de elementos culinarios como cacerolas, ollas y cubiertos que mejoran notablemente las propiedades de adherencia, conductividad, termoestabilidad, resistencia a abrasiones, y durabilidad que cumple con altos estándares de calidad.

Adicionalmente, me permito resaltar que existen diferentes solicitudes de patentes hechas por parte de estas entidades, que protegen recubrimientos con matrices novedosas que se caracterizan por otorgarle al elemento culinario propiedades físicas, químicas y mecánicas mejoradas, lo que da solución a diversas desventajas en elementos culinarios ya existentes. Por lo tanto, el recubrimiento cerámico definido en la invención de SEB S.A. de ninguna manera puede ser novedoso o tener nivel inventivo, ya que elementos culinarios con características como las que el recubrimiento cerámico de SEB S.A. presenta, son plenamente conocidos por el estado del arte e incluso son productos comercializados hoy en día.

Así entonces, es importante resaltar que la mención de los anteriores documentos y entidades permite evidenciar que existen dispositivos de cocción en el estado de la técnica anterior que se basan en el mismo principio de contener revestimientos cerámicos que permiten al dispositivo tener mayor resistencia a abrasiones y a altas temperaturas.

Consecuentemente, **me permito declarar que la invención reclamada en la patente colombiana 13-258.452 de SEB S.A. carece tanto de Novedad como de Nivel Inventivo.**

5. **SOLICITUD.**

En razón de los anteriores argumentos, atentamente solicito a ese Despacho declarar que la solicitud colombiana CO **13-258.452** no cumple con los requisitos de patentabilidad exigidos en los Artículos 14, 16 y 18 de la Decisión 486 de 2000 y por lo tanto proceder a rechazar dicha solicitud de patente.

6. **ANEXOS.**

Anexo al presente memorial me permito presentar:

(a) Copia del documento de patente US 6.372,290 (D1),

(b) Copia del documento de patente EP 0810301 (D2),

(c) Copia del documento de patente EP 2141138 (D3)

7. **NOTIFICACIONES.**

Reitero que la suscrita como apoderada de dicha sociedad, recibirá notificaciones en la Secretaría de ese Despacho y en la Calle 72 No. 5-83, Piso 6o. de la ciudad de Bogotá, D. C.

Del Señor Superintendente,

ALICIA LLOREDA RICAURTE
T.P. 53.215

(Anexo 9)

7



US006372290B1

(12) **United States Patent**
Berkenkoetter et al.

(10) **Patent No.: US 6,372,290 B1**
(45) **Date of Patent: Apr. 16, 2002**

(54) **METHOD OF MAKING A TEMPERATURE AND SCRATCH RESISTANT ANTI-STICKING COATING**

(75) Inventors: **Herbert Berkenkoetter**, Oelde; **Friedel Kaup**, Guetersloh; **Thomas Kruempelmann**, Guetersloh; **Walter Mangen**, Guetersloh; **Ulrich Sillmen**, Guetersloh, all of (DE)

(73) Assignee: **Miele & Cie. GmbH. & Co.**, Guetersloh (DE)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/254,520**

(22) PCT Filed: **Jul. 3, 1998**

(86) PCT No.: **PCT/EP99/04126**

§ 371 Date: **Mar. 5, 1999**

§ 102(e) Date: **Mar. 5, 1999**

(87) PCT Pub. No.: **WO99/02463**

PCT Pub. Date: **Jan. 21, 1999**

(51) **Int. Cl.**[7] **C23C 16/00**

(52) **U.S. Cl.** **427/255.18**; 427/255.13; 427/255.14; 427/387; 427/409; 427/419.4; 427/419.5

(58) **Field of Search** 428/428, 429, 428/447, 448, 450; 427/255.13, 255.14, 255.18, 255.19, 387, 409, 419.4, 419.5

(56) **References Cited**

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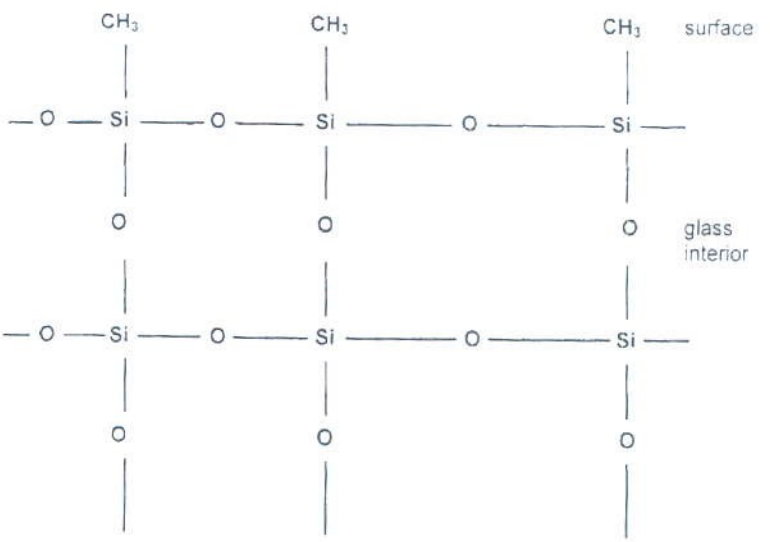
* cited by examiner

Primary Examiner—D. S. Nakarani
(74) *Attorney, Agent, or Firm*—Karl Hormann

(57) **ABSTRACT**

The invention relates to a carrier material having an inorganic molecular structure and a surface coating produced by applying a substance and by heat treatment. The invention also relates to a method for the production and to the appropriate uses of said surface coating. Carrier materials made of glass, metal or ceramic should be provided with a surface coating with anti-sticking properties against water-based and/or oil-based organic materials or water-oil emulsions while exhibiting at the same time essentially better temperature-resistant and anti-scratch characteristics than conventional PTFE or silicon coatings. The requirements are met by an inventive surface coating consisting of a combination of inorganic molecules of the carrier material and organic molecules of an applied substance on the uppermost molecular layer of said coating. In order to produce such a surface, an inorganic substance with silicone-like networks is initially applied. Subsequently, heat treatment is carried out, whereby the temperature and duration of said treatment are chosen in such a way that the purely organic coating applied is fully decomposed and/or removed so that a combination of inorganic molecules of the carrier material and organic molecules of the applied substance is formed. The appropriate carrier material with the inventive surface coating can be advantageously use above all in household appliances and kitchenware.

11 Claims, 3 Drawing Sheets



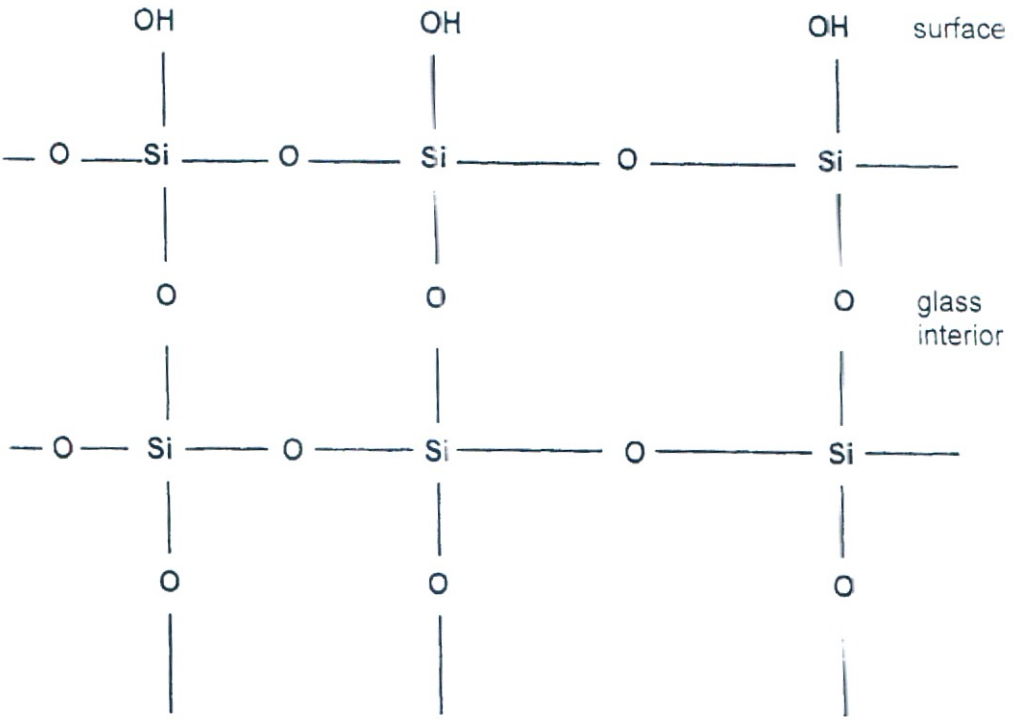

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Fig. 1

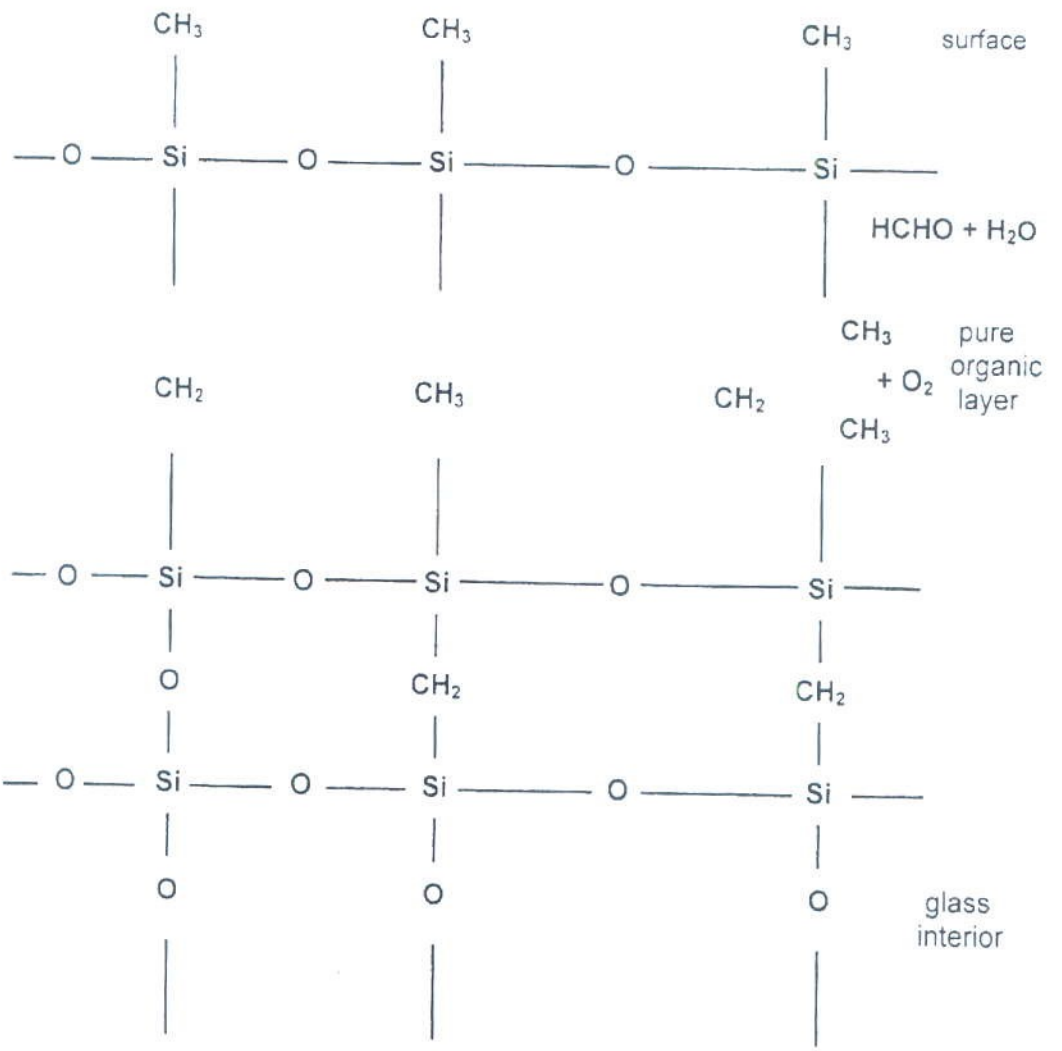

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Fig. 2

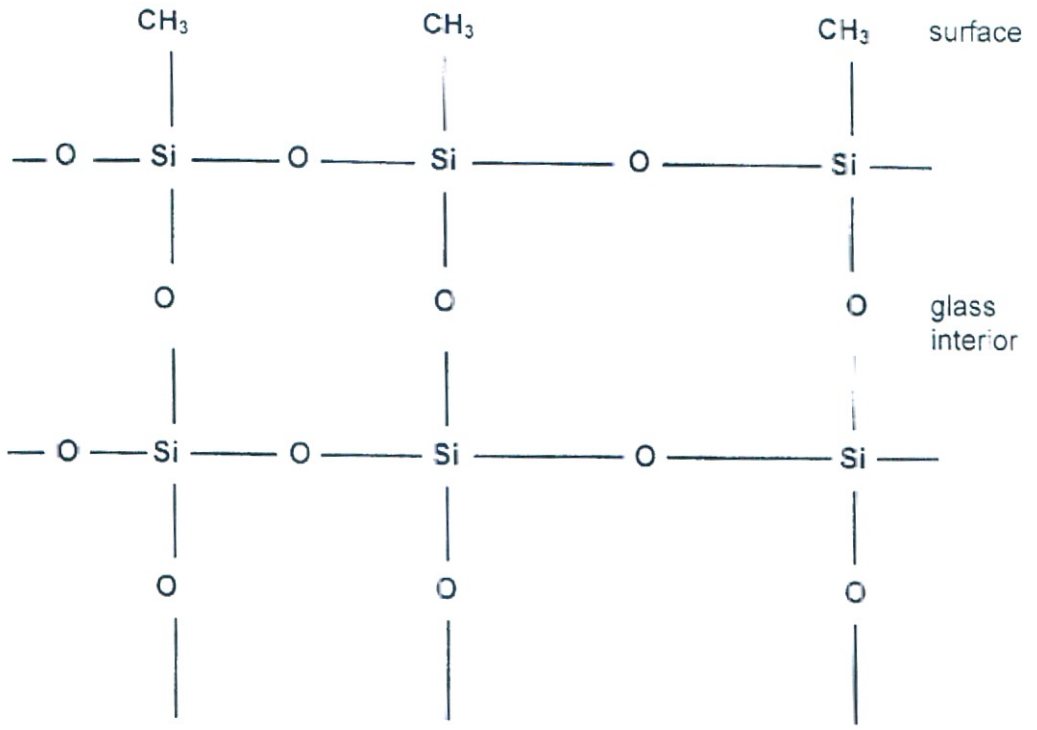

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Fig. 3

METHOD OF MAKING A TEMPERATURE AND SCRATCH RESISTANT ANTI-STICKING COATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a carrier substance of an inorganic molecular structure and provided with a surface coating produced by application of a substance and heat treatment. Furthermore, the invention relates to a method of producing, as well as suitable uses for, the surface coating.

2. The Prior Art

For providing a scratch and temperature resistant surface, it is generally known to use surfaces of enamel, glass, glass ceramics or similarly structured systems, i.e. networks particularly of silicon dioxide and/or other metal oxides. Also, metal surfaces such as, for instance, steel, stainless steel, aluminum, and chromium, which while inferior as regards these properties, are, nevertheless, acceptable compared to surfaces of organic materials. The above mentioned properties are especially needed in surfaces used in the field of household appliances.

Also, surfaces coated with polytetrafluoroethylene (Teflon®) or silicone are known which are distinguished by their non-stick properties. The excellent non-stick properties of PTFE and silicone-like surface systems against burnt-in food are particularly noticeable in baking pans, cooking and baking utensils. However, since those coatings are relatively thick their maximum useful temperatures are below 250° C. to 300° C. Moreover, because of its relatively thick coating such a surface will suffer significant damage when used frequently and abusively, and will lose its favorable charateristics in those areas which have been damaged. A further disadvantage of the known surface coating is that bonding agents have to be applied to a scratch and temperature resistant surface prior to the application of the organic coating. While non-sticking is the resultant new property, the scratch and temperature resistance of the surface of the carrier material will be lost. While in its new state a non-stick surface requires no scrubbing or scouring to be cleaned, its non-stick properties will deteriorate after several uses particularly close to their maximum useful temperature, and cleaning is possible only with greater effort. The surface will thus be damaged mechanically, and the non-stick property of the surface will deteriorate.

Bonding with water or oil based materials or with water/oil emulsions is accomplished by bonding forces between molecular groups of the surface and corresponding atoms/molecules of the bonded organic material. Typical reactive molecular groups of the surface are, for instance, OH groups which to a great extent define the surfaces of silicone based systems. The OH groups at the carrier surface are either absorbed by bonding the coating, or they escape from the system as a result of chemical reaction. The remaining few reactive molecular groups of the coating material then define the non-stick characteristics. A substantial draw back is that such relatively thick surface coating behaves very much like organic materials of low scratch and temperature resistance. The properties of the underlying inorganic layer cannot permeate to the outer surface.

OBJECTS OF THE INVENTION

It is, therefore, an object of the invention to provide a surface on metallic, ceramic and glass-like carrier materials with non-stick properties against water and/or oil based organic materials or water/oil emulsions while at the same time being substantially more temperature and scratch resistant than conventional coatings of PTFE or silicone.

SUMMARY OF THE INVENTION

In accordance with the invention the object is accomplished by a carrier material and a surface coating in which the surface coating in its uppermost molecular layers consists of a compound of inorganic molecules of the carrier material and organic molecules of an applied substance. In another advantageous embodiment, the invention proposes a novel method of producing a non-stick surface on a base carrier surface by applying to the surface an organic substance including silicone-like networks followed by a heat treatment for cross-linking the molecules of the carrier surface and of the substance and removing, by evaporation, any excess substance whereby a new network is formed of surface and substance molecules. Other objects will in part be obvious and will in part appear hereinafter.

Aside from a scratch and temperature resistant surface the advantages attainable by the invention are, in particular, that the surface is resistant even against temperatures in excess of 300° C. and that it has non-stick properties with respect to water and/or oil based organic materials or water/oil emulsions. On a molecular plane the surface of the substrate has at least local network structures with at least one layer of molecules of reactive bonding molecular groups being bonded to the uppermost network plane. A layer-forming organic substance with silicone-like networks is applied to this surface. In the upper molecular layer of the substrate surface close to the surface the reactive bonding molecular groups react chemically with the molecules of the organic substance and form a transitional range with respect to the organic surface without leading to the formation of a pure organic layer. Within this transitional range the reacting molecular groups are substituted by hydrophobic and/or oleophobic atoms or molecules or groups of molecules. If the non-stick coating does not reject another surface when in use, the latter surface will define the surface characteristics of the entire system. In accordance with a further embodiment unintended organic protective films on the non-stick surface can be removed without loss of the non-stick properties. Except in the mentioned transitional range between inorganic and organic substances the growth of an organic layer is prevented at the end of or during a heat treatment process above the decomposition temperature of the silicone-like substance. As a result, the organically modified uppermost plane of the inorganic substrate remains. An advantageous field of application of surfaces modified in this manner relates to enameled surfaces of substrates. The modified surface is used especially in connection with electrical household appliances or kitchen furniture. The use of a modified surface imparts especially advantageous properties to a glass-ceramic cooking surface, baking, roasting, broiling and/or microwave oven and/or to components to be placed into a roasting chamber and/or to baking, roasting, cooking containers, for instance, cooked food containers.

BRIEF DESCRIPTION OF THE SEVERAL DRAWINGS

The novel features which are considered to be characteristic of the invention are set forth with particularity in the appended claims. The invention itself, however, in respect of its structure, construction and lay-out, as well as manufacturing techniques, together with other objects and advantages thereof, will best be understood from the following

description of preferred embodiments when read with reference to the appended drawings, in which:

FIG. 1 depicts a silicon oxygen network of a conventional glass surface or of a surface of a glass-like material (prior art);

FIG. 2 depicts the silicon oxygen network of FIG. 1 with a conventional surface coating (prior art); and

FIG. 3 depicts the silicon oxygen network of FIG. 1 with a surface modified in accordance with the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

In use, the properties of a surface are always defined by its final exposed coating. A surface made, i.e. modified in accordance with the invention and a method for producing a surface thus modified will hereafter be described in connection with a substrate surface similar to glass or ceramic. The description is not, however, intended to exclude the modification of other types of substrate surfaces.

FIG. 1 depicts a silicon oxygen network of a conventional glass or glass-like carrier material without coating. Typically, molecular groups similar to the OH groups shown are formed at the surface of such a carrier material. By a chemical reaction, for instance by condensation, these molecular groups may be made to react with aqueous and/or water based coatings on the surface. They also react strongly with vegetable and/or animal fats. In use this leads to the formation on the surface of strongly bonded residues which can only be removed with difficulties.

FIG. 2 depicts a network which exhibits structures resulting from applying to the carrier material an inherently permanent organic coating. Though an improved non-stick effect is obtained by low reactive molecular groups (CH_3) formed at the outer molecular layers, yet the inherently permanent relatively thick organic coating is prone to suffer from mechanical action.

FIG. 3, by contrast, depicts a network produced in accordance with the invention in which even the uppermost molecular layer is formed by substantially non-reactive molecules of the CH_3 group immediately adjacent to which there is positioned the molecular structure of the carrier material.

Hence, the terminal or final molecular groups shown in FIG. 1 as OH groups are substituted by substantially non-reactive molecular groups of the applied substance. The methyl groups depicted here have hydrophobic and oleophobic properties. The OH groups of the prior art may, however, also be substituted by phenyl groups. It is essential that the organic modification of the surfaces, i.e. the incorporation of carbon (C atoms) is restricted to the uppermost layer of the surface, but in any event to the upper several layers. In this manner, the thermal and mechanical characteristics of the inorganic material will be substantially maintained. In connection with the modified surfaces it was experimentally proved that, for instance, methyl groups are retained in the SiO nets even at very high temperatures (>500° C.).

The reactive bonding molecular groups forming the uppermost molecular layer of the initial substrate surface are substituted by atoms, molecules or molecular groups which are hydrophobic, oleophobic or both hydrophobic and oleophobic. The surface of the modified system consists of only one, but in no case more than very few net layers in which substantially non-reactive molecular groups are bound. Hence, an organically modified inorganic system is produced only in the uppermost layer of the surface. Any excess organic substance is substantially dissolved during the heat treatment of the coating process, without forming a permanent layer of its own. The surface produced by this process may be mechanically cleaned with impunity by the same means as a glass or ceramic surface. It is stable at temperatures up to about 500° C. and possesses non-stick characteristics.

The organic substance may be applied in various ways. In a manner known per se the surface of the carrier material which exhibits a local network structure is brought into contact at a low temperature with at least one silicone-like component or thermal decomposition products thereof, in liquid form or in a gaseous phase. This leads to cross-linking within the liquid with the reactive bonding molecular groups of the carrier material. Thereafter, for a time dependent upon the thickness of the layer, the changed surface (including the carrier) is tempered at a temperature above the decomposition temperature of the silicone-like network. The organic layer of the cross-linked silicone-like liquid which may have become too thick during the coating process will evaporate and will thus decompose pyrolytically. Only the one required molecular layer of this substance with non-stick properties remains, which connect to the silicone oxide or other metal oxide net or to the exterior, e.g., OH groups. The preferred tempering temperature is a temperature in the range between 300° C. and 700° C. The silicone-like liquid contains polydimethylsiloxanes or polydimethylsiloxanes with special ends, such as phenyl, vinyl, hybrid, silanol, amino, epoxy, or carbinol ends. The silicone liquids are substantially non-reactive or they are modified by reactive groups. The silicone-like liquid may contain additional components such as, for instance, silicone resins and organic solvents and thinners, water, emulsifiers, cleaning compounds, cross-linking accelerators, encapsulation systems and the like.

Another way of modifying the surface of the carrier material is preferably carried out by heating the substrate surface, as well as the oven into which the surface has been placed for modification, to about the same elevated temperature. Following this, a liquid or solid silicone-based substance is evaporated, preferably in a separate chamber, and the substance converted into a gaseous state is brought into contact with the surface of the substrate. To this end, the temperature of the substrate surface is to be chosen to be higher than the evaporation temperature of the silicone-like substance. At the same time, the temperature of the substrate surface should be higher than the decomposition temperature of the silicone-like substance. Since the temperature of the source (evaporator) is lower than that of the surface to be modified (sink) the formation of "thicker" layers on the surface to be modified is prevented. In the event, but for the concentration gradient between source and sink no accumulation would occur. Raising the temperature of the surface to a temperature above the decomposition temperature of the organic substance will additionally result in preventing organic layers from accumulating. Only the desired organic modification of the inorganic surface will remain. The temperature of the evaporator lies between 150° C. and 600° C., whereas the temperature of the surface is between 300° C. and 700° C.

The carrier material provided with the surface coating in accordance with the invention is particularly useful either where frequent cleaning is unavoidable or where improved corrosion protection is necessary against thermal corrosion or chemical attacks (laundry lye, salt water). A modified surface is of special advantage in household appliances, for instance cooking surfaces of glass ceramics, baking,

roasting, broiling and/or microwave ovens, including parts thereof, baking, roasting and cooking vessels with enameled, chromium-plated or stainless steel surfaces, washing machine drums, or dish washing sinks of stainless steel. In addition, many advantages such as, for instance, repelling chemicals (e.g. starch from laundry) are derived from a modified surface in clothes mangles having aluminum parts, aluminum oxide with or without anodized hardened surfaces and/or laundry iron surfaces. Scarcely any lime or calcium sediments are formed on tubular heaters the carrier material surfaces of which have been modified, for instance, in water boilers, washing machines and dish washers. Such a modification may also be applied, however, to glass and glass-like carrier materials, such as, for instance, bottles for beverages, laboratory glasses, glass, glass ceramic and ceramic surfaces, systems of a similar chemical structure, such as glass shop counters, glass door panels in general, shop windows, large surface three-dimensional glass structures of vapor vent hoods, (kitchen) cupboard windows or on plain metal and coated metal surfaces, such as, for instance, any kind of stainless steel or aluminum surfaces. In many individual cases a surface of a carrier material of the kind described supra is structured more smoothly which results in reduced sliding friction and often, because of it, lower noise.

At least the interior surface of the coated carrier material of cooking, roasting, baking or frying vessels of enameled steel, glass, glass ceramic, ceramic, porcelain and the like (e.g. pots or cake forms) which comes into contact with the food to be prepared should be treated by one of the processes described above. Of course, it would be best if their other surface would be additionally treated in accordance with the process. Also, in door glass panes with IR reflecting properties of known tin dioxide coatings, the tin dioxide reflector may be provided with an organically modified surface coating made be the same process as silicone dioxide and other glass or glass ceramic-like metal oxide surfaces.

Surfaces suitable for modification may be applied to glass, glass ceramic, ceramic surfaces and systems of a similar chemical structure on electric household appliances such as, for instance, glass service panels, door panes in general, display windows, large surface 3D glass structures on venting hoods, doors of (kitchen) cupboards and so forth. Components of a warming chamber made of glass, glass ceramic, ceramic or related materials, such as baking sheets, drip pans, removable side and surface panels, lamp covers, interior door panes of a stove, such as a baking oven or a microwave apparatus. At least one side, preferably all sides, however, of their surface are organically modified for the above described non-stick properties. In cooking, roasting, baking and frying vessels of glass, glass ceramic, ceramic, porcelain and the like (e.g. pot or cake forms) at least the inner surface which comes into contact with the food to be processed should be modified as described above. It is best, however, to modify their exterior surfaces as well. IR reflectors based upon known tin dioxide coatings of door panes may be organically modified as well by the same process as silicone dioxide and other glass, and ceramic-like metal oxide surfaces.

The enamel as described above may also be modified in a pyrolysis oven provided with an oven chamber and components coated with pyrolysis enamel at a pyrolytic cleaning cycle at conventional temperatures between 400° C. and 600° C. The modified non-stick layer is also resistant against the usual pyrolytic temperatures of 480° C. The interior door pane should be modified to be stick resistant. Preferably the pyrolysis oven is provided with a glass door including a glass ceramic interior pane without a structural frame and, preferably, the glass ceramic interior pane should also be modified. Its temperature resistance makes it possible after each cleaning cycle to regenerate its modified surface followed by an exposure to a high temperature. But even in an oven with chrome-plated accessories or stainless steel parts in or at the roasting chamber, such as broiling grids, broiling skewers, support grids for baking sheets, telescoping arms, vapor vanes and/or air exhaust vanes (outside of the oven chamber !) and the like, the surfaces of those parts should be modified in the manner described supra.

If, in use, another layer adheres to the non-stick coating the former layer defines the surface characteristics of the entire system. Hence, it is apparent that the sedimentation of undesired layers is to be prevented. Some cleaning agents, for instance stainless steel cleaners, are combinations of cleaning agents and protective agents specifically developed to form such protective layers on the surfaces to be treated by them. Such protective films on non-stick surfaces are contraindicative, for either their non-stick property is such that the protective films cannot adhere, or a simple method has to be developed for removing such foreign protective film in order to reestablish the non-stick properties. It is for this reason that the surface should have non-stick as well as scratch and scouring resistant properties. A conventional enamel coated surface may be the basis of such a treated surface. The modified surface is regenerated by exposing the non-stick surface previously cleaned, serviced and/or protected for a short time to a temperature above the decomposition temperature of the protective film. This eliminates the undesired protective film of the treatment agent by evaporation or pyrolytic decomposition. Since its non-stick properties suffer no damage as a result of such heat treatment, the surface will be fully reuseable after each cleaning, servicing and/or protective treatment. The organically modified layer with non-stick properties below an undesired organic cover layer may be regenerated by heat treatment.

Baking ovens equipped in their baking chambers with surfaces or components modified in the above described manner are suitable for regeneration of the modified surfaces. They should be equipped with a user actuated switching element for cycling the oven through a regeneration. In this manner, a user, after first carefully cleaning the oven and its accessories with little effort in the usual manner, may then cause the modified surface to regenerate itself. To this end, the accessories are placed in an empty state into the oven chamber. Under its function or setting "Regeneration of the non-stick property" the oven executes regeneration cycle along a time/temperature curve, and any organic protective films formed by cleaning agents are removed from the modified surface. The surface is cleaned from any organic layer present and the modified non-stick surface will again be exposed. By input means, the user may alter duration and temperature of the regeneration process within predetermined limits (from a minimum to a maximum effect). Preferably, the treatment temperature is between 200° C. and 400° C. and the holding time is from 15 to 30 min.

Since a stainless steel surface is not particularly scratch resistant, it may be desireable to provide it with a surface coating without changing the expensive look of the stainless steel. Since at higher temperatures stainless steel quickly and irreversibly takes on heat-tinting colors, a way has to be found of modifying the surface coating without discoloring the stainless steel. Such a way consists of directly applying, at low temperatures (e.g. <100° C.), a very thin coating of transparent glass or ceramic (e.g. water glass) to the stainless

steel surface in order to prevent a change in color of the stainless steel. Thereafter the surface is treated by the above described process.

What is claimed is:

1. A method of forming a temperature and scratch resistant coating on a surface of an inorganic carrier material comprising at least one organo-functional molecular group, comprising the steps of:

applying to the surface a coating of an organic substance comprising silicone-like networks;

heat-treating the carrier material with the coating of the organic substance thereon at a temperature in excess of the permissible operating temperature of the organic substance and for a duration selected to ensure a reaction for cross-linking the organo-functional molecular groups with the silicone-like networks of the substance, and

evaporating excess organic substance.

2. The method of claim 1, wherein the surface of the carrier material comprises stainless steel and wherein the application of the coating is preceded by applying a layer of one of glass and ceramic to the surface.

3. The method of claim 1, wherein the organic substance is applied to the surface in a chamber maintained at a temperature not falling below the operating temperature of the organic substance.

4. The method of claim 1, further including the steps of converting the organic substance to its gaseous phase and precipitating it on the carrier surface within a heated treatment chamber.

5. The method of claim 4, further including the step of raising the temperature of the organic substance to above its decomposition temperature and of thereafter applying the organic substance in a gaseous phase to the surface.

6. The method of claim 4, further including the steps of raising the temperature of the organic substance to below its decomposition temperature and of thereafter applying the organic substance in a gaseous phase to the surface.

7. The method of claim 4, further including the step of conveying the organic substance to the treatment chamber at a temperature not lower than the temperature of the carrier material.

8. The method of claim 1, wherein the organic substance when coated on the carrier material surface is at a temperature below its decomposition temperature and that following coating the carrier material and the organic substance are subjected to a heat treatment.

9. The method of claim 1, wherein the heat treatment is performed at a temperature between about 300° C. and about 700° C.

10. The method of claim 1, wherein the organo-functional groups of the surface of the carrier material comprises one of methyl groups and phenyl groups.

11. The method of claim 1, wherein the organic substance has one of hydrophobic and oleophobic properties.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,372,290 B1
DATED : April 16, 2002
INVENTOR(S) : Berkenkoetter et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [86], please correct to read as follows:
-- [86] PCT No.: PCT/EP98/04126 --

Signed and Sealed this

Eleventh Day of June, 2002



Attest:

Attesting Officer

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

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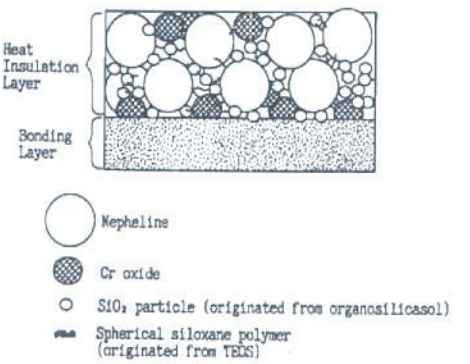
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(54) Ceramic heat insulating layer and process for forming same

(57) A ceramic heat insulating layer formed on an iron-based base material with or without a bonding layer interposed therebetween, comprising: aggregate particles of a nepheline mineral; and a binder composed of silica particles and of a metalloxane polymer, the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer. The ceramic heat insulating layer may alternatively comprise: aggregate particles of a nepheline mineral; a binder composed of silica particles and a metalloxane polymer, the binder intervening between the aggregate particles to leave voids and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer; and a sealing layer sealing the voids in a surface region of the ceramic heat insulating layer. A process of forming the ceramic heat insulating layer comprises the steps of: mixing aggregate particles of a nepheline mineral, a binder of an alcoxide and an organosilicasol, and a dispersing medium to form a slurry; applying the slurry either on the surface of an iron-based base material, or on any bonding layer formed on the surface; and firing the iron-based base material having the applied slurry; wherein the mixing is either carried out in a sufficiently acidic or sufficiently alkaline solution such that the surface potential of particles dispersed in the slurry does not pass an isoelectric point due to an increase in a pH value of the slurry because of alkaline metal ions dissolved from the aggregate particles of the nepheline mineral, or the mixing is carried out after coating the aggregate particles of the nepheline mineral with a coating layer which prevents dissolution of alkaline metal ions from the aggregate particles of the nepheline mineral.

Fig.5



EP 0 810 301 A1

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a ceramic heat insulating layer formed on an iron-based base material with or without an interposed bonding layer therebetween, and to a process for forming the heat insulating layer.

2. Description of the Related Art

It is known in the art that a ceramic layer having good heat resistance and heat insulation efficiency can be formed on an iron-based structural member in which the heat resistance and the heat insulation are necessary, such as the cylinder, piston, cylinder head, and other members of the exhaust system of diesel engines, gasoline engines, and other internal combustion engines.

Japanese Unexamined Patent Publication (Kokai) No. 61-26781 proposed forming a ceramic layer mainly composed of oxides of Fe, Al and Cr on a base material made of a iron-based metal or alloy such as cast iron forming part of an internal combustion engine, which part is exposed to high temperatures. The ceramic layer preferably comprises Fe_2O_3, Fe_2O_3-Cr, or other iron oxide-based ceramic having a linear thermal expansion coefficient close to that of the iron-based base material.

The proposed iron oxide-based ceramic layer, however, has a drawback in that, at service temperatures of 900°C or higher, a reduction reaction of Fe_2O_3 and a sintering shrinkage occur to cause cracking of the ceramic layer and/or exfoliation of the ceramic layer from the base material or from the bonding layer formed on the base material.

To eliminate this drawback, it is necessary to form a heat insulating layer which is stable at temperatures of 900°C or higher, has a thermal expansion coefficient comparable with or greater than that of the iron-based base material, and has a thermal conduction coefficient comparable with or less than that of the iron oxide-based ceramic.

Nepheline minerals (typically, $NaAlSiO_4$) have been considered to have an optimal property to form an aggregate of the above-mentioned heat insulating layer.

Nepheline minerals, however, cannot be practically used because, when preparing a slurry from a nepheline mineral powder, alkaline metal ions (typically, Na^+) of the nepheline mineral cause rapid progress of both agglutination of the powder particles and reaction of a binder, and therefore, controllec preparation of slurry cannot actually be realized on commercial scale.

Even on laboratory scale, there is still a problem that, at service temperatures of 1000°C or higher, the nepheline mineral aggregate sinters and the ceramic layer then shrinks to cause cracking and exfoliation of the ceramic layer to occur.

SUMMARY OF THE INVENTION

The object of the present invention is to solve the above-mentioned conventional problems and to provide a ceramic heat insulating layer containing a nepheline mineral as an aggregate, having a thermal expansion coefficient comparable with that of the iron-based base material, having an improved strength of bonding to the iron-based base material or to a bonding layer interposed between the ceramic layer and the base material, and having an improved heat resistance and strength, and also to provide a process for forming the ceramic heat insulating layer.

To achieve the object according to one aspect of the present invention, there is provided a ceramic heat insulating layer formed on an iron-based base material with or without a bonding layer interposed therebetween, comprising:

aggregate particles of a nepheline mineral, and

a binder composed of silica particles and of a metalloxane polymer, the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer.

The ceramic heat insulating layer contains an aggregate of a nepheline mineral having a heat resistance at temperatures of 1000°C or higher and a high thermal expansion coefficient comparable with that of an iron-based base material, to ensure an improved heat resistance and to prevent cracking and exfoliation due to a difference in thermal expansion coefficient relative to the iron-based base material; contains a binder composed of silica particles and a metalloxane polymer, which binder fills spaces between the aggregate particles, to ensure a good heat resistance while providing a buffer against a sintering shrinkage of the aggregate, thereby preventing cracking and exfoliation at high temperatures of 1000°C or higher, the binder also chemically bonding the aggregate particles to each other and to the base material or to the interposed bonding layer, to ensure an improved strength.

According to another aspect of the present invention, the ceramic heat insulating layer may contain a binder which intervenes between the aggregate particles leaving unfilled pores or voids between the aggregate particles, except for the surface region of the ceramic layer in which the voids are sealed with a sealing layer. In this structure, the voids left between the aggregate particles preserve air in the ceramic layer while the voids are isolated by the sealing layer from the environment to provide an improved heat insulation.

For either of the above-mentioned aspects of the present invention, there is also provided a process of forming a ceramic heat insulating layer on an iron-based base material, comprising the steps of:

mixing aggregate particles of a nepheline mineral, a binder of an alcoxide and an organosilicasol, and a dispersing medium to form a slurry,

applying the slurry either on the surface of an iron-based base material, or on a bonding layer formed on the surface, and

firing the iron-based base material having the applied slurry,

wherein the mixing is either carried out in a sufficiently acidic or sufficiently alkaline solution such that the surface potential of particles dispersed in the slurry does not pass an isoelectric point due to an increase in pH value of the slurry because of alkaline metal ions dissolved from the aggregate particles of the nepheline mineral, or the mixing is carried out after coating the particles of the nepheline mineral with a coating layer which prevents dissolution of alkaline metal ions from the aggregate particles of the nepheline mineral.

The process of forming a ceramic heat insulating layer of the present invention utilizes a sol-gel process, including applying a slurry in a sol state on the surface of a base material, causing the applied layer of the slurry to gel, and firing the thus-formed gel layer to form a ceramic layer.

In the conventional art, during this process, alkaline metal ions (typically, Na^+) from a nepheline mineral cause agglutination of particles in the slurry to occur in a very short time and gelation proceeds rapidly, so that controlled preparation of a slurry cannot actually be carried out and a ceramic heat insulating layer utilizing a nepheline mineral was not practically realized.

The basic concept of the present invention is that the agglutination of particles in a slurry, or the gelation of the slurry, proceeds rapidly because alkaline metal ions from a nepheline mineral increases the pH value of the slurry, during which the surface potential of particles in the slurry passes an isoelectric point to cause agglutination of particles.

In one aspect, the process of the present invention uses a slurry which is either sufficiently acidic to overcome or cancel the increase in pH value due to the alkaline metal ions from the nepheline mineral, or is sufficiently alkaline to provide an initial pH value on an alkaline side, to prevent the surface potential of particles in the slurry from passing the isoelectric point.

In another aspect of the process of the present invention, particles of the nepheline mineral are coated, prior to the preparation of slurry, to prevent dissolution of the alkaline metal ions from the particles.

According to any of these aspects, the gelation during preparation of a slurry can be substantially delayed so that controlled preparation of a slurry on commercial scale can be practically achieved to provide a ceramic heat insulating layer utilizing a nepheline mineral as an aggregate and having an improved heat resistance and strength.

In the ceramic heat insulating layer of the present invention, particles of a nepheline mineral form an aggregate and spaces between the aggregate particles are filled with a binder composed of silica particles and a metalloxane polymer which also chemically bonds the aggregate particles to each other and to a base material, or to any bonding layer formed on the base material.

The term "metalloxane" is herein used as a generic name of the chemical compounds having M-O bonds and consisting of a metal M, oxygen O, and hydrogen. The metal M is not necessarily limited but may be any metal which cooperates with the silica particles to chemically bond the aggregate particles of a nepheline mineral to each other and to the base metal, or to any bonding layer formed on the base metal to provide good stability at high temperatures of 900°C or higher, preferably 1000°C or higher. From the viewpoint of easy handling, those chemical compounds in which polycondensation does not proceed rapidly but proceeds slowly are preferred.

Siloxane is one of the most preferred embodiments of metalloxane, which contains Si as the metal M and has Si-O bonds, i.e., siloxane bonds. Siloxane may preferably be produced from tetraethoxysilane (TEOS), in which polycondensation is easy to control.

Polycondensation of tetraethoxysilane can be easily controlled to selectively produce either linear or spherical siloxane polymers. A linear siloxane polymer provides a stiff ceramic heat insulating layer. In contrast, a spherical siloxane polymer has a relatively lower stiffness and is suitably used to provide a buffer against sintering shrinkage where it is significant.

A ceramic heat insulating layer having the aggregate particles of a nepheline mineral according to the present invention may not be directly formed on a base material but may be formed on a bonding layer formed on the base material in order to provide a further strengthened bond to the base material. The bonding layer is typically composed of a Fe-Ni alloy and a Cr oxide. In this case, the ceramic heat insulating layer also preferably contains a Cr oxide. To this

end, a Cr powder is added in the slurry for forming the ceramic heat insulating layer.

A strengthened bond to the base material can also be achieved without forming a bonding layer by an alternative method including initially applying a slurry directly on a base material, drying the applied layer, then firing in an inert atmosphere to cause formation of a dense oxide layer chemically bonded to the base material while a ceramic heat insulating layer of the present invention is formed on the dense oxide layer. This provides an improved bond strength between the base material and the ceramic heat insulating layer because the dense oxide film protects the base material from oxidation to prevent exfoliation of the ceramic layer due to oxidation of the base material and because the bond between the ceramic layer and the base material is substantially effected by chemical bonding through the dense oxide film.

In the above-mentioned embodiment, in which a bonding layer containing a Cr oxide is not formed on the base material, a ceramic heat insulating layer need not contain Cr oxides. Because Cr oxides have a heat conduction coefficient of about 150 times that of nepheline minerals, the absence of Cr oxides advantageously provides an improved heat insulation of the ceramic heat insulating layer. Moreover, because Cr oxides exhibit green color whereas nepheline minerals are white, the absence of Cr oxides also advantageously reduces radiant heat absorption to further improve the heat insulation.

In the preparation of a slurry for forming a ceramic heat insulating layer according to the present invention, the rapid gelation of the slurry caused by alkaline metal ions dissolved from a nepheline mineral is prevented either by (1) the mixing of a binder and an aggregate is performed in (a) an acidic solution or (b) an alkaline solution, or by (2) coating particles of a nepheline mineral with a suitable coating layer to prevent dissolution of alkaline metal ions from the nepheline mineral particles.

In case (1)-(a), the aggregate particles of a nepheline mineral are agitated in an acid solution to form a suspension, prior to being mixed with a binder, to prevent the surface potential of the aggregate particles from reaching an isoelectric point in the process of the increase in pH of the slurry because of alkaline metal ions.

The acid solution is advantageously composed of a carboxylic acid and an alcohol containing a small amount of an inorganic acid to form an alkaline metal salt of alkaline metal ions from a nepheline mineral and an ester, which salt acts as a surfactant to improve the dispersivity and stability of a slurry while preventing retention of inorganic salts other than the binder sources to provide an improved strength of a ceramic heat insulating layer.

From this point of view, it is preferred that the carboxylic acid may be composed of an anhydrous carboxylic acid which does not cause formation of inorganic acids, or may further contain at least one selected from the group consisting of polyamine, polyphosphine, and polyether, to fix alkaline metal ions from a nepheline mineral as a chelate complex, thereby substantially improving the dispersivity and stability of a slurry.

In case (1)-(b), the pH value of a dispersed liquid composed of the binder and the dispersing medium is suitably adjusted to 8 or greater, prior to the mixing step. This holds the pH value of the dispersed liquid on the alkaline side to prevent the surface potential of the dispersed particles from passing an isoelectric point even when the pH value is increased by alkaline metal ions dissolved from the nepheline mineral.

In case (2), the particles of a nepheline mineral are suitably coated with an inorganic coating by an alcoxide, prior to the mixing step according to the present invention. The inorganic coating on the nepheline mineral particles is suitably formed by using a solution containing a metal alcoxide, particularly a non-aqueous solution containing an unhydrolyzed metal alcoxide, preferably a stock solution of a metal alcoxide, so that polycondensation preferentially proceeds more on the surface of the nepheline mineral particles than between the molecules of the metal alcoxide.

In this case, it is advantageous that hydroxyl groups are preliminarily added on the surface of the nepheline mineral particles by exposure to water vapor or boiling in pure water, etc., to form, or increase the number of, bonding hands on the nepheline mineral particles for coupling with the metal alcoxide and the metalloxane polymer, thereby forming a dense coating. Preferably, hydrochloric acid is used as a nucleophilic reaction catalyst to facilitate graft polymerization of the metal alcoxide molecules on the surface of the nepheline mineral particles to form a dense coating of an inorganic oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow chart showing a slurry preparation step of the present inventive process for forming a ceramic heat insulating layer having particles of a nepheline mineral as a main aggregate and a linear siloxane polymer as a main binder;

Fig. 2 is a schematic illustration of the cross-sectional structure of a nepheline mineral-based ceramic heat insulating layer formed from a slurry prepared by the step shown in Fig. 1;

Fig. 3 is a graph showing the gelation time of a slurry prepared by mixing and the bond strength of ceramic heat insulating layer formed by firing, in relation to the acid treatments of the aggregate particles mainly composed of a nepheline mineral before mixing of the particles with a binder mainly composed of tetraethoxysilane (TEOS) in the slurry preparation step shown in Fig. 1;

Fig. 4 is a flow chart showing a slurry preparation step of the present inventive process for forming a ceramic heat

insulating layer having particles of a nepheline mineral as a main aggregate and a spherical siloxane polymer as a main binder;

Fig. 5 is a schematic illustration of the cross-sectional structure of a nepheline mineral-based ceramic heat insulating layer formed from a slurry prepared by the step shown in Fig. 4;

Fig. 6 is a graph showing the relationship between the gelation time of slurry prepared by mixing and the adjusted pH value of a dispersed liquid of a binder mainly composed of tetraethoxysilane (TEOS) in the slurry preparation step shown in Fig. 4;

Fig. 7 is a graph showing the relationship between the exposure temperature and the bond strength for two types of the ceramic heat insulating layers formed by using spherical and linear siloxane polymers as a binder, respectively, according to the present invention;

Fig. 8 is a flow chart of a slurry preparation step of the present inventive process, in which nepheline mineral particles are coated with a linear siloxane polymer and then mixed with a binder component;

Fig. 9 schematically illustrates a processing sequence of the slurry preparation step shown in Fig. 8, in which hydroxylic groups are added on the surface of nepheline mineral particles and a linear siloxane polymer coating is then formed;

Fig. 10 is a schematic illustration of the cross-sectional structure of a nepheline mineral-based ceramic heat insulating layer formed from a slurry prepared by the step shown in Fig. 8;

Fig. 11 is a flow chart of a slurry preparation step in which the nepheline mineral particles coated with a linear siloxane polymer in the slurry preparation step shown in Fig. 8 are mixed with a conventional aluminum phosphate binder to form a slurry, to demonstrate the advantageous effect of coating the nepheline mineral particles;

Fig. 12 is a graph showing the gelation time of a slurry prepared by the step shown in Fig. 11 and the bond strength of a nepheline mineral-based ceramic heat insulating layer formed from the slurry, comparing two cases in which nepheline mineral particles are coated and non-coated, respectively;

Fig. 13 is a graph showing the gelation time of slurry and the bond strength of a ceramic heat insulating layer, in relation to the conditions for coating the nepheline mineral particles;

Fig. 14 is a schematic illustration of the cross-sectional structure of a nepheline mineral-based ceramic heat insulating layer not containing Cr oxides, which layer is formed from a slurry prepared by the same step as shown in Fig. 8 except that no Cr powder is added;

Fig. 15 is a schematic illustration of the cross-sectional structure of a porous nepheline mineral-based ceramic heat insulating layer not containing Cr oxides and having a sealing layer of Cr oxides in the surface region, which layer is formed from a slurry prepared by the same step as shown in Fig. 8 except that no Cr powder is added and that the mixing proportion is varied;

Fig. 16 is a scanning electron micrograph of a fracture surface of the porous nepheline mineral-based ceramic heat insulating layer schematically illustrated in Fig. 15;

Fig. 17 is a graph showing the relationship between the metal alcoxide concentration C1 of slurry and the bond strength of porous nepheline mineral-based ceramic heat insulating layer;

Fig. 18 is a graph showing the bond strength and the heat insulation of a porous nepheline mineral-based ceramic heat insulating layer in relation to the powder concentration (nepheline mineral powder concentration) C2 of slurry; and

Fig. 19 is a graph showing the relationship between the heat insulation of a porous nepheline mineral-based ceramic heat insulating layer and the solid concentration of binder C3.

In the drawings, the abbreviations have the following meanings:

TEOS = tetraethoxysilane,
Et-OH = ethanol,
ME = 2-methoxyethanol,
AA = anhydrous acetic acid,
NAS = nepheline mineral, and
$NaAlSiO_4$ = nepheline mineral.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

According to the present invention, a bonding layer was formed on a base material and a ceramic heat insulating layer having a main binder of a linear siloxane polymer was formed on the bonding layer. A slurry was prepared by using the blend components summarized in Table 1 and in the process sequence shown in Fig. 1.

Table 1

Phase	Blend component	Blend ratio		
		M.R (*1)	W.R. (*2)	
1	2-methoxyethanol	1	-	1.5
	tetraethoxysilane	1		
	ethanol	1		
	H_2O	2		
	HCl	0.01		
2	2-methoxyethanol	-	1	
	oraganosilicasol	1/5 (*3)	1	
3	2,4-pentandione	1/4	-	
4	nepheline mineral particles	-	1.5	3.5
	chromium particles	-	0.5	
	2-methoxyethanol	-	1.2	
	anhydrous acetic acid	-	0.3	

Note

*1) M.R.: molecular ratio

*2) W.R.: weight ratio

*3) the value reduced to the amount of SiO_2 for SiO_2 equivalent)

A binder was prepared through the processing phases 1, 2 and 3, in which, in phase 1, tetraethoxysilane (TEOS) was dispersed in 2-methoxyethanol (ME) and agitated in the presence of H_2O and HCl for 2 hours to cause hydrolysis and polycondensation (condensation polymerization) of the tetraethoxysilane (TEOS) to produce a linear siloxane polymer, which was then, in phase 2, adsorbed on the surface of silica particles originated from an organosilicasol in the form of a silanol (agitation at room temperature for 1 hour), and finally, in phase 3, the hydrolysis and polycondensation was terminated (agitation at room temperature for 0.5 hour).

An aggregate component was separately prepared in phase 4 in which a nepheline mineral powder (average particle size of 5 μm) and a Cr powder (average particle size of 10 μm or less) were dispersed in 2-methoxyethanol, which was then maintained acidic by adding therein anhydrous acetic acid (AA).

The binder prepared by phases 1 to 3 and the aggregate component prepared by phase 4 were mixed to form a slurry.

A bonding layer composed of a Fe-Ni alloy and a Cr oxide was formed on the surface of a cast iron base material and the slurry was then applied on the bonding layer, dried, and then fired in air at 850°C for 5 hours to form a ceramic heat insulating layer having a thickness of 1 mm.

Figure 2 schematically illustrates the cross-sectional structure of the ceramic heat insulating layer observed by a scanning electron microscope and a transmission electron microscope. The ceramic heat insulating layer is formed on the bonding layer formed on the cast iron base material (not shown), and has aggregate particles composed of nepheline mineral particles (large blank circles in Fig. 2) and Cr oxide particles (cross-hatched circles) and a binder composed of silica particles (small blank circles) and a linear siloxane polymer (hatched portions between particles), the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the bonding layer.

For comparison, the same bonding layer was formed on the same base material as the above, and on the bonding layer, a conventional iron-oxide-base ceramic heat insulating layer having Fe_2O_3 particles as an aggregate and aluminum phosphate as a binder and having the same thickness of 1 mm as the above was formed.

The bond strength and the heat insulation of these ceramic heat insulating layers were measured by the following methods, which were also used in the other examples which will be described later.

To evaluate the bond strength, a slice is cut from a sample having a ceramic heat insulating layer along the cross section in the direction of the thickness of the ceramic layer (the direction of the depth in the base material), the base material portion of the slice is held by a jig from both sides to only expose the ceramic layer portion of the slice from the jig, and a pressing force is applied to the exposed ceramic layer portion by another jig in the direction of the thickness of the slice (the direction along an interface between the base material and the heat insulating layer) until shear fracture

occurs at the interface between the base material and the heat insulating layer, at which fracture a shear stress f is measured as the bond strength.

To evaluate the heat insulation, a heat insulating layer is formed on the inner wall of a hollow cylindrical base material, the atmosphere within the cylinder is held at 850°C to simulate a heat flux in an exhaust manifold of an automobile engine, a pair of thermocouples are inserted in the cylinder from the circumferential surface in the direction toward the center thereof to measure a temperature at the interface between the base material and the heat insulating layer and a temperature at the free surface of the heat insulating layer, and the temperature difference Δt between the two temperatures is used for the evaluation.

The measured results for the above two samples are summarized in Table 2.

Table 2

Heat insulating layer	Δt (°C)	f (MPa)
Present invention	60	60
Fe_2O_3-aluminum phosphate	30	25
Δt: heat insulation, f: bond strength.		

It can be seen from Table 2 that, in comparison with the conventional iron oxide-based ceramic heat insulating layer, the ceramic heat insulating layer according to the present invention not only has a significantly improved bond strength (invention: 60 MPa, conventional: 25 MPa) because the aggregate particles are chemically bonded to each other and to the base material (or to the bonding layer) by siloxane bonding and because the number of the bonding points is increased by the presence of a linear siloxane polymer, but also has a significantly improved heat insulation (invention: 60°C, conventional: 30°C) because the aggregate particles are mainly composed of nepheline mineral particles.

Example 2

In the process of forming a ceramic heat insulating layer in Example 1, nepheline mineral particles were subjected to different acid treatments prior to mixing with a binder for comparison.

Slurries were prepared with the same blend composition and the same process phases as in Example 1, except that, in phase 4, anhydrous acetic acid (AA) was (1) not used or was replaced by (2) HCl or (3) glacial acetic acid.

A bonding layer was formed on the base material in the same way as in Example 1, and the above-prepared three types of slurries were applied on the bonding layer, dried, and then fired under the same conditions as in Example 1 to form three types of ceramic heat insulating layers having a thickness of 1 mm.

Fig. 3 compares the gelation time of slurry and the bond strength of ceramic heat insulating layer between these three slurries and the slurry using anhydrous acetic acid used in Example 1.

It can be seen that the gelation time is significantly increased by acid-treating the nepheline mineral particles according to the present invention ((2), (3) and (4) in Fig. 3) in comparison with that achieved without acid-treating ((1) in Fig. 3), i.e., the gelation time is increased from several minutes of the non-treated case (1) to several hours of the acid-treated cases (2), (3) and (4), which means a sufficient stability of the slurry for commercial use. The bond strength of ceramic heat insulating layer is also significantly more improved by acid treatment in (2), (3) and (4) than that achieved without acid treatment in (1). In particular, (3) and (4), in which organic acid treatment was used, provided the most improved strength because a reduction in the number of the bonding points due to retained inorganic acid was suppressed.

Example 3

According to the present invention, a bonding layer was formed on a base material and a ceramic heat insulating layer having a main binder of a spherical siloxane polymer was formed on the bonding layer. A slurry was prepared with the blend composition shown in Table 3 and in the process sequence shown in Fig. 4.

Table 3

Phase	Blend component	Blend ratio		
		M.R. (*1)	W.R. (*2)	
1	2-methoxyethanol	1	-	4
	tetraethoxysilane	1		
	NH_3	0.01		
	H_2O	2		
2	oraganosilicasol	1 (*3)	-	
	NH_3	depends on pH-adjust		
3	nepheline mineral particles	-	4	5
	chromium particles	-	1	

Note
*1) M.R.: molecular ratio
*2) W.R.: weight ratio
*3) SiC_2 equivalent

A binder was prepared by dispersing tetraethoxysilane (TEOS) in 2-methoxyethanol (ME), adding therein NH_3 to adjust the pH of the dispersed liquid to a value of greater than 7 and less than or equal to 8, and under the presence of H_2O, causing hydrolysis and polycondensation to produce a spherical siloxane polymer by agitating at room temperature for 1 hour. Organosilicasol, and then NH_3 were added in the dispersed liquid to adjust the pH of the liquid to a value of greater than 8 and less than 11.

In the above-prepared binder, nepheline mineral particles (average particle size of 5 μm) and a Cr powder (particle size of 10 μm or less) were added as aggregate particles to form a slurry.

A bonding layer was formed on a base material in the same way as in Example 1 and the above-formed slurry was applied on the bonding layer, dried, and then fired under the same conditions as in Example 1 to form a ceramic heat insulating layer having a thickness of 1 mm.

Figure 5 schematically illustrates the cross-sectional structure of the ceramic heat insulating layer observed by a scanning electron microscope and a transmission electron microscope. The ceramic heat insulating layer is formed on the bonding layer formed on the cast iron base material with (not shown), and has aggregate particles composed of nepheline mineral particles (large blank circles in Fig. 5) and Cr oxide particles (cross-hatched circles) and a binder composed of silica particles (small blank circles) and a spherical siloxane polymer (short segments between particles), the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the bonding layer.

In the process of preparing a slurry shown in Fig. 4, the pH of a dispersed liquid of a binder mainly composed of tetraethoxysilane (TEOS) was adjusted to different values prior to mixing with the aggregate mainly composed of nepheline mineral particles. Figure 6 shows the relationship between the adjusted pH value and the gelation time of slurry.

As can be seen from Fig. 6, the gelation of slurry occurred in a few minutes when the binder dispersed liquid has a pH value of 7 or less before the mixing. This is because, when mixed with the aggregate, the pH value of the dispersed liquid is increased by alkaline metal ions dissolved from the nepheline mineral, and in the process of increase of the pH value, the surface potential of the dispersed binder and aggregate particles passes an isoelectric point to cause agglutination of the dispersed particles.

When the pH value of the dispersed liquid is preliminarily increased to 8 or more, the surface potential does not pass an isoelectric point if the pH is increased, and also the resulting agglutination of the dispersed particles does not occur, so that the gelation of slurry can substantially be delayed, i.e., the gelation time can be increased to several hours or more.

The gelation time, however, reaches a peak at a pH value of 10 and is then decreased as the pH value is further increased. This is because, when the pH value exceeds 10, polycondensation of TEOS rapidly proceeds to accelerate the gelation of slurry.

It can be seen from Fig. 6 that the pH of the binder dispersed liquid is suitably adjusted to within the range of from 8 to 12 before the liquid is mixed with the aggregate particles.

Figure 7 compares the bond strength at high temperatures between the ceramic heat insulating layer having a spherical siloxane polymer as a main binder produced in Example 3 and the ceramic heat insulating layer having a lin-

ear siloxane polymer as a main binder produced in Example 1.

The ceramic heat insulating layer of Example 1 containing a linear siloxane polymer and having a stiff structure exhibits a high bond strength corresponding to the stiff structure at temperatures up to 1000°C, but at higher temperatures, sintering of the nepheline mineral particles proceeds and the stiff structure only has a poor buffer effect against the sintering shrinkage causing easy occurrence of cracking and exfoliation to reduce the bond strength.

In contrast, the ceramic heat insulating layer of Example 3 containing a spherical siloxane polymer and having a less stiff or soft structure exhibits a relatively lower bond strength corresponding to the low stiffness of the structure at temperatures up to 1000°C, but at higher temperatures, the low stiffness advantageously provides a substantial buffer effect against the sintering shrinkage of nepheline mineral particles to ensure a high bond strength. As the result, when a spherical siloxane polymer is used as a binder, the bond strength can be maintained substantially constant at a high level over the whole testing temperatures ranging from room temperature to 1200°C.

Example 4

According to the present invention, nepheline mineral particles were coated with a linear siloxane polymer and mixed with a binder to form a slurry, which was then used to form a ceramic heat insulating layer on a bonding layer formed on a base material in the same manner as in Example 1.

A slurry was prepared with the blend composition shown in Table 4 and in the process sequence shown in Fig. 8.

Table 4

Phase	Blend component	Blend ratio		
		M.R. (*1)	W.R. (*2)	
1	nepheline mineral particles	-	100	2
	H_2O	-	800	
	Cr particles	-	25	
2	tetraethoxysilane	1	300	
	ethanol	0.1	-	
	HCl	0.01	-	
3	ethanol	50	-	2.5
	tetraethoxysilane	4	-	
	H_2O	15.2	-	
	HCl	0.01	-	
	2-methoxyethanol	1.4	-	
	organosilicasol	4 (*3)	-	

Note

*1) M.R.: molecular ratio

*2) W.R.: weight ratio

*3) SiO_2 equivalent

To prepare an aggregate, in phase 1, nepheline mineral particles having an average particle size of 5 μm were H_2O-treated by either exposing to water vapor or boiling in water to add hydroxyl groups to the surface of the particles, which were then recovered by suction filtration and the recovered powder was dried at 110°C for 2 hours. Next, in phase 2, HCl as a nucleophilic reaction catalyst was added in tetraethoxysilane (TEOS) and the hydroxyl group-added nepheline mineral powder prepared in phase 1 was then added therein and the mixture was agitated at 75°C for 5 hours, followed by suction filtration to recover a powder, which was then dried at 250°C for 3 hours. This yielded a nepheline mineral powder with the particles coated with a linear siloxane polymer. Figure 9 schematically illustrates the reaction process through phases 1 and 2.

In phase 3, a binder was prepared by adding tetraethoxysilane (TEOS) in a dispersing medium of 2-methoxyethanol (ME), adding H_2O and HCl, agitating the mixture at 75°C for 1 hour, adding the rest of 1-methoxyethanol, fractionally distilling the mixture at 95°C for 1 hour, adding organosilicasol, and agitating at room temperature.

The nepheline mineral aggregate prepared by phases 1 and 2 and the binder prepared by phase 3 were mixed to

form a slurry.

A bonding layer was formed on a base material as in Example 1 and the slurry was applied on the bonding layer, dried, and then fired under the same conditions as in Example 1 to form a ceramic heat insulating layer having a thickness of 1 mm.

Figure 10 schematically illustrates the cross-sectional structure of the ceramic heat insulating layer observed by a scanning electron microscope and a transmission electron microscope. The ceramic heat insulating layer is formed on the cast iron base material with the bonding layer interposed therebetween, and has an aggregate composed of nepheline mineral particles (large blank circles in Fig. 10) and Cr_2O_3 oxide particles (cross-hatched) and a binder composed of silica particles (small blank circles) and a linear siloxane polymer (hatched portions between particles), the binder chemically bonding the particles of the aggregate to each other and to the bonding layer. The nepheline mineral particles shown by a large blank circle are coated with the linear siloxane polymer shown by a hatched case surrounding the large blank circle.

Table 5 shows the heat insulation (Δt) and the bond strength (f) of the ceramic heat insulating layer of Example 4 in comparison with those of the conventional iron oxide-based ceramic heat insulating layer.

Table 5

Heat insulating layer	Δt (°C)	f (MPa)
Present invention	70	80
Fe_2O_3-aluminum phosphate	30	25

Δt: heat insulation,
f: bond strength.

The linear siloxane polymer present as a coating on the nepheline mineral particles, as well as that present as a binder, also provides bonding hands between the aggregate particles and the base material (or the bonding layer on the base material) to provide a further improved heat insulation and bond strength in comparison with those obtained in Example 1.

Example 5

To demonstrate the advantageous effect of the linear siloxane polymer coating on the nepheline mineral particles according to the present invention, the following comparative experiments were conducted.

An aggregate was prepared in the same manner as in Example 4, i.e., with the blend composition shown in Table 4 and through phases 1 and 2 shown in Fig. 8 to coat the nepheline mineral particles with a linear siloxane polymer. A conventional aluminum phosphate-based binder was prepared with the blend composition shown in Table 6 and a slurry was prepared by the process sequence shown in Fig. 11.

Table 6

	Blend component	Weight ratio	
Powder	nepheline mineral particles	4	2
	Cr particles	1	
Dispersing medium containing binder	aqueous solution of aluminum phosphate (solid conc. = 30%)	-	

A bonding layer was formed on a base material in the same manner as in Example 1 and the slurry was applied on the bonding layer, dried and then fired under the same conditions as in Example 1 to form a ceramic heat insulating layer having a thickness of 1 mm.

Figure 12 compares the gelation time of a slurry prepared by mixing the aggregate and the binder and the bond strength of a ceramic heat insulating layer formed by applying the slurry, drying and firing, between the cases (1) having and (2) not having the coating on nepheline mineral particles respectively.

In the non-coat case (2), alkaline metal ions dissolved from the nepheline mineral reacted with the phosphoric acid of the binder to form an insoluble salt and causes rapid gelation or setting of the slurry. Moreover, the formation of the

insoluble salt only provided a low polymerization degree of aluminum phosphate and the bare nepheline mineral particles only had a small number of bonding bands and failed to provide a high bond strength as achieved in case (1) in which the nepheline mineral particles were coated.

Example 6

Comparative experiments were conducted by varying the conditions for coating nepheline mineral particles in phases 1 and 2 shown in Fig. 8 used in Example 5.

In Comparative Examples 1 and 2, a ceramic heat insulating layer was formed under the same conditions as in Example 5, except that, at stage (A) in phase 2 shown in Fig. 8, either (1) the same molar amount or (2) double the molar amount of H_2O was added to the tetraethoxysilane (TEOS).

In Comparative Example 3, a ceramic heat insulating layer was formed under the same conditions as in Example 5, except that hydroxyl groups were not added in phase 1 shown in Fig. 8.

In Comparative Example 4, a ceramic heat insulating layer was formed under the same conditions as in Example 5, except that HCl was not added in the phase 2 shown in Fig. 8.

Figure 13 compares the gelation time of slurry and the bond strength of ceramic heat insulating layer, between Comparative Examples 1 to 4 and Example 5.

In Comparative Examples 1 and 2, the addition of H_2O to TEOS for use in phase 2 promoted formation of the coating to provide a small increase in the gelation time of slurry relative to Example 5. On the other hand, polymerization between alkoxide molecules was promoted during the formation of the coating causing bonding between the powder particles to increase the aggregate particle size and the packing density of the aggregate particles was thus reduced to lessen the number of the sites for bonding between particles, with the result that the ceramic heat insulating layer had a significantly reduced bond strength. This tendency is particularly remarkable in Comparative Example 2 in which a relatively greater amount of H_2O was added in TEOS.

In Comparative Example 3, because hydroxyl groups were not added to the surface of nepheline mineral particles, a linear siloxane polymer coating formed on the particles was not dense and failed to prevent dissolution of alkaline metal ions, with the result that the gelation of the slurry occurred in a short time. Thus, the slurry was not suitably prepared and the ceramic heat insulating layer had a low bond strength.

In Comparative Example 4, because HCl was not present as a nucleophilic reaction catalyst, polycondensation did not preferentially occur on the surface of nepheline mineral particles and a linear siloxane polymer coating formed on the particles was not dense and failed to prevent dissolution of alkaline metal ions, with the result that the gelation of slurry occurred in a short time. Thus, the slurry was not suitably prepared and the ceramic heat insulating layer had a low bond strength.

In the preceding Examples 1 to 6, a ceramic heat insulating layer was formed on a bonding layer on a base material, the bonding layer being composed of a Fe-Ni alloy and Cr oxides.

In the following Examples 7 and 8, a ceramic heat insulating layer will be formed directly on a base material having no bonding layer thereon.

Example 7

According to the present invention, a ceramic heat insulating layer was formed directly on a base material having no bonding layer thereon, by applying a slurry directly on the base material, drying, and then firing in an inert atmosphere.

As in Example 4, a linear siloxane polymer coating was formed on the surface of nepheline mineral particles, which was then mixed with a binder to form a slurry.

The slurry had the blend composition shown in Table 7, which is the same as that shown in Table 4 used in Example 4, except that no Cr powder was added. The slurry was prepared in the same process sequence as shown in Fig. 8 used in Example 4.

Table 7

Phase	Blend component	Blend ratio		
		M.R. (*1)	W.R. (*2)	
1	nepheline mineral particles	-	100	2
	H_2O	-	800	
2	tetraethoxysilane	1	300	
	ethanol	0.1	-	
	HCl	0.01	-	
3	ethanol	50	-	2.5
	tetraethoxysilane	4	-	
	H_2O	15.2	-	
	HCl	0.01	-	
	2-methoxyethanol	1.4	-	
	organosilicasol	4 (*3	-	

Note
*1) M.R.: molecular ratio
*2) W.R.: weight ratio
*3) SiO_2 equivalent

The slurry was applied on a cast iron base material to a thickness of 1 mm, dried, and then fired in an Ar gas atmosphere at 850°C for 5 hours to form a ceramic heat insulating layer (Sample 1)

Figure 14 schematically illustrates the cross-sectional structure of the ceramic heat insulating layer observed by a scanning electron microscope and a transmission electron microscope. The ceramic heat insulating layer has a dense SiO_2 layer formed on the cast iron base material and has an aggregate composed of nepheline mineral particles (large blank circles in Fig. 14) and a binder composed of silica particles (small blank circles) and a linear siloxane polymer (hatched portions between particles), the binder filling spaces between particles and chemically bonding the particles of the aggregate to each other and to the SiO_2 layer on the base material. The nepheline mineral particles shown by a large blank circle are coated with the linear siloxane polymer shown by a hatched case surrounding the large blank circle.

For comparison, a ceramic heat insulating layer was formed by using the same slurry and firing in air (Sample 2), and also, ceramic heat insulating layers were formed by using the same slurry except that a Cr powder having an average particle size of 10 μm was added in an amount of 20 wt% based on the nepheline mineral powder and by firing in an Ar gas atmosphere (Sample 3) and in air (Sample 4), respectively.

The bond strength f and the heat insulation Δt were measured for Samples 1 to 4, in which a ceramic heat insulating layer was formed directly on a base material having no bonding layer. The measured results are summarized in Table 8.

Table 8

No.	Cr	Firing atmosphere	f (MPa)	Δt (°C)
1	None	Ar	50	85
2		air	5	-
3	Added	Ar	61	60
4		air	11	-
Δt: heat insulation, f: bond strength.				

In Sample 1, prepared by using no Cr powder and firing in an Ar atmosphere, a dense SiO_2 layer was formed by chemical bonding of siloxane polymer on the base material to prevent exfoliation due to oxidation of the base material

and the SiO_2 layer is strongly bonded with the aggregate mainly by chemical bonding, thereby providing a high bond strength.

The ceramic heat insulating layer of Sample 1 also had an improved heat insulation in both heat conduction and heat radiation because it contained no Cr oxides having a heat conductivity about 150 times that of a nepheline mineral and because it exhibited a white color of the nepheline mineral present as a main aggregate due to the absence of Cr oxides exhibiting a green color.

In Sample 2 prepared by using no Cr powder and firing in air, no SiO_2 layer was formed on the base material and oxidation of the base material occurred, with the result that no substantial formation of a ceramic heat insulating layer was achieved.

In Sample 3 prepared by adding a Cr powder and firing in an Ar gas atmosphere, a ceramic heat insulating layer was formed which was strongly bonded to the base material through Cr oxides produced during the firing to provide a high bond strength although the heat insulation was lower than Sample 1 in both heat conduction and heat radiation because of inclusion of Cr oxides.

In Sample 4 prepared by adding a Cr powder and firing in air, oxidation of the base material occurred as in Sample 2 and no substantial formation of a ceramic heat insulating layer was achieved.

Example 8

A first slurry containing no Cr powder as in Example 7 was applied on a base material having no bonding layer thereon, dried, and then fired in an inert atmosphere to form a porous ceramic heat insulating layer, and thereafter, a second slurry having a Cr powder as an aggregate was applied on the porous layer, dried, and then fired to form a sealing layer composed of Cr oxides in the surface region of the porous ceramic layer.

The first slurry was prepared in basically the same process sequence as in Example 4, i.e., through phases 1, 2 and 3, except that no Cr powder was added in phase 1 for preparing an aggregate and that an increased amount of a dispersing medium for diluting a binder was used in phase 3 for preparing a binder.

The blend composition of the first slurry was varied in the following compositional parameters C1, C2 and C3 by varying the weight ratios Wp, W1, W2 and W3 shown in Table 9.

C1 = concentration of metal alcoxide (TEOS in this example)
= W1/(W2 + W3),
C2 = concentration of powder (nepheline mineral powder)
= Vp/Vt, and
C3 = concentration of solid component of binder
= (a1W1 + a2W2)/(W1 + W2 + W3),
wherein
W1 = mass of metal alcoxide binder,
W2 = mass of organosilicasol binder,
W3 = mass of diluting and dispersing medium,
Vp = volume of powder material (calculated from Wp),
Vt = volume of slurry,
a1 = concentration of solid component of metal alcoxide binder, and
a2 = concentration of solid component of organosilicasol binder.

Table 9

Phase		Blend component	Blend ratio		
			M.R. (*1)	W.R. (*2)	
1		nepheline mineral particles	-	100	Wp
		H_2O	-	800	
2		tetraethoxysilane	1	300	
		ethanol	0.1	-	
		HCl	0.01	-	
3	Binder 1	ethanol	50	W1	
		tetraethoxysilane	4		
		H_2O	15.2		
		HCl	0.01		
		2-methoxyethanol	1.4		
	Binder 2	organosilicasol	-	W2	
4	Solvent for diluting binder	2-methoxyethanol	-	W3	

Note
*1) M.R : molecular ratio
*2) W.R. weight ratio

The second slurry was prepared with the blend composition shown in Table 10.

Table 10

Blend component	Weight ratio	Volume ratio
Cr powder (d = 10 μm, average)	-	17.5
Binder 1	1	82.5
Binder 2	1	
Solvent for diluting binder (2-methoxyethanol)	8.2	

The first slurry was first applied on a cast iron base material to a thickness of 1 mm, dried, and then fired in an Ar atmosphere at 850°C for 5 hours to form a porous ceramic heat insulating layer. The second slurry was then applied on the porous ceramic layer, dried, and then fired in air at 850°C for 5 hours to form a sealing layer composed of Cr oxides in the surface region of the porous ceramic heat insulating layer.

Figure 15 schematically illustrates the cross-sectional structure of the ceramic heat insulating layer observed by a scanning electron microscope and a transmission electron microscope. The ceramic heat insulating layer has a dense SiO_2 layer formed by a siloxane polymer on the cast iron base material and has an aggregate composed of nepheline mineral particles (large blank circles in Fig. 15) and a binder composed of silica particles (not shown) and a linear siloxane polymer (not shown), the binder intervening between particles leaving voids and chemically bonding the particles of the aggregate to each other and to the SiO_2 layer, and further, in the surface region, a sealing layer composed of Cr oxides (cross-hatched) filling spaces between the aggregate particles of a nepheline mineral. The nepheline mineral particles shown by a large blank circle are coated with the linear siloxane polymer shown by a hatched case surrounding the large blank circle.

Figure 16 shows a scanning electron microscope image of the thus-formed ceramic heat insulating layer in which the bright portions are aggregate particles and the dark portions are voids between the aggregate particles.

The heat insulation and the bond strength were measured for ceramic heat insulating layers formed with different values of the compositional parameters C1 of 20 to 80%, C2 of 5 to 30% and C3 of 5 to 25%, which were varied by varying the weight ratios Wp, W1, W2 and W3.

Figures 17, 18 and 19 shows the variations of the measured values in relation to the variations of C1, C2 and C3, respectively.

Referring to Fig. 17, in the region where the TEOS concentration C1 is low (i.e., the organosilicasol concentration is high), bonding is mainly effected by organosilicasol having fewer bonding hands per volume relative to those of TEOS and the bond strength f is low. The bond strength has a peak when Cl = 50% at which the TEOS binder 1 and the organosilicasol binder 2 are present in the same amount and is lowered at higher TEOS concentrations, and cracking occurs when the TEOS concentration is more than 80%. C1 is suitably within the range of from 40 to 60% to provide a bond strength substantially greater than 25 MPa achieved by the conventional iron oxide-based ceramic heat insulating layer.

Referring to Fig. 18, as the concentration of aggregate powder is increased, the ceramic layer is made more dense to provide an increased bond strength while the number of voids is decreased by the increased density to result in a reduced heat insulation. When the powder concentration is more than 30%, the amount of aggregate is excessive relative to that of binder and a ceramic heat insulating layer is not successfully formed. Referring to Fig. 19, the heat insulation is also reduced for the same reason as described above referring to Fig. 18. The powder concentration C2 is suitably within the range of from 15 to 20% and the binder solid component concentration C3 is suitably within the range of from 5 to 15% in order to ensure a bond strength f of at least 50 MPa or more and a heat insulation ΔT of at least 85°C, which values were achieved in Example 7, in which a ceramic heat insulating layer was formed directly on a base material as in this example. If C3 is less than the lower limit of 5%, the amount of binder solid component is too small to successfully form a ceramic heat insulating layer.

As described herein above, the present invention provides a ceramic heat insulating layer having an aggregate of a nephelin mineral realized by controllable preparation of a slurry free from the influence of alkaline metal ions characteristic to the nepheline mineral, thereby having a linear thermal expansion coefficient comparable with that of an iron-based member, an improved strength of bonding to the iron-based member or to a bonding layer formed on the member, and an improved heat resistance and strength.

A ceramic heat insulating layer formed on an iron-based base material with or without a bonding layer interposed therebetween, comprising: aggregate particles of a nepheline mineral; and a binder composed of silica particles and of a metalloxane polymer, the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer. The ceramic heat insulating layer may alternatively comprise: aggregate particles of a nepheline mineral; a binder composed of silica particles and a metalloxane polymer, the binder intervening between the aggregate particles to leave voids and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer; and a sealing layer sealing the voids in a surface region of the ceramic heat insulating layer. A process of forming the ceramic heat insulating layer comprises the steps of: mixing aggregate particles of a nepheline mineral, a binder of an alcoxide and an organosilicasol, and a dispersing medium to form a slurry; applying the slurry either on the surface of an iron-based base material, or on any bonding layer formed on the surface; and firing the iron-based base material having the applied slurry; wherein the mixing is either carried out in a sufficiently acidic or sufficiently alkaline solution such that the surface potential of particles dispersed in the slurry does not pass an isoelectric point due to an increase in a pH value of the slurry because of alkaline metal ions dissolved from the aggregate particles of the nepheline mineral, or the mixing is carried out after coating the aggregate particles of the nepheline mineral with a coating layer which prevents dissolution of alkaline metal ions from the aggregate particles of the nepheline mineral.

Claims

1. A ceramic heat insulating layer formed on an iron-based base material with or without a bonding layer interposed therebetween, comprising:

   aggregate particles of a nepheline mineral, and
   a binder composed of silica particles and of a metalloxane polymer, the binder filling spaces between the aggregate particles and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer.

2. A ceramic heat insulating layer according to claim 1, further comprising chromium oxide particles.

3. A ceramic heat insulating layer according to claim 2, wherein the metalloxane polymer is a linear siloxane polymer.

4. A ceramic heat insulating layer according to claim 2, wherein the metalloxane polymer is a spherical siloxane polymer.

5. A ceramic heat insulating layer according to claim 1, wherein the aggregate particles of the nepheline mineral are coated with an inorganic oxide such as alumina and silica.

6. A ceramic heat insulating layer according to claim 2, wherein the aggregate particles of the nepheline mineral are coated with an inorganic oxide such as alumina and silica.

7. A ceramic heat insulating layer formed on an iron-based base material with or without an interposed bonding layer therebetween, comprising:

aggregate particles of a nepheline mineral,
a binder composed of silica particles and a metalloxane polymer, the binder intervening between the aggregate particles to leave voids and chemically bonding the aggregate particles to each other and to the base material or to the bonding layer, and
a sealing layer sealing the voids in a surface region of the ceramic heat insulating layer.

8. A process of forming a ceramic heat insulating layer on an iron-based base material with or without a bonding layer interposed therebetween, comprising the steps of:

mixing aggregate particles of a nepheline mineral, a binder of an alcoxide and an organosilicasol, and a dispersing medium to form a slurry,
applying the slurry either on the surface of an iron-based base material, or on any bonding layer formed on the surface, and
firing the iron-based base material having the applied slurry
wherein the mixing is either carried out in a sufficiently acidic or sufficiently alkaline solution such that the surface potential of particles dispersed in the slurry does not pass an isoelectric point due to an increase in a pH value of the slurry because of alkaline metal ions dissolved from the aggregate particles of the nepheline mineral, or the mixing is carried out after coating the aggregate particles of the nepheline mineral with a coating layer which prevents dissolution of alkaline metal ions from the aggregate particles of the nepheline mineral.

9. A process according to claim 8, wherein the slurry further comprises chromium particles.

10. A process according to claim 9, wherein the mixing is carried out using the aggregate particles of the nepheline mineral held in suspension in an acid solution.

11. A process according to claim 10, wherein the acid solution is a solution of a carboxylic acid and an inorganic acid.

12. A process according to claim 11, wherein the carboxylic acid is an anhydrous carboxylic acid.

13. A process according to claim 8, wherein the slurry further comprises at least one selected from the group consisting of polyamine, polyphosphine, and polyether.

14. A process according to claim 9, wherein, prior to the mixing, the pH value of a dispersed liquid composed of the binder and the dispersing medium is adjusted to 8 or more.

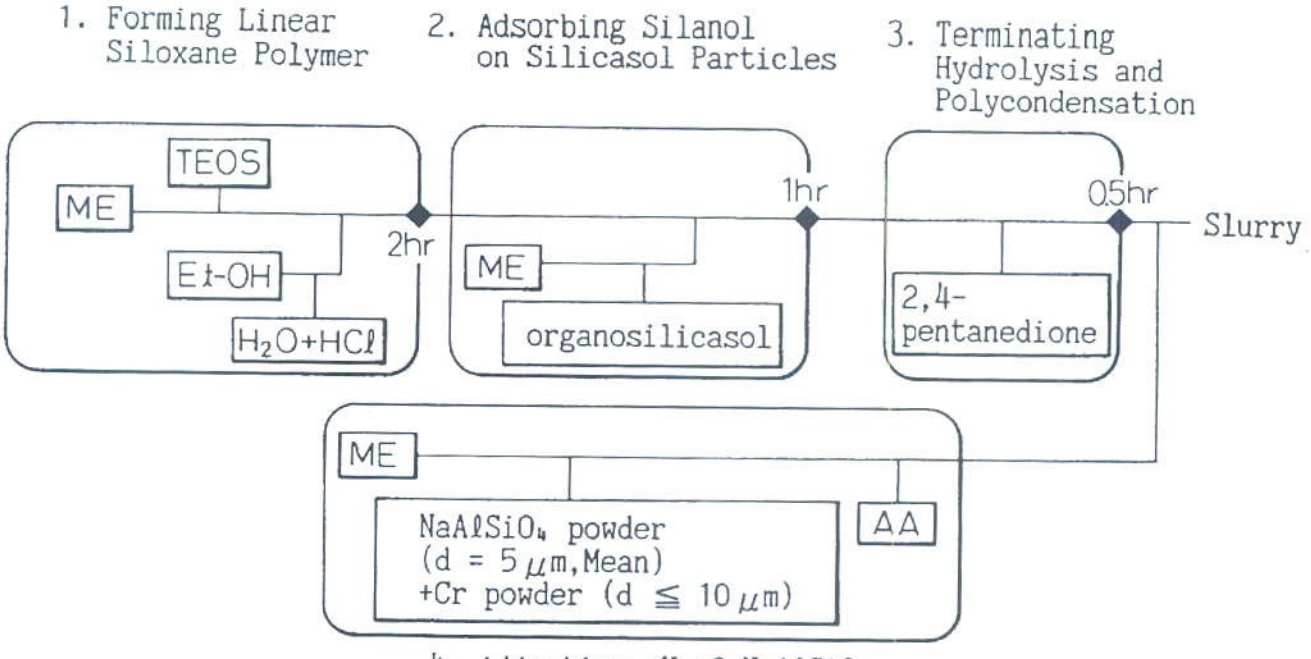
15. A process according to claim 8, wherein, prior to the mixing, an inorganic coating is formed on the aggregate particles of the nepheline mineral by an alcoxide.

16. A process according to claim 15, wherein hydroxyl groups are added to the surfaces of the aggregate particles of the nepheline mineral before use.

17. A process according to claim 15, wherein hydrochloric acid is used as a nucleophilic reaction catalyst.

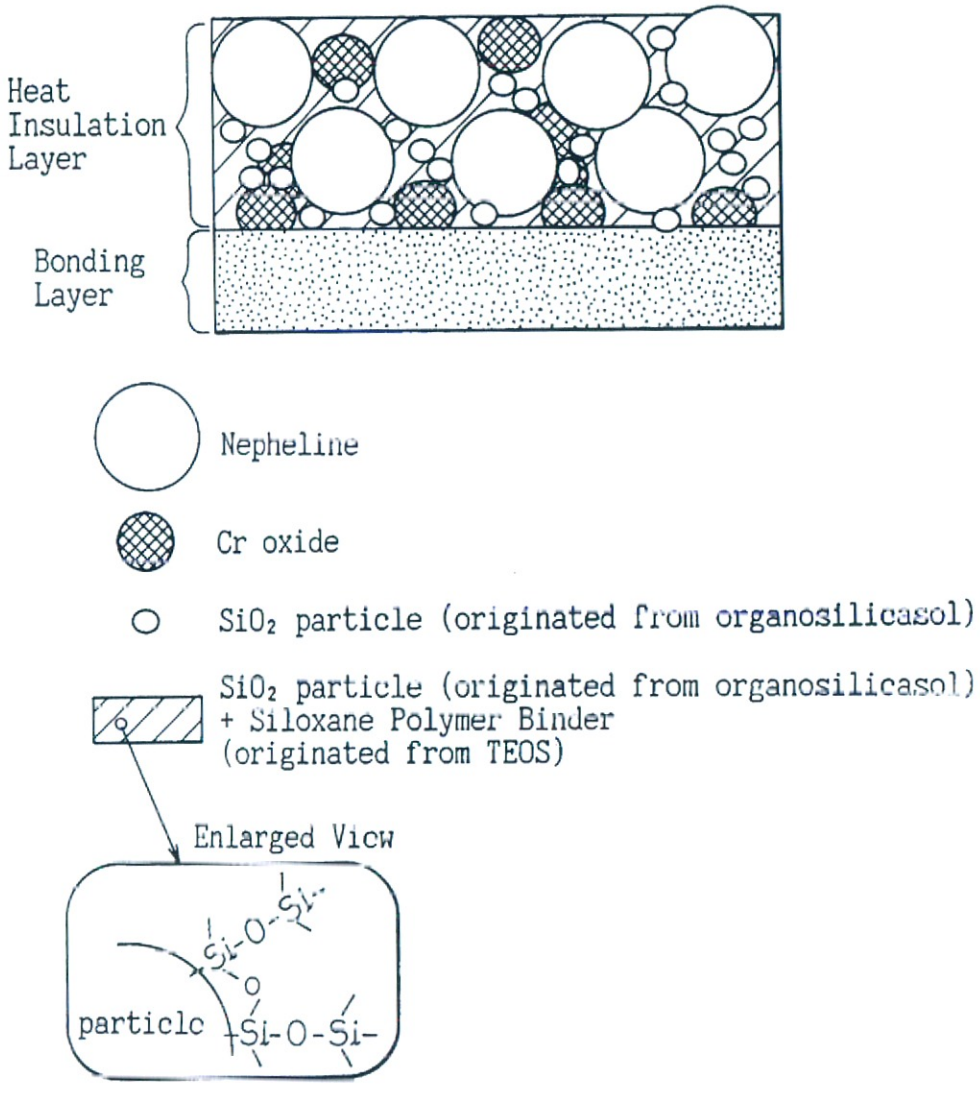
18. A process according to claim 15, wherein the firing is carried out in an inert atmosphere.

Fig.1



EP 0 810 301 A1

Fig.2


Heat
Insulation
Layer
Bonding
Layer
Nepheline
Cr oxide
SiO_2 particle (originated from organosilicasol)
SiO_2 particle (originated from organosilicasol)
+ Siloxane Polymer Binder
(originated from TEOS)
Enlarged View
particle
Si-O-Si
O
Si-O-Si

21

Fig.3

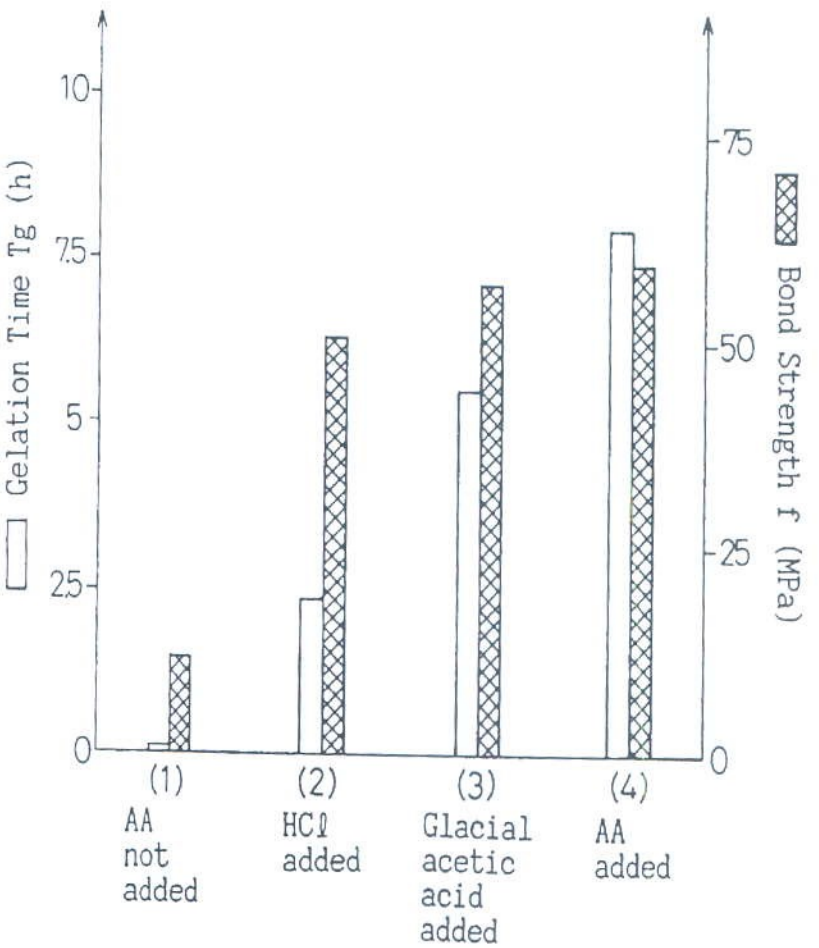

Gelation Time Tg (h)
10
7.5
5
2.5
0
Bond Strength f (MPa)
75
50
25
0
(1)
AA not added
(2)
HCl added
(3)
Glacial acetic acid added
(4)
AA added

Fig. 4

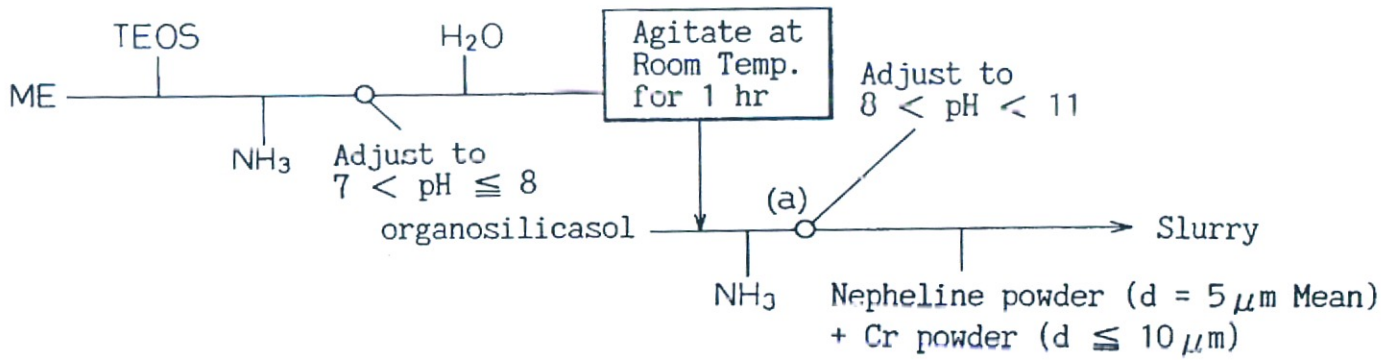

TEOS
H_2O
Agitate at Room Temp. for 1 hr
ME
Adjust to 8 < pH < 11
NH_3
Adjust to 7 < pH ≦ 8
(a)
organosilicasol
Slurry
NH_3
Nepheline powder (d = 5 μm Mean)
+ Cr powder (d ≦ 10 μm)

Fig.5

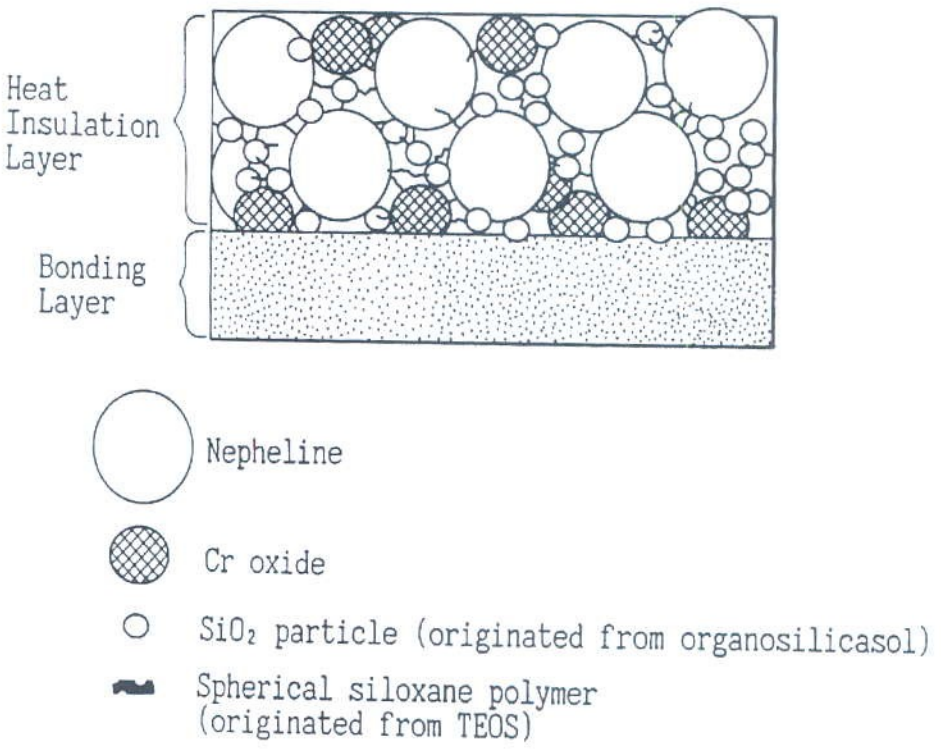

Heat
Insulation
Layer
Bonding
Layer
Nepheline
Cr oxide
SiO_2 particle (originated from organosilicasol)
Spherical siloxane polymer
(originated from TEOS)

Fig. 7

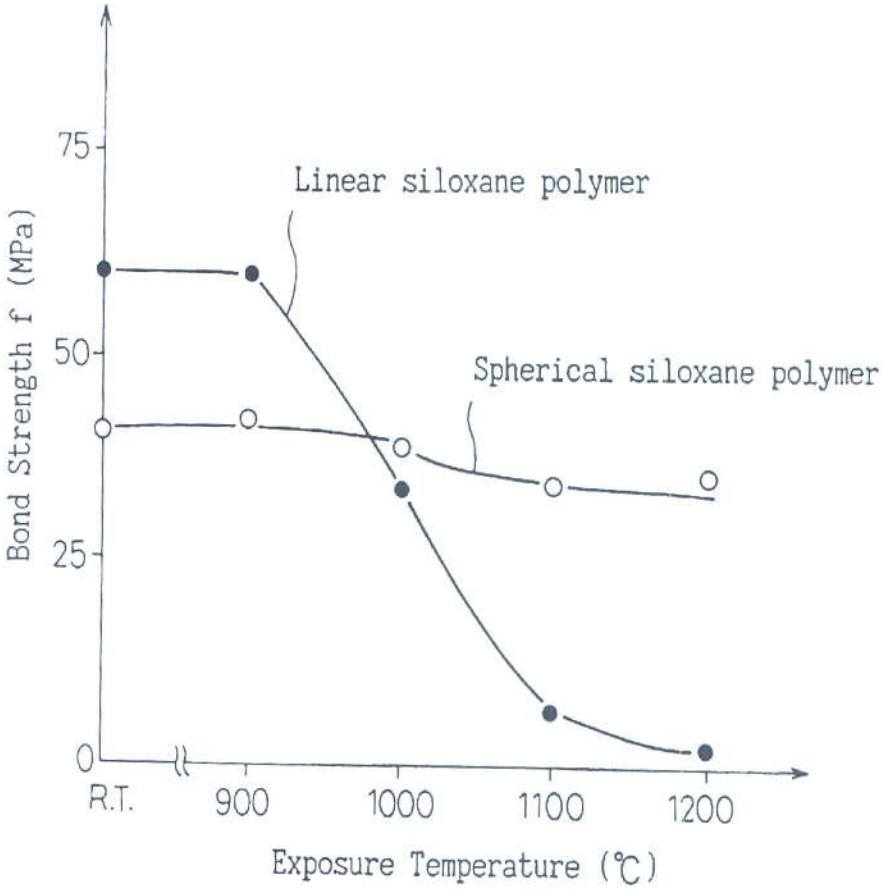
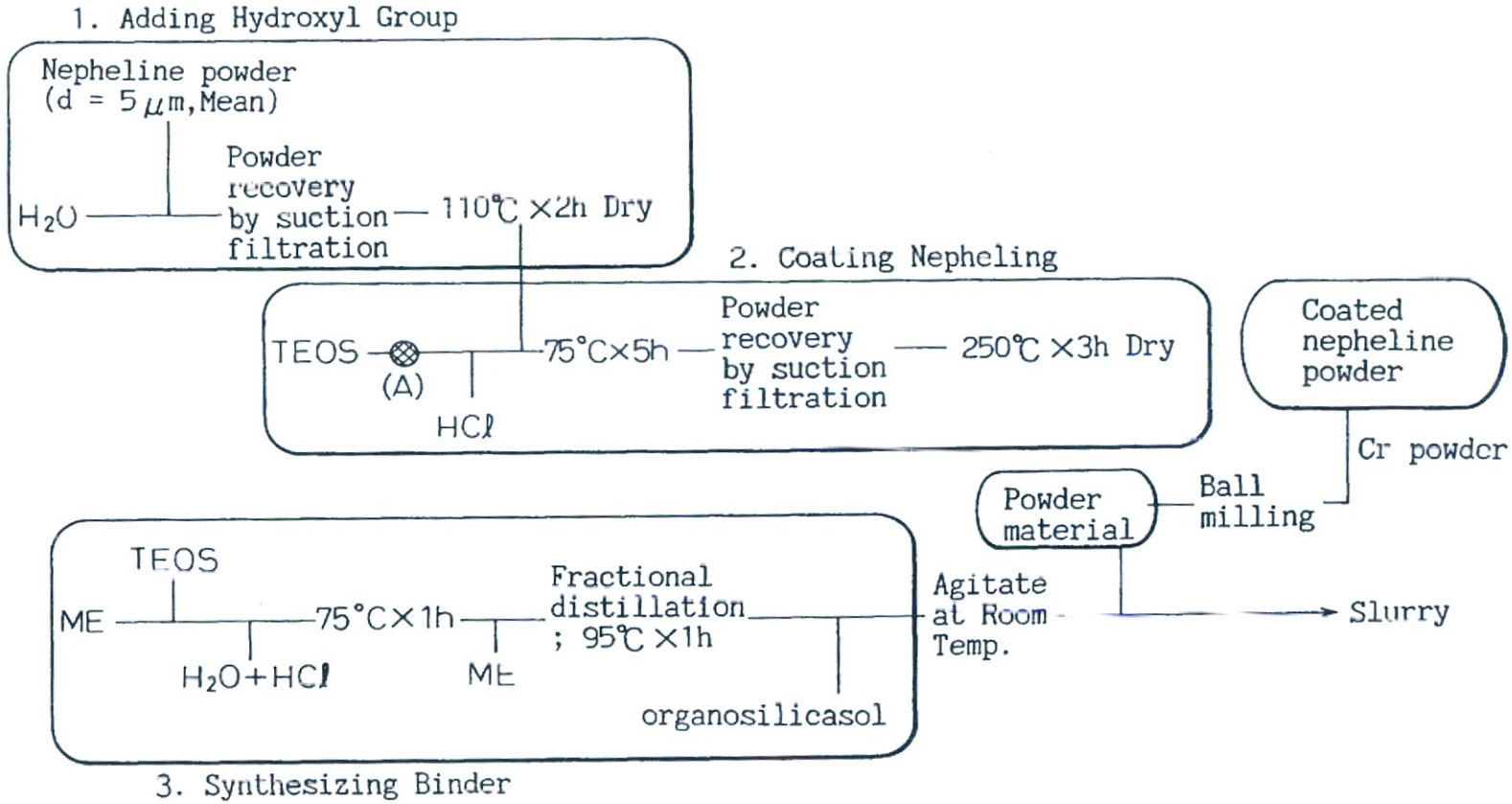
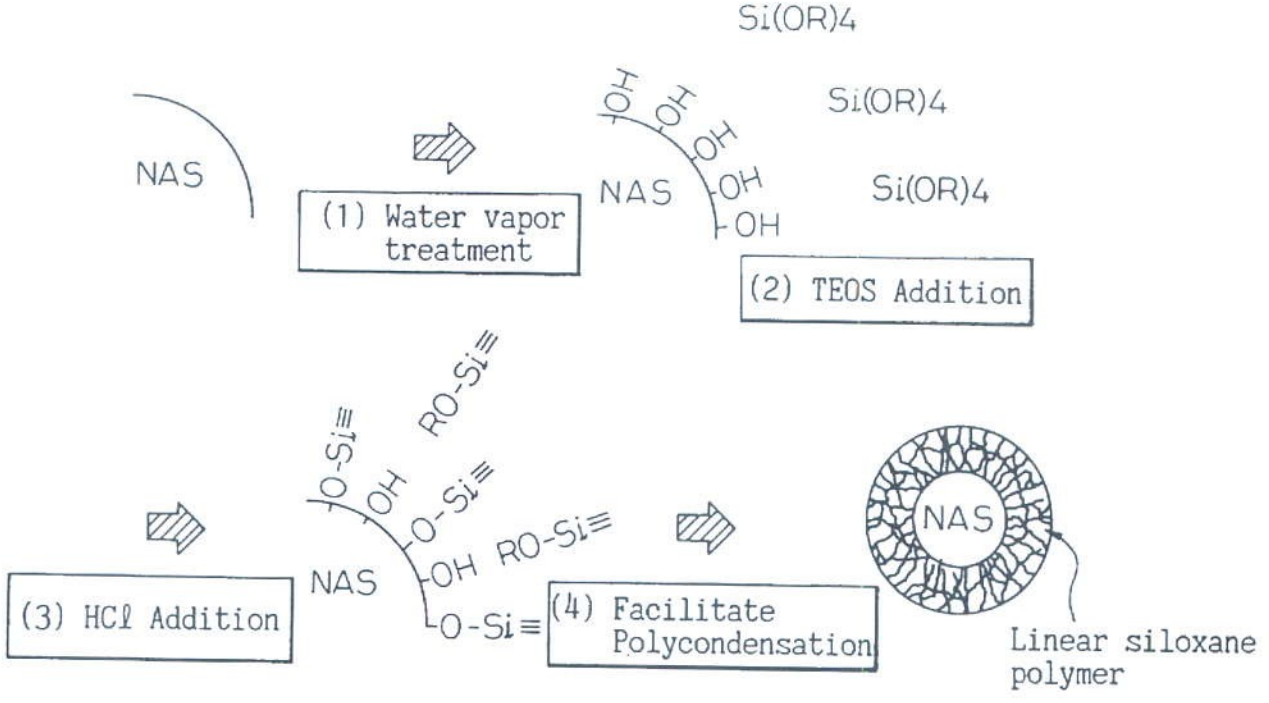

Bond Strength f (MPa)
75
50
25
0
Linear siloxane polymer
Spherical siloxane polymer
R.T.
900
1000
1100
1200
Exposure Temperature (℃)

Fig.8



EP 0 810 301 A1

Fig.9



EP 0 810 301 A1

Fig.10

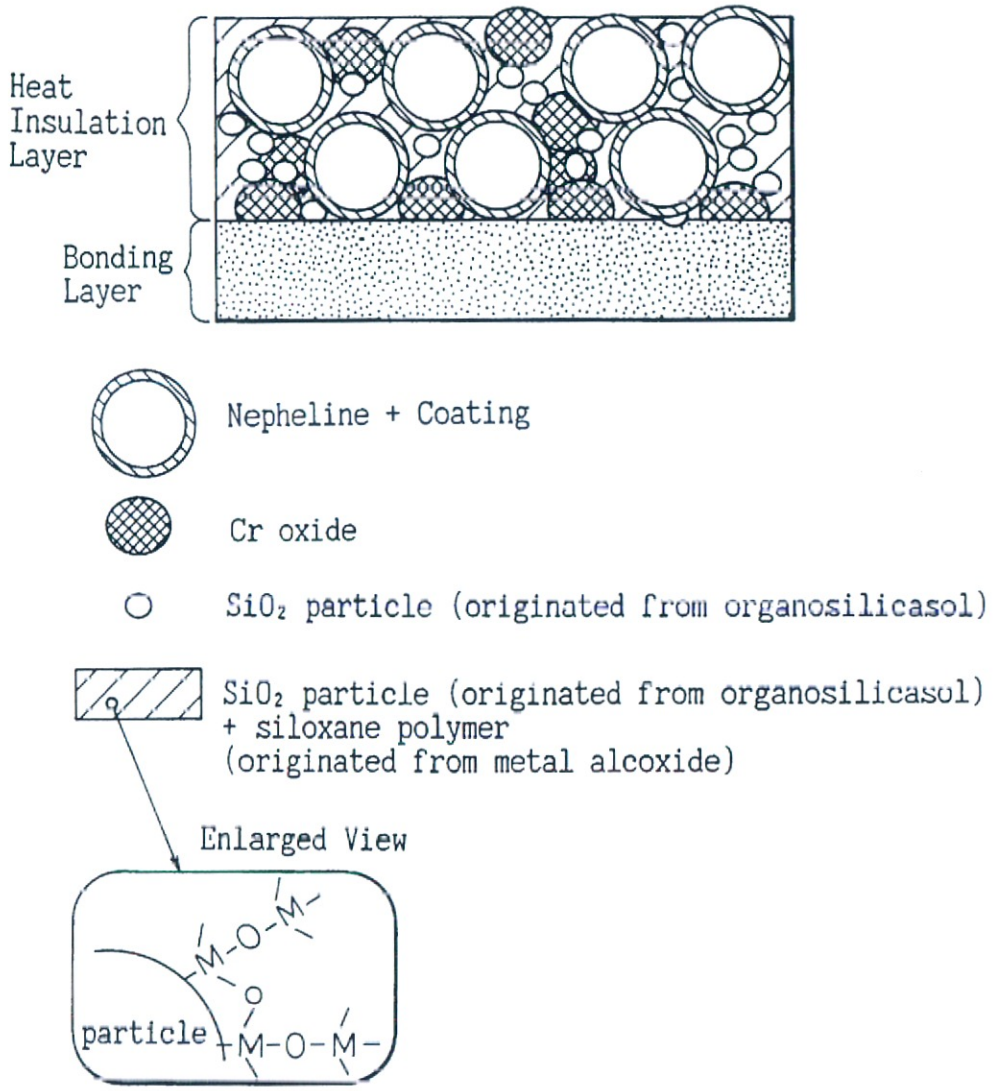

Heat
Insulation
Layer
Bonding
Layer
Nepheline + Coating
Cr oxide
SiO_2 particle (originated from organosilicasol)
SiO_2 particle (originated from organosilicasol)
+ siloxane polymer
(originated from metal alcoxide)
Enlarged View
particle
M-O-M
O
M-O-M

Fig.11

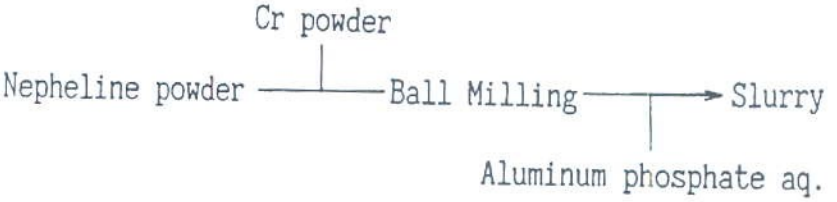

Cr powder
Nepheline powder
Ball Milling
Slurry
Aluminum phosphate aq.

Fig.12

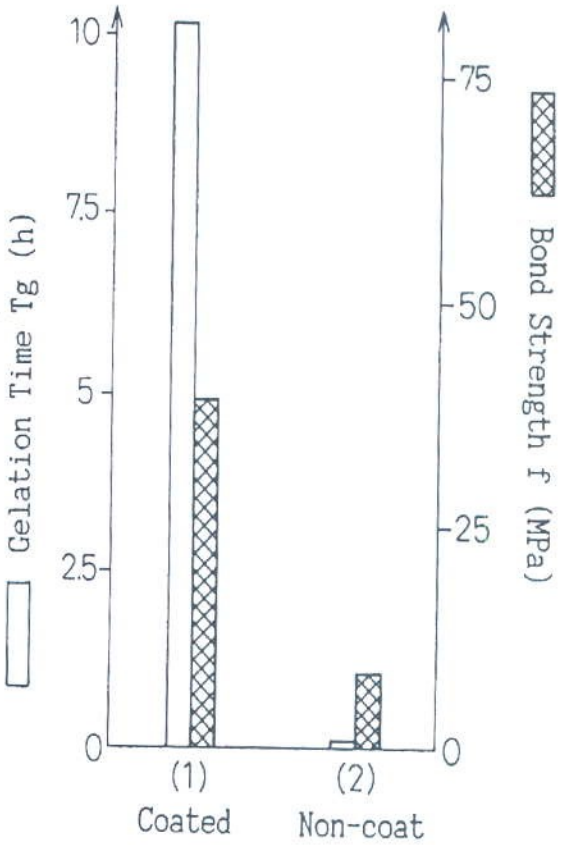

10
7.5
5
2.5
0
Gelation Time Tg (h)
75
50
25
0
Bond Strength f (MPa)
(1)
Coated
(2)
Non-coat

Fig.13

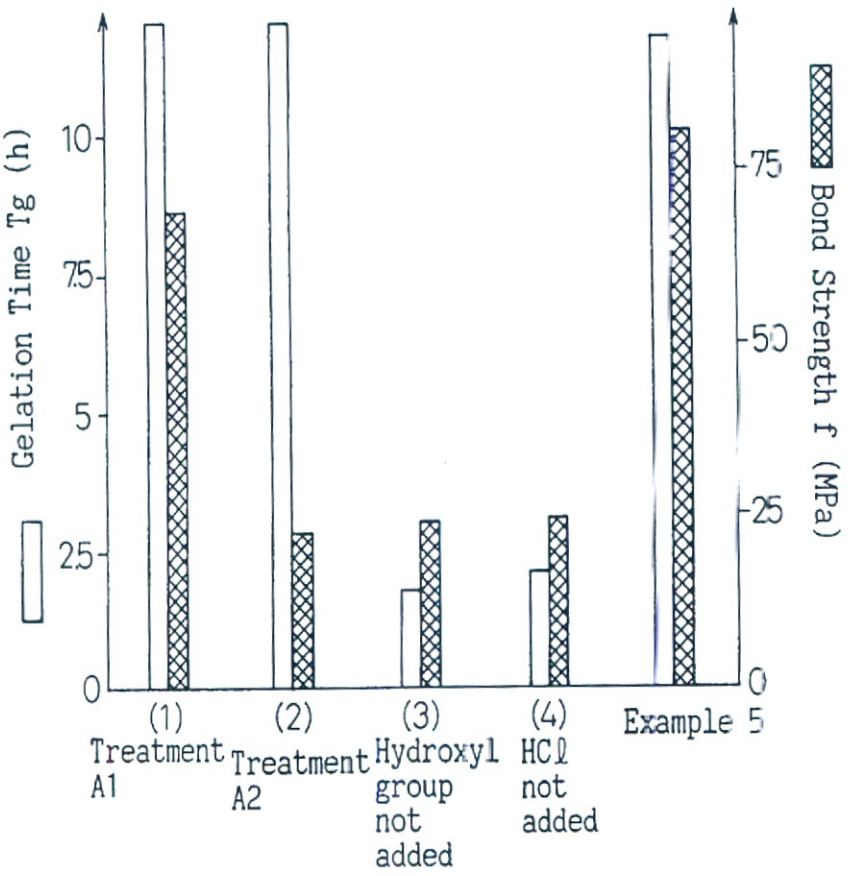

Gelation Time Tg (h)
10
7.5
5
2.5
0
Bond Strength f (MPa)
75
50
25
0
(1)
Treatment A1
(2)
Treatment A2
(3)
Hydroxyl group not added
(4)
HCl not added
Example 5

Fig.14

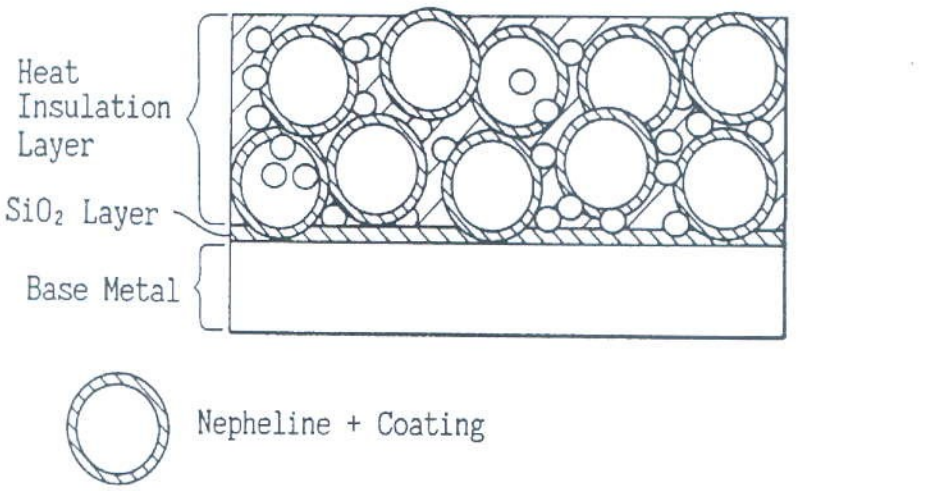

Heat
Insulation
Layer
SiO2 Layer
Base Metal
Nepheline + Coating
SiO2 particle (originated from organosilicasol)
SiO2 particle (originated from organosilicasol)
+ siloxane polymer
(originated from metal alcoxide)
Enlarged View
particle
M-O-M
O
M-O-M

Fig.15

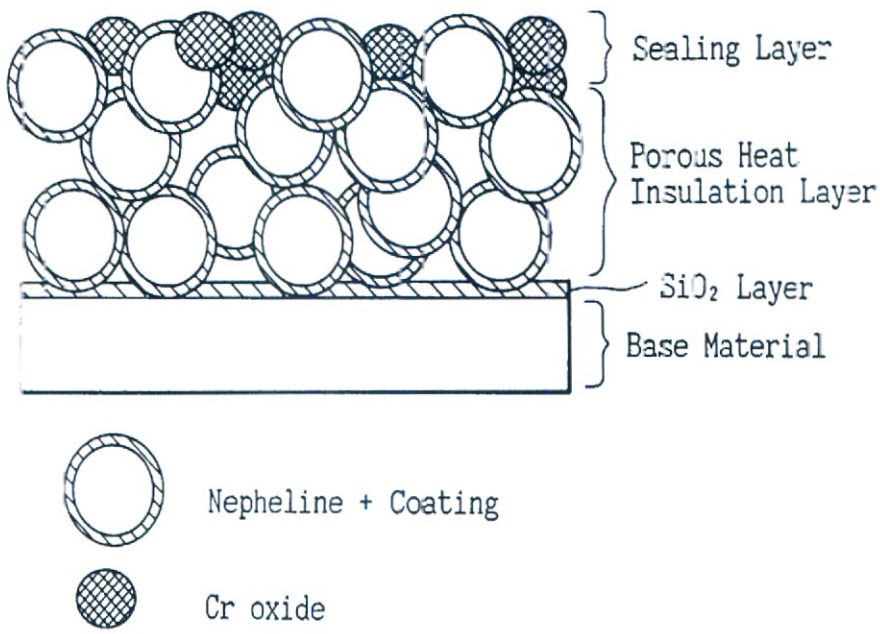

Sealing Layer
Porous Heat Insulation Layer
SiO_2 Layer
Base Material
Nepheline + Coating
Cr oxide

Fig.16



Fig.18

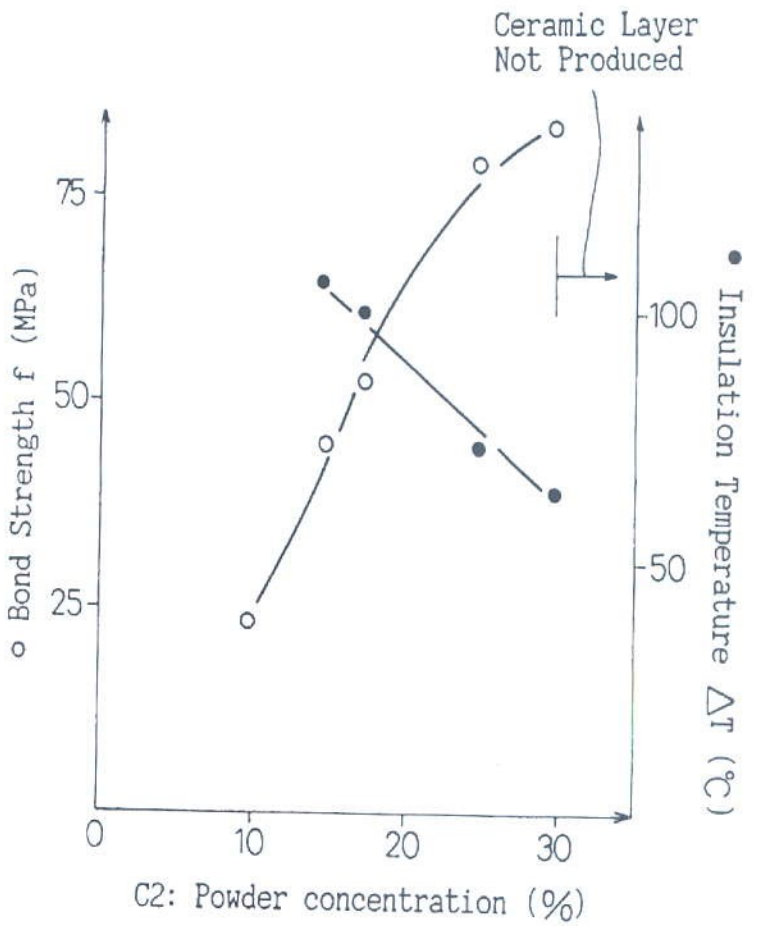
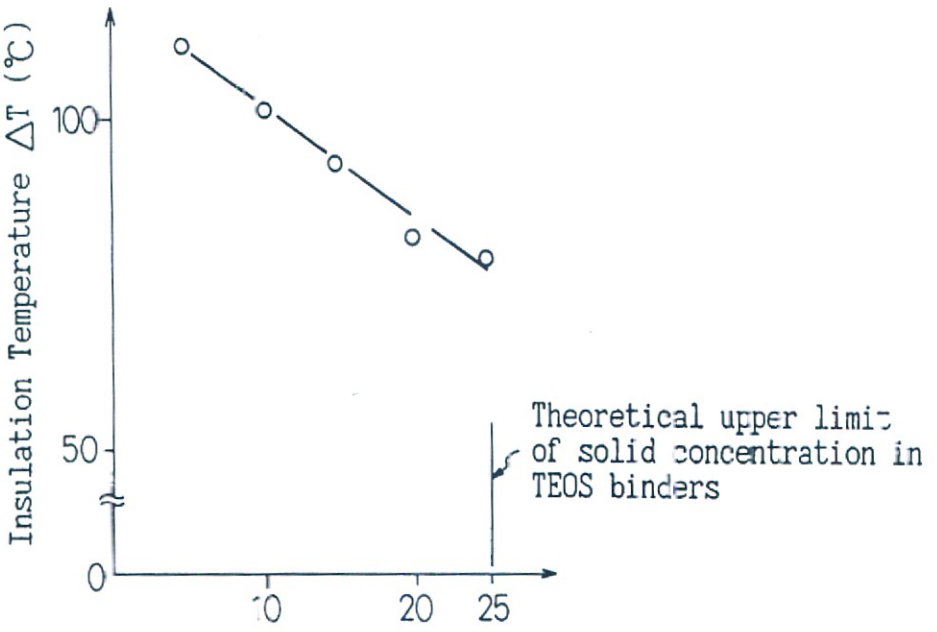

Ceramic Layer
Not Produced
o Bond Strength f (MPa)
75
50
25
0
10
20
30
100
50
• Insulation Temperature ΔT (℃)
C2: Powder concentration (%)

Fig.19


Insulation Temperature ΔT (℃)
100
50
0
10
20
25
Theoretical upper limit of solid concentration in TEOS binders
C3: Solid concentration of blnder (%)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8695

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 330 794 A (PAUL N. BOSCO) * claims 1-29 *	1-3,8	C23C24/08 C23C26/00
A	US 5 164 003 A (PAUL N. BOSCO) * claims 1-20 *	1-3,8	
A	JOURNAL OF THE CERAMIC SOCIETY OF JAPAN, INTERNATIONAL EDITION, vol. 103, no. 7, 1 July 1995, pages 731-733, XP000547586 NISHIMORI H ET AL: "DISPERSITY AND SIZE OF SILICA PARTICLES CONSTRUCTING THICK FILMS PREPARED BY ELECTROPHORETIC SOL-GEL DEPOSITION"		
A	US 5 436 083 A (LOREN A. HALUSKA)		
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 84-198178 c32 XP002037687 & JP 59 113 051 A (KANEGAFUCHI CHEM KK) , 29 June 1984 * abstract *		TECHNICAL FIELDS SEARCHED (Int.Cl.6) C23C
A	US 3 013 897 A (MARTIN E. CUPERY)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 August 1997	Elsen, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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(Anexo C)

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(54) Method of repairing a thermal barrier coating and repaired coating formed thereby

(57) A coating composition and repair method suitable for repairing thermal barrier coatings (TBCs), and particularly TBCs based on alumina-silica compositions. The method includes preparing a coating composition containing solid ceramic particles, hollow ceramic particles, and a silica precursor binder, applying the coating composition on a surface area of a component exposed by an opening, for example, spallation of the TBC, and then reacting the binder to yield a repair coating that covers the surface area of the component. The resulting repair coating contains the solid ceramic particles and the hollow ceramic particles in a silica matrix formed by thermally decomposing the binder.

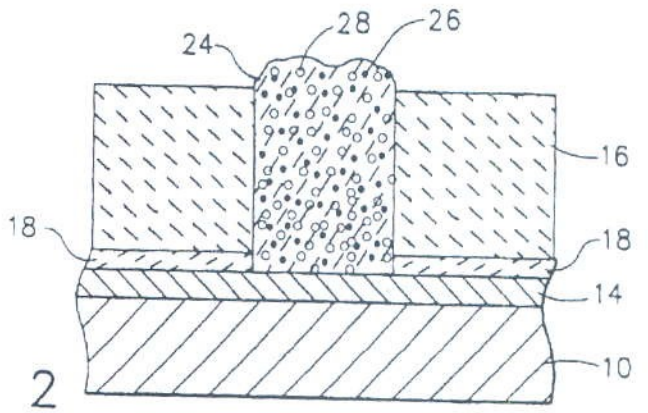


FIG. 2

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Description

BACKGROUND OF THE INVENTION

[0001] This invention relates to coatings for components exposed to high temperatures, such as the hostile thermal environment of a gas turbine. More particularly, this invention is directed to a method for repairing thermal barrier coatings that have suffered localized spallation.

[0002] Hot section components of aircraft and industrial (power generation) gas turbine engines are often protected by a thermal barrier coating (TBC), which reduces the temperature of the underlying component substrate and thereby prolongs the service life of the component. Ceramic materials and particularly yttria-stabilized zirconia (YSZ) are widely used as TBC materials because of their high temperature capability, low thermal conductivity, and relative ease of deposition by plasma spraying, flame spraying, and physical vapor deposition (PVD) such as electron beam physical vapor deposition (EBPVD). Air plasma spraying (APS) is often preferred over other deposition processes due to relatively low equipment costs and ease of application and masking.

[0003] Analysis has shown that YSZ TBC's deposited by APS are about 20% to 70% transparent to thermal radiation (wavelengths of about 780 nm to about 1 mm) when deposited at typical thicknesses of about 250 to 500 micrometers. As a result, the thermal protection provided by such TBC's is compromised by their infrared (IR) transmissivity in environments that have high thermal radiation loads, such as within the combustor section of a gas turbine. In response, other materials have been proposed for insulating combustion section hardware and other hardware subject to similar operating conditions. Notable examples include materials containing alumina and silica that are non-transparent to IR wavelengths of particular concern in the combustor, for example, wavelengths of about 0.3 to about 6 micrometers. These coating materials also have the advantage of having lower mass and excellent insulating properties. Particular examples of TBC's formed of these coating materials involve the use of a mixture containing alumina powder particles and a silica precursor, which are applied to the surface to be protected and heated to thermally decompose the precursor to form a silica matrix in which the powder particles are dispersed. The mixture can be preformed as a tape that is applied to the surface or can be sprayed onto the surface. As examples, see commonly-assigned U.S. Patent Nos. 6,165,600, 6,177,186, 6,210,791, 6,465,090, and 6,827,969.

[0004] To be effective, TBC systems must have low thermal conductivity, strongly adhere to the component, and remain adherent throughout many heating and cooling cycles. The latter requirement is particularly demanding due to the different coefficients of thermal expansion between the ceramic materials of the TBC and the substrates they protect, which are typically metallic superalloys. To promote adhesion and extend the service life of a TBC system, an oxidation-resistant bond coat is often employed. Bond coats are typically in the form of overlay coatings such as MCrAlX (where M is iron, cobalt and/or nickel, and X is yttrium, rare earth elements, and/or reactive elements), or diffusion aluminide coatings. During the deposition of the ceramic TBC and subsequent exposures to high temperatures, such as during engine operation, these bond coats form a tightly adherent alumina (Al_2O_3) layer or scale that adheres the TBC to the bond coat.

[0005] The service life of a TBC system is typically limited by a spallation event driven by bond coat oxidation, increased interfacial stresses, and the resulting thermal fatigue. Though significant advances have been made, there is the inevitable requirement to repair components whose thermal barrier coatings have spalled. Though spallation typically occurs in localized regions or patches, the conventional repair method has been to completely remove the thermal barrier coating, restore or repair the bond layer surface as necessary, and then recoat the entire component. As an alternative, U.S. Patent No. 5,723,078 to Nagaraj et al. teach a process for selectively repairing a spalled region of a TBC using a plasma spray technique.

[0006] In the case of large power generation turbines, completely halting power generation for an extended period in order to remove components whose TBC's have suffered only localized spallation is not economically desirable. As a result, components identified as having spalled TBC are often analyzed to determine whether the spallation has occurred in a high stress area, and a judgment is then made as to the risk of damage to the turbine due to the reduced thermal protection of the component, which if excessive can lead to catastrophic failure of the component. If the decision is to repair the TBC, the spalled component is removed and new TBC material is deposited by plasma spraying on the spalled surface region. Such repair processes have found wide use for the repair of YSZ TBC's. However, there is an ongoing need for new repair materials and techniques, including those particularly adapted to repair the aforementioned alumina-silica TBC materials.

BRIEF DESCRIPTION OF THE INVENTION

[0007] The present invention provides a coating composition and repair method suitable for repairing a TBC on a component, and particularly TBC materials based on alumina-silica compositions.

[0008] According to a first aspect of the invention, the method includes preparing a coating composition comprising

solid ceramic particles, hollow ceramic particles, and a silica precursor binder, applying the coating composition on an exposed surface area of the component, for example, exposed by localized spallation, and then reacting the binder to yield a repair coating that covers the surface area of the component. The resulting repair coating comprises the solid ceramic particles and the hollow ceramic particles in a silica matrix formed by thermally decomposing the binder. Also encompassed by the invention is the coating composition and the repaired TBC.

[0009] Coating compositions and the resulting repair coatings described above are compatible with alumina-silica based TBC materials, and the hollow ceramic particles provide the additional benefit of reducing density and enhancing the insulative and erosion-resistant properties of the repair coating. Preferred materials for the solid and hollow ceramic particles are non-transparent to IR wavelengths of particular concern in the combustor section of a turbine engine, for example, wavelengths of about 0.3 to about 6 micrometers. As such, preferred materials for the repair coating do not degrade the thermal reflectivity of the TBC being repaired.

[0010] In view of the above, it can also be appreciated that the method of this invention does not require the TBC to be completely removed, and does not require removal of the component in order to repair its TBC. The method also does not require a high temperature treatment, as the silica precursor binder may be initially cured to enable the repair coating to exhibit sufficient strength to withstand engine operation, during which time the precursor binder is gradually converted to form the silica matrix. As a result, minimal downtime is necessary to complete the repair and resume operation of the turbine engine. In the case of large power generation turbines, the cost is avoided of completely halting power generation for an extended period in order to remove, repair and then reinstall a component that has suffered only localized spallation.

[0011] The method of this invention can be used to repair ceramic coatings on a wide variety of components exposed to thermal loads, including but not limited to TBCs formed of materials other than alumina-silica compositions and applied to hot section components of aircraft and industrial (power generation) gas turbine engines.

[0012] Other objects and advantages of this invention will be better appreciated from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is a cross-sectional representation of a component surface protected by a thermal barrier coating that has suffered localized spallation.

FIGS. 2 and 3 are cross-sectional representations of the component surface of Figure 1 during the repair of the thermal barrier coating in accordance with a preferred embodiment of this invention.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention is directed to components protected by thermal barrier coatings for operation within environments characterized by relatively high temperatures, and are therefore subjected to severe thermal stresses, cycling, and radiation loads. Notable examples of such components include the high and low pressure turbine nozzles and blades, shrouds, combustor liners, secondary seals, and augmentor hardware of gas turbine engines for use in aircraft and industrial applications. The present invention is particularly directed to thermal barrier coatings (TBCs) that exhibit thermal insulating properties to conduction and thermal radiation. The advantages of this invention will be described as particularly applicable to combustor components of turbine engines, though the invention is generally applicable to any components in which thermal barrier-type coatings as described herein may be used to thermally insulate a component from its environment.

[0015] Represented in Figure 1 is a surface region of a component 10 with a thermal barrier coating (TBC) system 12 having an exposed region 20, for example, as a result of localized spallation. The TBC system 12 is shown as being composed of a bond coat 14 on the surface of the component 10, and a ceramic layer (TBC) 16 deposited on the bond coat 14 as the thermal barrier coating. As is the situation with high temperature components of gas turbine engines, the component 10 may be formed of a nickel, cobalt or iron-base superalloy. The bond coat 14 is preferably formed of a metallic oxidation-resistant material, so as to protect the underlying component 10 from oxidation and enable the ceramic layer 16 to more tenaciously adhere to the component 10. Suitable materials for the bond coat 14 include, but are not limited to, MCrAlX overlay coatings and diffusion aluminide coatings. Following deposition of the bond coat 14, an oxide scale 18 forms on the surface of the bond coat 14 at elevated temperatures. The oxide scale 18 provides a surface to which the ceramic layer 16 more tenaciously adheres, thereby promoting the spallation resistance of the ceramic layer 16.

[0016] The ceramic layer 16 may be formed of a variety of materials, including YSZ materials widely employed as TBC materials, though results of the repair method of this invention will depend in part on the extent to which the thermal expansion properties of the ceramic layer 16 are compatible with the repair materials discussed below. In a preferred

embodiment of the invention, the ceramic layer 16 is an alumina/silica-based material (alumina, silica, and/or aluminosilicates are the predominant constituents) that is non-transparent to IR wavelengths of particular concern in the combustion sections of turbine engines. Particular examples of such materials include the aforementioned U.S. Patent Nos. 6,165,600, 6,177,186, 6,210,791, 6,465,090, and 6,827,969, whose contents regarding coating compositions and coating processes are referenced here. The ceramic layer 16 may have been formed from tapes applied to the surface of the component 10, or a composition sprayed or to the component surface, or another suitable deposition process. Preferred examples of these coating materials contain alumina powder particles, optionally additional ceramic particles, and a silica precursor, which are mixed and applied to the component surface and then heated to thermally decompose the precursor to form a silica matrix in which the powder particles are dispersed. The coating material is deposited to a thickness that is sufficient so that the resulting ceramic layer 16 is capable of providing the required thermal protection for the component 10.

[0017] If located within the combustion section of a turbine engine, surfaces of the component 10 are subjected to hot combustion gases during operation of the engine and are therefore subjected to severe attack by oxidation, corrosion and erosion. Accordingly, the component 10 must remain protected from its hostile operating environment by the TBC system 12. Loss of the ceramic layer 16 due to spallation leads to premature and often rapid deterioration of the component 10. As such, the localized spalled region 20 of the ceramic layer 16 represented in Figure 1 must be repaired or the component 10 scrapped. A preferred TBC repair process of this invention is represented in Figures 2 and 3. Each of the following steps performed in the repair of the component 10 can be performed while the component 10 remains installed in the turbine engine, thereby completely avoiding the requirement to remove and later reinstall the component.

[0018] The repair process begins with clearing the surface 22 exposed by the localized spalled region 20 so as to remove loose oxides and contaminants such as grease, oils and soot without damaging the undamaged ceramic layer 16. The oxide scale 18 as well as any well-adhered remnants of the ceramic layer 16 exposed by the spalled region 20 may remain to promote adhesion of a coating composition 24 deposited in the spalled region 20, as represented by Figure 2. According to the invention, the coating composition 24 is a mixture containing one or more powders of solid (non-hollow) ceramic particles 26, one or more powders of hollow ceramic particles (microballoons) 28, and a silica precursor that when sufficiently heated forms a ceramic repair coating 30 shown in Figure 3. In addition, the coating composition 24 may contain other filler materials, including glass compositions.

[0019] The solid particles 26 are preferably alumina, though the use of other ceramic materials or mixtures thereof is also foreseeable. Preferred materials are refractory oxides that are non-transparent to IR wavelengths, including alumina, magnesia (MgO), titania (TiO_2), and calcia (CaO). Additionally, YSZ particles may be included as part of the solid particles 26 as scattering sites for wavelengths of about 0.9 about 2.5 micrometers. Suitable particle sizes for the powder particles 26 and other solid constituents of the coating composition 24 are generally in a range of about 0.01 to about 100 micrometers, more preferably about 0.1 to about 25 micrometers. Depending on the particular application and desired construction of the coating 30, preferred alumina powders for the solid particles 26 may include A-14 (an unground calcined alumina powder; particle size range of about 3 to 5.5 micrometers) available from Almatis, A-16SG (a superground thermally reactive alumina powder; particle size range of about 0.3 to 0.5 micrometer) also available from Almatis, and SM8 (particle size range of about 0.10 to 0.6 micrometer) available from Baikowski International Corp.

[0020] Depending on the particular application and desired construction of the coating 30, the hollow ceramic particles 28 may be alumina, another ceramic material, or a mixture of one or more ceramic materials, with preferred materials being those non-transparent to IR wavelengths such as alumina and silicates including aluminosilicates. Though shown throughout the coating composition 24 and repair coating 30 in FIGS. 2 and 3, the hollow particles 26 may be limited to certain regions of the composition 24 and coating 30, for example, their innermost, outermost, and/or intermediate regions. According to a preferred aspect of the invention, an important role played by the hollow ceramic particles 28 is to increase the insulation properties of the repair coating 30 without diminishing the overall non-transparency of the alumina-silica ceramic layer 16 to IR wavelengths of particular concern in the combustion sections of turbine engines. Other potential benefits include improved erosion resistance of the repair coating 30 with minimal or no adverse increase in weight. The low density of the hollow powder particles 28 compared to the solid powder particles 26 allows for greater thicknesses of the repair coating 30 without exceeding the weight of a similar coating composition containing only the solid particles 26, or a repair coatings 30 of similar thicknesses but lower weight. Preferred materials for the hollow particles 28 include aluminosilicates having a particle density of less than 0.40 g/cm^3. Various sources of hollow ceramic powders exist, including Sphere One, Inc. (Extendospheres®), 3M® (Zeeospheres), Sphere Services Inc. (cenospheres), and Trelleborg Emerson & Cuming, Inc. (Eccospheres®). Preferred hollow ceramic particles 28 include aluminosilicates with a particle size range of about 0.05 to about 200 micrometers, such as Extendospheres® SL (about 10 to about 150 micrometers) available from Sphere One, Inc. and Zeeospheres (D50 of about 18 micrometers) available from 3M.

[0021] The silica precursor serves as a binder in the coating composition 24. Preferred silica precursors are believed to be silicone-based compositions such as polymethylsiloxane, though it is foreseeable that other silicon sources and ceramic precursors could be used, such as TEOS (tetra-ethyl-ortho-silicate) or possibly a colloidal silicon source. Particularly suitable precursors include methylsesquisiloxane mixtures of the polysiloxane family available from sources

such as Apollo Plastics Corporation (for example, SR350 and SR355) and Dow Chemical Corporation, and a polyvinyl butyral available under the name B-79 from Monsanto Co.

[0022] The remaining constituents for the composition 24 are preferably organics, primarily a carrier liquid or solvent and optionally surfactants, dispersants, and/or additional binders/plasticizers capable of adhering the powder particles 26 and 28 together to yield a composition 24 that can be applied to the surface 22. Depending on the types and amounts of the additional ingredients, the composition 24 may be formulated and processed as solid but pliable tapes that can be individually applied to the surface 22, or a more pliable and malleable material that can be applied as a putty or paste. A suitable carrier liquid/solvent is an anhydrous alcohol such as ethanol, denatured alcohol and isopropyl alcohol, though acetone, trichloroethylene, and others compatible with silicone materials could be used. Suitable plasticizers include dibutyl pthalate (DBP) and polyvinyl butyral (for example, the aforementioned B-79). If the composition 24 is to be used in the form of a tape, a sufficient fraction of binders and plasticizers should be present to allow the tape to be applied and chemically or mechanically bonded to the surface 22 with the use of heat and pressure. Surfactants can also be used to achieve a suitably tacky consistency that enables the composition 24, particularly those prepared as a tape, to adhere to the surface 22 exposed by the spalled region 20. Suitable surfactants include an alkyl organic phosphate ester acid surfactant commercially available as PS21A from Whitco Chemical. Another surfactant that can be used is available under the name Merpol A from Stephan.

[0023] The fraction of organics used in the composition 24 may also depend on whether the repair process is intended to produce a coating 30 whose structural properties vary through its thickness, in which case multiple layers of the composition 24 with different compositions are applied to the surface 22. For example, it may be desirable that the innermost layer or region of the applied coating material 24 contains sufficient binders/plasticizers to produce submicron voids and yield a desirable porosity level that increases the thermal insulation capability of the coating 30, while the fraction of organics used in the outermost layer or any intermediate layers is preferably lower to minimize porosity to promote abrasion and infiltration resistance.

[0024] Whether formulated as a paste or tape, it may be desirable to formulate certain regions of the coating 30 to have additional enhanced properties. For example, the outermost surface region of the coating 30 may incorporate IR-reflective or IR-absorbing particles, as well as other constituents such as erosion- and/or corrosion-resistant materials. Another example is to formulate the outermost surface region of the coating 30 to achieve a smoother surface finish that promotes the aerodynamics of the component 10. In this case, it may be desirable to apply as the outermost layer a coating composition 24 that uses finer solid and/or hollow particles 26 and 28. For example, the interior of the coating 30 may be formed by a composition 24 that contains an alumina powder material such as A14, while the exterior of the coating 30 may be formed by a composition 24 that contains a finer alumina powder material such as A16SG, and may completely omit the hollow particles 28.

[0025] Approximate broad and preferred ranges are stated in weight percents in Tables I and II below for individual constituents for coating compositions 24 in the form of pastes and tapes, respectively.

TABLE I

CONSTITUENTS	BROAD	PREFERRED	EXAMPLE
Solvent	10 - 60%	15 - 45%	29.3%
Solid Powder Particles	5 - 55	12 - 35	22.0
Hollow Powder Particles	5 - 45	10 - 35	30.2
Silica Precursor (binder)	6 - 40	10 - 25	18.5

[0026] For the quantities indicated for the Example in Table I, the solvent is preferably denatured alcohol or acetone, the solid powder particles are preferably A16SG or A14 alumina, and the silica precursor is preferably SR350.

TABLE II

CONSTITUENTS	BROAD	PREFERRED	EXAMPLE
Solvent	10 - 60%	12 - 40%	21.5%
Solid Powder Particles	5 - 55	15 - 40	28.4
Hollow Powder Particles	5 - 45	10 - 40	33.3
Silica Precursor (binder)	3 - 40	5 - 20	8.5
Other binders	2 - 20	3 - 10	4.0

(continued)

CONSTITUENTS	BROAD	PREFERRED	EXAMPLE
Plasticizer(s)	1 - 10	1 - 5	2.0
Surfactant(s)	0 - 9	1 - 5	2.6

[0027] For the quantities indicated for the Example in Table II, the solvent is preferably denatured alcohol or acetone, the solid powder particles are preferably A16SG alumina, the silica precursor is preferably SR355, the additional binder is preferably B-79, the plasticizer is preferably DBP, and the surfactant is preferably PS21A. The solvent is evaporated from the tape compositions of Table II prior to application of the tape to the component surface 22 and sintering to form the repair coating 30.

[0028] The choice of silica precursor in Tables I and II is due in part to their differing silica yields. The SR350 binder indicated in Table I yields silica in an amount of about 60 to about 75 weight percent of the original amount of SR350 binder present in the coating composition 24, whereas a like amount of the SR355 binder indicated in Table II yielding silica in lower amounts of about 30 to about 40 weight percent of the original amount of SR355 binder present in the tape coating composition 24.

[0029] A suitable process for forming coating compositions 24 of this invention as a paste involves combining the above-noted constituents of Table I to achieve a suitable paste-like consistency, after which the composition 24 can be applied to fill the spalled region 20 in any suitable manner, such as with a trowel. Depending on its composition, the binder of the paste composition 24 may react at room temperature, or its reaction accelerated by heating such as with a heat lamp, torch, or other heat source until the strength of the resulting repair coating 30 has reached a required level for operation in the turbine engine. A suitable cure treatment is about sixteen hours at room temperature to cure the preferred silicone binders, though cure times can be significantly reduced at elevated temperatures. Conformance of the paste composition 24 to the spalled region 20 and curing of the binder can be promoted by using a thermal treatment that includes pressing the applied composition 24 with a heated iron. Thereafter, post processing operations can be performed to prepare the component 10 for use.

[0030] During operation of the turbine engine, the repair coating 30 continues to react, associated with an increase in the strength and other mechanical properties of the coating 30. The preferred silicone binders initially cure by polymerization to form a silicone matrix whose strength is sufficient for engine operation. With extended use at high temperatures, the silicone thermally decomposes to silica, forming a silica matrix in which the ceramic particles 26 and 28 are dispersed.

[0031] A suitable process for forming coating compositions 24 of this invention as a tape involves casting the one or more tapes on a tetrafluoroethylene (i.e., TEFLON®) sheet. Compositions within the ranges defined in Table II are applied to the TEFLON sheet and then dried for a duration sufficient to evaporate the solvent. The dried tapes are then removed from the TEFLON sheet and transferred to the component surface to be protected by the repair coating 30. If a coating 30 with multiple layers of different properties is desired, a tape formulated to produce an innermost layer or region of the coating 30 may be applied first, followed by one or more tapes to form the outermost and any intermediate layers or regions of the coating 30. Alternatively, a single multilayer tape may be cast that contains the desired different coating compositions 24, such that only a single tape application is required. An advantage with using a single multilayer tape is that the relative amounts of the solid particles 26, hollow particles 28, and binder can be varied to achieve different porosity levels within the coating 30 (for example, greater porosity near the surface 22 of the component 10 and lower porosity near the outer surface of the coating 30. As noted above, the smoothness of the surface of the repair coating 30 can also be improved by appropriately selecting the relative sizes of the solid and hollow particles 26 and 28, and the relative amounts of the solid and hollow particles 26 and 28 and binder.

[0032] Following tape application, pressure is preferably applied to the outer surface of the tape(s) through the use of a caul plate, rubber form, or other suitable means in order to produce the desired final surface finish and geometry for the coating 30. If the component 10 has been removed, a vacuum bag can be used in conjunction with an autoclave to apply the heat and pressure required to chemically or mechanically bond the tape(s) to the component 10. The unsintered tape or tapes can then be sintered by operating the engine or an additional thermal treatment to consolidate and set the tape(s). In either case, sintering is performed at a temperature that will not adversely affect the desired properties for the component 10, but above the temperatures at which the binders and plasticizers will burn off and the ceramic particles 26 and 28 will sinter.

[0033] While the invention has been described in terms of particular embodiments, it is apparent that other forms could be adopted by one skilled in the art. Accordingly, the scope of the invention is to be limited only by the following claims.

Claims

1. A method for repairing a thermal barrier coating on a component that is formed of an alumina/silica-based material, the method comprising the steps of:

   preparing at least a first coating composition comprising solid ceramic particles, hollow ceramic particles, and a silica precursor binder;
   applying the first coating composition on a surface area of the component exposed by an opening in the thermal barrier coating; and then
   reacting the binder to yield a repair coating that covers the surface area of the component, the repair coating comprising the solid ceramic particles and the hollow ceramic particles in a silica matrix formed by thermally decomposing the binder.

2. The method according to claim 1, wherein the solid ceramic particles comprise at least one ceramic material chosen from the group consisting of alumina, magnesia, titania, and calcia.

3. The method according to claim 1 or claim 2, wherein the hollow ceramic particles comprise at least one ceramic material chosen from the group consisting of alumina and aluminosilicates.

4. The method according to any preceding claim, wherein the preparing step comprises preparing the first coating composition as a paste and the applying step comprises applying the paste to the surface area.

5. The method according to claim 4, wherein the first coating composition is prepared to contain, by weight, about 10 to about 60 percent of a solvent, about 5 to about 55 percent of the solid ceramic particles, about 5 to about 45 percent of the hollow ceramic particles, and about 6 to about 40 percent of the silica precursor binder, the balance incidental impurities, and at least a portion of the solvent is removed from the first coating composition prior to applying the first coating composition to the surface area.

6. The method according to any one of claims 1 to 3, wherein the preparing step comprises preparing the first coating composition as a tape and the applying step comprises applying the tape to the surface area.

7. The method according to claim 6, wherein the first coating composition is prepared to further contain at least a second binder, at least one plasticizer, and optionally at least one surfactant.

8. The method according to claim 7, wherein the first coating composition is prepared to contain, by weight, about 10 to about 60 percent of a solvent, about 5 to about 55 percent of the solid ceramic particles, about 5 to about 45 percent of the hollow ceramic particles, about 6 to about 40 percent of the silica precursor binder, about 2 to about 20 percent of the at least one second binder, about 1 to about 10 percent of the at least one plasticizer, and up to about 9 percent of the at least one surfactant, the balance incidental impurities, and at least a portion of the solvent is removed from the first coating composition to form the tape and prior to applying the tape to the surface area.

9. The method according to any preceding claim, further comprising preparing a second coating composition comprising the solid ceramic particles, the hollow ceramic particles, the silica precursor binder, and an additional constituent chosen from the group consisting of particles that are more IR-reflective, IR-absorbing, erosion-resistant, and/or corrosion-resistant than the solid ceramic particles and the hollow ceramic particles of the first coating composition, and the second coating composition is applied to form an outermost surface region of the repair coating.

10. The method according to any one of claims 1 to 8, further comprising preparing a second coating composition comprising the silica precursor binder and at least one of second solid ceramic particles and second hollow ceramic particles that are finer than the solid ceramic particles and the hollow ceramic particles of the first coating composition, and the second coating composition is applied to form an outermost surface region of the repair coating having a smoother surface finish than otherwise possible with the first coating composition to promote the aerodynamics of the repair coating.

11. The method according to any preceding claim, wherein the reacting step comprises initially curing the silica precursor binder by polymerization to form a silicone matrix, and then heating the component to thermally decompose the silicone matrix and form the silica matrix.

12. The method according to any preceding claim, wherein the applying and reacting steps are performed while the component remains installed in the gas turbine engine.

13. The method according to claim 12, wherein the gas turbine engine is operated during the reacting step.

14. The method according to any preceding claim, wherein the alumina/silica-based material of the thermal barrier coating comprises alumina particles in a silica matrix.

15. A component repaired by the method of any preceding claim, wherein the opening in the thermal barrier coating is the result of localized spallation of the thermal barrier coating.

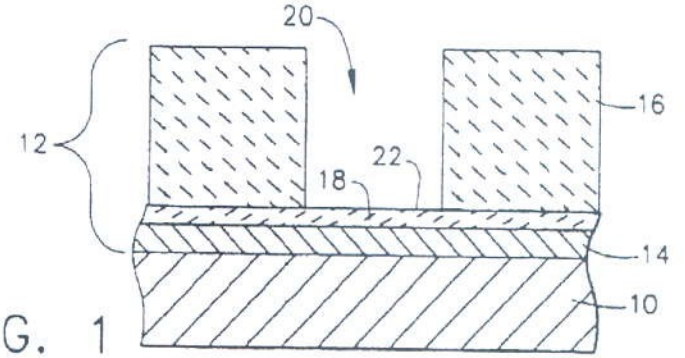


FIG. 1

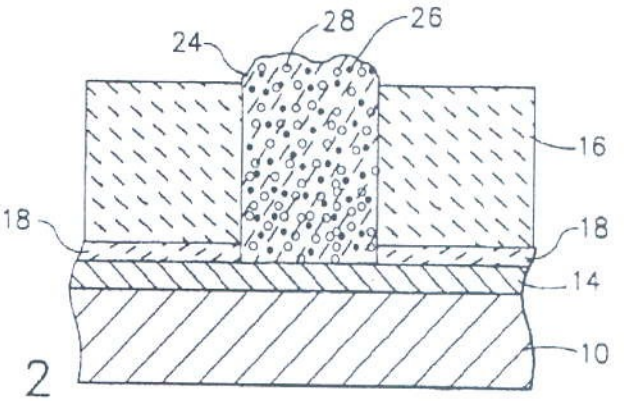


FIG. 2

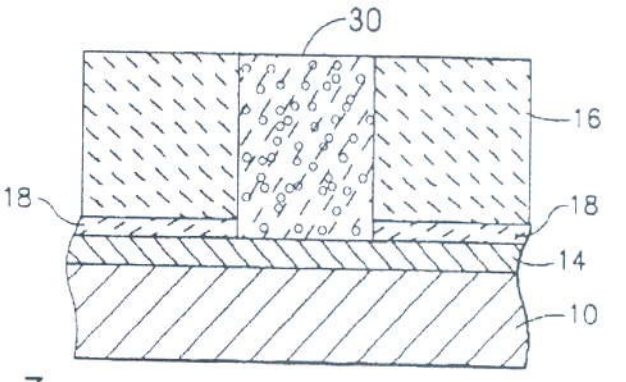


FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 09 16 2700

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 September 2009	Vathakis, S

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