

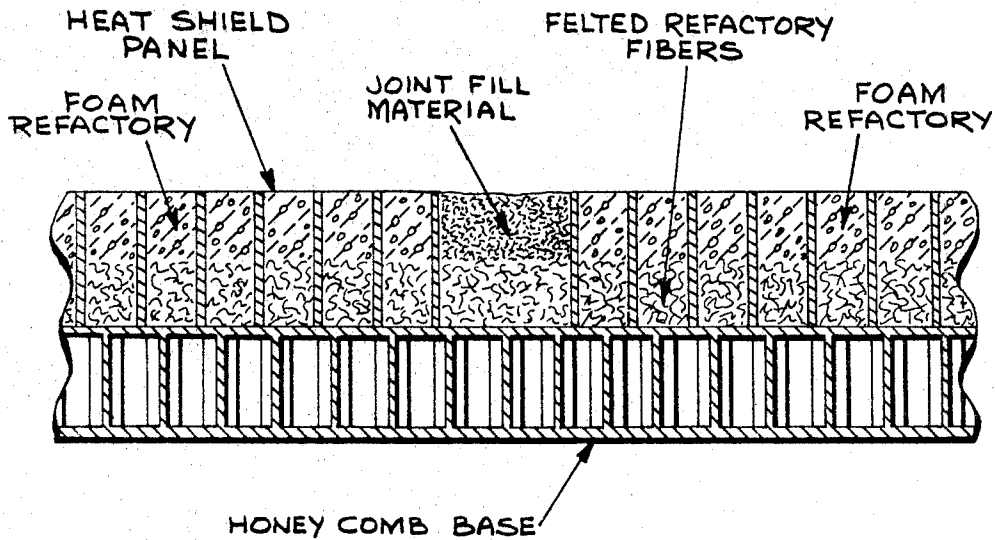
March 25, 1969

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3,434,854

METHOD AND MATERIAL FOR MAKING JOINTS BETWEEN REFRACTORY PANELS

Filed March 12, 1965



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**METHOD AND MATERIAL FOR MAKING JOINTS
BETWEEN REFRACTORY PANELS****Wendell G. Voss, Middletown, Ohio, assignor to Aeronca
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Filed Mar. 12, 1965, Ser. No. 439,154

Int. Cl. C04b 35/66, 35/48

U.S. Cl. 106—57

6 Claims

ABSTRACT OF THE DISCLOSURE

A method for the production of a high temperature insulative, mechanically strong joint between adjacent refractory panels, such as heat shield panels in aerospace vehicles, which includes placing in the joint area a joint fill material containing a mixture of refractory fibers and a binder sol of an organic acid salt of zirconium and permitting the joint to fill to harden at room temperature. A self-hardenable insulating material including refractory fibers mixed with a zirconium salt sol of zirconium acetate, butyrate and propionate which develops increasing compressibility when subjected to temperatures on the order of 800° F. and higher.

This invention relates to means for forming joints between adjacent panels of refractory insulating material, and more particularly, to the production of panel-to-panel joints in heat shields which provide a high degree of mechanical as well as thermal protection to the underlying structure. The invention also relates to a refractory joint fill material which demonstrates the property of compressibility at high temperatures for accommodation of thermal expansion of adjoining insulative panels.

The high temperatures generated by present-day aerospace vessels such as satellite boosters and manned rockets, when passing through the earth's atmosphere, have necessitated an extensive search for new materials of construction which can withstand such temperatures. While heat shields are commonly used to protect these vessels from the high exterior temperatures generated by the friction of air moving over their exterior surfaces, in actual practice substantial difficulties still remain in constructing heat shields of large area by methods which are satisfactory for production outside the laboratory.

One of the problems encountered in producing heat shields of large area is that as size increases, casting or forming the heat shield in one piece from refractory materials becomes increasingly difficult; and it becomes necessary to construct large heat shields from smaller panels which are mounted onto a base or support. In this case the joints or areas between the individual panels are usually filled with an insulative joint fill material.

The present method of constructing a large heat shield is to assemble the individual insulative units or panels onto the base and then to apply a hardenable semi-liquid joint fill material which is chemically cured or hardened in the spaces between the panels. Various silicone resins and phenolic resins have, for example, been tested as joint fill materials. Materials which require firing or sintering in place during manufacture to develop properties present obvious production problems, and are unsatisfactory.

The assembled heat shield is inevitably subjected, before actual launch, to mechanical strains in handling, shipment and final assembly onto the aerospace vehicle, and these strains must be withstood by the joint fill material without rupture of the joints. During launching of the vehicle the joints are subjected to the severe vibration loads then encountered, followed by compression stresses which arise as the insulative panels undergo thermal expansion caused by aerodynamic heating in re-entry.

What has been needed as a joint fill material for the commercial construction of heat shields for aerospace use is a high temperature insulating material which can be formed in place, without firing, with strength sufficient to withstand the usual mechanical forces prior to and during launch. It must, moreover, have sufficient compressibility to accommodate the thermal expansion of the heat shield panels in re-entry without itself failing and without generating failure stresses in the heat shield panels. It should have sufficient strength to withstand aerodynamic shear loads acting on the joint area, and a temperature capability in excess of 3000° F. A material which powders under compression in re-entry would lead to complete removal of the filler material with subsequent exposure, followed by probable rapid destruction, of the joint area.

Joint fill materials previously suggested for use in heat shields have displayed a rather high susceptibility to damage in use, because these materials have either lacked the necessary strength and flexibility to withstand the disruptive mechanical forces encountered, or they have not retained sufficient compressibility or flexibility when subjected to temperatures of the magnitude encountered in re-entry.

It has been a major purpose of this invention to provide a high temperature insulating material for protection of joint areas between refractory panels which can be formed in place at room temperature to provide joint protection between panels which is sufficient to withstand the varying mechanical forces that act on it as well as the thermal stresses of re-entry.

The development of a joint fill material with a temperature capability in excess of 3000° F. and which demonstrates compressibility and bond strength after prolonged exposure above 3000° F. represents a significant achievement. Simulated environmental and physical property tests of the present joint fill material have shown that it permits thermal expansion of the heat shield without generation of excessive buckling stresses in the panels, yet at the same time it restricts heat transfer through the joint area to a value approximating the heat transfer through the heat shield panels themselves. This fill material retains flexibility after high temperature exposure, and when it is used in a simple butt joint configuration, removal and replacement of the fill material can be easily accomplished should excessive surface degradation occur.

The joint fill material I have discovered is formed from a mixture consisting essentially of a fibrous refractory ceramic material having a melting point higher than about 3000° F. and a bonding agent comprising a sol of zirconium acetate or another zirconium salt of a weak acid having a logarithmic dissociation constant between approximately 2.5 and 6.0. Exemplary of such acids are acetic acid, propionic acid, butyric acid and the like. The ratio of zirconium salt to fiber is important, and should be in the range of about 0.2 to 0.3 grams/gm. fiber.

This mixture self hardens or sets in several hours at room temperature to form what is believed to be a new composition of matter wherein the fibers are chemically bonded to the zirconium salt particles from the sol. Experimental tests indicate that the zirconium acetate or other sol used according to this invention has colloidal particles with very active surface structures which give extensive "cross-linking" between the elements of the fibrous ceramic material and the zirconium acetate, so that the resultant product is an actual reaction product as opposed to an aggregate of fibers and a binder.

In this respect the material of this invention differs from materials using colloidal zirconia as a binder. When a colloidal zirconia sol prepared from a zirconium salt of a strong acid such as hydrochloric, nitric, or sulfuric, is used, for example as shown in Alexander and Bugosh

Pat. No. 2,984,576, the resultant structure lacks certain very desirable properties possessed by the material of the present invention, as will be shown. Such colloidal zirconia sols prepared from strong mineral acids apparently suffer considerable surface deactivation during preparation, which renders them unreactive or chemically inert with respect to the fibers, so that no strong chemical bonds between fibers and sol particles are formed.

Insulating materials derived from colloidal zirconia sols prepared from zirconium salts by means of strong mineral acids are considerably inferior in compressive strength and completely disintegrate (i.e., powder) under high compression whereas the insulating materials of the present invention cured at room temperature have over twice the compressive strength and are not powdered at the same high compression. In addition, insulating materials derived from colloidal zirconia sols undergo undesirable drying shrinkage during room temperature cure whereas the insulating material of the present invention shows no drying shrinkage at room temperature.

Description

The insulating materials of the present invention are prepared by mixing fibers of a refractory material such as zirconia fibers, aluminum silicate fibers, alumina fibers, or the like, which are capable of resisting temperatures above about 3000° F., that is to say, which have a melting point higher than about 3000° F., with a colloidal sol prepared from zirconium acetate or other salt of zirconium with a weak acid having a logarithmic dissociation constant in the range of approximately 2.5–6.0. The sol may for example, be prepared by the action of aqueous acetic acid on a zirconium salt at elevated temperatures. A commercially available zirconium acetate sol which has been found suitable for mixture with zirconia or other refractory fibers is produced and sold by Zirconium Corp. of America, Cleveland, Ohio, under the trademark "Zircoa Bond #6." This material has a specific gravity of 1.324 and contains about 40% by weight of zirconium salt solids, in a dispersing liquid. The zirconium acetate sol is mixed with the fiber, which has preferably been chopped into short lengths, in preferred proportions of 40–55 cc. of the "Zircoa" sol (i.e., about 20–30 grams of zirconium salt solids) to each 100 grams by weight fiber.

The joint is prepared by pressing a matted or felted refractory fibrous material into the bottom part of the joint between the panels, so that it preferably fills about the bottom half of the height of the joint. The fiber-bonding agent mix is then placed into the joint area over the fibrous matted material and is compacted by troweling. The material self-cures at room temperature within several hours, and is not fired.

At room temperature the fiber-bonding agent mixture dries and hardens to a plaster-like consistency and provides a binder with a greater mechanical strength than if cured at high temperature. In the in-plant production of the joint, no temperatures higher than room temperature are needed to cure the filler. It has been found that the room temperature dried condition imparts to the joint fill material a higher strength and greater resistance to damage from vibration loads in launching than the high temperature cured condition. However, although mechanical strength is higher in the unfired state, compressibility is relatively low. When the heat shield is subjected in use to temperatures of 800° F. or more, as in re-entry, compressibility markedly increases. Such curing in service reduces the strength to the order of that of the panels, but increases the compressibility of the joint to accommodate expansion of the adjacent panels without setting up severe stresses. In other words, the requisite compressibility is developed as it is needed in service.

The differences between the zirconium acetate sol bonding agent used in the present invention and colloidal zirconia sol binders can be readily demonstrated, as seen by the following test results. A joint fill material in ac-

cordance with this invention was prepared by adding 54 cc. of "Zircoa Bond #6," as supplied, to 100 grams of chopped zirconia fiber. A standard of comparison was prepared by adding a corresponding amount (64 cc.) of a colloidal zirconia to 100 gms. of chopped zirconia fibers. Properties before and after curing at 800° F. are recorded in the table following:

	Zirconium acetate bonding agent	Colloidal zirconia binder
Initial drying shrinkage, percent -----	0	3.8
Room temperature cure:		
Compressive strength, p.s.i.	699	333
Percent compression at failure -----	2.39	3.05
Type of failure -----	(1)	(2)
Cured for 4 hours at 800° F.:		
Compressive strength, p.s.i.	264	278
Percent compression at failure -----	7.21	4.10
Type of failure -----	(1)	(2)

¹ Vertical crack sample intact.

² Powdered-sample disintegrated.

The test data show that substituting a colloidal zirconia sol for a modified zirconium acetate sol reduces strength at room temperature with no significant change in compressibility. Even more significant results are the drying shrinkage and mode of failure experienced with the colloidal zirconia material. The 3.8% drying shrinkage of itself limits the use of colloidal zirconia, and the mode of failure under compression is another serious defect. Powdering of a colloidal zirconia-filled joint under compression could, in service, lead to complete removal of the filler with subsequent exposure and destruction of the joint area. Simulated re-entry tests have shown that the insulating material of the present invention will remain in place affording sufficient protection to the joint area.

As shown in the table, the properties of the insulating material of this invention change quite markedly with curing. The material cured at 800° F. or higher has much greater compressibility than that cured at room temperature. This was originally unexpected, but it demonstrates that one great value of the material resides in the fact that heat shield joints filled with it develop greater compressibility as thermal conditions require it. In comparison, the zirconia-containing material completely powdered under an approximately similar degree of compression; at failure, the present material only developed a crack and the sample remained intact.

For best results, using a zirconium acetate sol containing 40% zirconium salt solids, at least 40 cc. of the bonding agent per 100 grams of fibrous material should be used; in terms of weight, at least about 20 gms. of zirconium salt solids should be used per 100 gms. fibers. Increasing the quantity of bonding sol over 60 cc. per 100 grams of fiber increases the drying shrinkage of the mix and tends to weaken strength after curing at high temperatures.

The drawing is a section of a joint area between two adjacent refractory panels in a heat shield, showing a preferred joint construction in accordance with this invention. The individual refractory heat shield panels may be of any conventional known type, for example comprising an open faced stainless steel honeycomb, and are shown brazed to a honeycomb sandwich base. The individual honeycomb cavities of the adjacent panels may be partially filled with a felted refractory covered with a foamed cast refractory, or they may be entirely filled with refractory.

In the joint area between the two panels a felted refractory material such as "Fiberax," an aluminum silicate fibrous material produced and sold by The Carborundum Company is inserted, suitably to about half the height of the joint. This material is cut into strips slightly wider than the joint and is pressed into place. Use of a fibrous material below the joint fill composition tends to impart greater compressibility to the joint to accommodate thermal expansion of the panel, and tests have indicated the

desirability of having a substantial fraction of the height of the joint filled with such material. The nature of the felted material, however, is not critical, however, as it is not exposed to the high thermal or mechanical stresses which are borne by the joint fill material in the outer portion of the joint.

The fibrous component of the joint fill material most suitably comprises zirconia fibers. These are supplied commercially in mat form, and are separated and reduced in size for example by "chopping" slowly in a mixer. The zirconium acetate sol is added in a ratio of 40 cc. for 100 grams of fiber and the two are mixed for several minutes. The fiber-bonding agent mix is then placed in the joint and compacted by trowelling. Hardening at room temperature is believed to effect chemical bonding of the fibers to the sol, and perhaps between the sol and the refractory oxide of the panels themselves.

When the insulating properties of heat shields having joints made in accordance herewith were tested under simulated re-entry conditions in comparison to other shields having joints filled with materials such as castable zirconna, silicone resin-silica mixtures and phenolic resins, for example, this material was the only one which performed satisfactorily. The other compositions tended to extrude from the joints or failed to yield in compression thereby causing the panels to buckle outwardly. The butt joints formed by this invention will withstand temperatures up to 3500° F., and have a thermal conductivity about equal to that of the heat shield itself.

Joint fill material in accordance with this invention was prepared by mixing 100 grams of chopped zirconia fiber, having an average fiber length of about 0.5 cm., with 40 cc. of "Zircoa Bond #6" as supplied. The composition was cast as cubes for testing of its properties. After air drying for 16 hours, density was 154 pcf. Average compression of the air dried material under 300 pounds load was 1.31% and the retained change after load removal was 0.60%. Failure load was 721 p.s.i. After curing for 4 hours at 800° F., density was 131 pcf. Compression under 300 pound load was 3.61% with a retained change after a load removal of 1.97%. Failure load was 373 p.s.i.

It should be understood that the invention is not limited to the examples cited but is generally applicable to any composition prepared from a ceramic fibrous material having a melting point over 3000° F. and a reactive zirconia bonding agent derived from a zirconium salt of a weak acid having a logarithmic dissociation constant be-

tween 2.5 and 6.0 which has been intimately mixed and cured at room temperatures.

What is claimed is:

1. A hardened composition consisting essentially of the room temperature reaction product of a fibrous refractory material characterized by a melting point over 3000° F. and a bonding agent which consists essentially of a zirconium acetate sol in the ratio of 40-60 cc. sol/100 grams fibrous material.

2. A joint fill material consisting essentially of a mixture of fibers of material characterized by a melting point over 3000° F. and a bonding agent which consists essentially of a sol of a zirconium salt selected from the group consisting of zirconium acetate, zirconium butyrate and zirconium propionate, said mixture containing about 40-60 cc. of said sol/100 grams of said fibers, said sol containing about 40% by weight zirconium salt.

3. The material of claim 2 wherein said fibers are of a material selected from the class consisting of zirconia, aluminum silicate, and alumina.

4. A high temperature insulating material consisting essentially of a room temperature reaction product of zirconia fibers and a bonding agent consisting essentially of a zirconium acetate sol, in which the ratio of components is about 40-60 cc. of zirconium acetate sol per 100 gms. fibers.

5. The insulating material of claim 4 wherein said sol contains about 40% by weight zirconium acetate.

6. A joint between a pair of adjacent refractory panels which joint contains a joint fill material consisting essentially of a room temperature cured, hardened mixture of fibers of a refractory material characterized by a melting point above 3000° F. and a bonding agent consisting essentially of a sol of a salt of zirconium selected from the group consisting of zirconium acetate, zirconium butyrate, and zirconium propionate, the mixture containing about 40-60 cc. of said sol/100 gm. of said fiber.

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U.S. Cl. X.R.

106-65, 69; 252-62; 52-404