

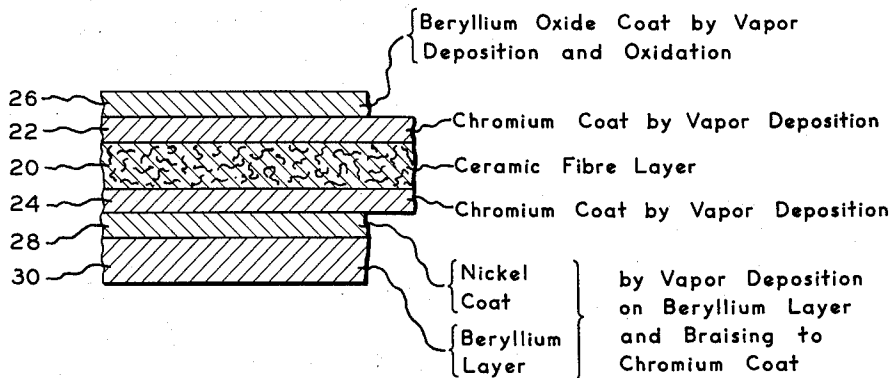
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THERMAL INSULATING CONSTRUCTION

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THERMAL INSULATING CONSTRUCTION

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The present invention relates to thermal insulation and, more particularly, to an insulating structure which is capable of sustaining an extraordinarily high temperature gradient in relation to its thickness. It is often desired to employ a thermally insulating sheet that is relatively thin, for example of the order of 100 mils thick, but that is capable of sustaining an extremely high temperature gradient thereacross, for example a temperature drop of the order of 2500° F. It is often required that such a sheet be characterized by good rigidity, good erosion and corrosion resistance and light weight. Because no single known material possesses a combination of all such characteristics, it is proposed now to provide a composite structure comprising discrete refractory metallic and inorganic fibrous strata, which together possess many or all of such characteristics. Difficulties have been encountered in bonding such strata, it having been found, for example that ceramic cements tend to provide an additional heavy stratum of undesirable brittle character that tends to destroy the original properties of the strata, for example, by rendering the fibrous stratum non-porous.

The present invention contemplates a novel composite insulating sheet structure, in which discrete metallic and inorganic fibrous strata are bonded securely in such a way that the individual properties of the strata are maintained. The object of the present invention is to provide such a structure by vapor depositing a thin metallic coat upon at least one face of the inorganic fibrous stratum and diffusion bonding the coat thus formed to the metallic stratum.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the construction, combination of elements and arrangement of parts, and the process involving the several steps and the relation and order of one or more of the steps with respect to each of the others, which are exemplified in the following detailed disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description, taken in connection with the accompanying drawing, wherein there is shown, in exaggerated cross-section, a preferred product embodying the present invention and wherein there is indicated the various steps of the process by which the preferred product is formed.

Generally, the process of the present invention comprises coating at least one face of a ceramic or glass fibrous stratum with a metal by reduction from or decomposition of a vapor containing a compound of the metal, and thereafter brazing, soldering, welding or otherwise diffusion bonding the metallic coat, which is relatively thin, to a metallic stratum, which is relatively thick. It has been found that a secure diffusion bond may be obtained when the metallic coat on the face of the fibrous stratum ranges from 0.1 micron to .001 inch in thickness.

The inorganic fibrous stratum, which is either woven or felted, is composed of a siliceous material, for example, a ceramic such as aluminum silicate (such as that sold by The Carborundum Company under the trademark Fiberfrax) or, for example, a glass such as soda glass or potash glass (such as that sold by Owens-Corning Fiber-

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glas Corp. under the trademark Fiberglas). The metallic stratum is composed of any suitable metal or alloy, particularly a metal or alloy having a melting point above 1000° C., such as beryllium, molybdenum, steel, tungsten, niobium and tantalum. The process illustrated herein is useful particularly in conjunction with an inorganic fibrous stratum ranging in thickness from 10 to 300 mils and in conjunction with a metallic support stratum ranging in thickness from 10 to 300 mils.

As indicated above, the inorganic fibrous and the metallic strata are diffusion bonded together after the inorganic fibrous stratum has been provided with an extremely thin coat of metal by vapor deposition. In order to secure a satisfactory bond between the metal coat and the fibrous stratum, it is necessary that the deposited coat be composed of a substantially pure metal either elemental or alloyed, it being particularly important that the metal being deposited is substantially oxygen free. Preferably, the metal bearing vapor has a first cationic component selected from the class consisting of the transition metals, rare earth metals, the actinide metals and combinations thereof, and an anionic component selected from the organics, halogens and combinations thereof. Examples of the foregoing are: ferric carbonyl, molybdenum carbonyl, nickel carbonyl, chromium chloride, tungsten chloride, molybdenum chloride; bis-cyclopentadienyl metals such as bis-cyclopentadienyls of iron, manganese, cobalt, nickel, rhodium and vanadium; bis-cyclopentadienyl metal halides such as bis-cyclopentadienyl chlorides, bromides and iodides of titanium, zirconium, hafnium, vanadium and tantalum; cyclopentadienyl carbonyls such as cyclopentadienyl manganese tricarbonyl; bis-cyclopentadienyl metal carbonyls wherein the metal is molybdenum, tungsten or iron; dibenzene metals such as dibenzene compounds of chromium, molybdenum and vanadium; and dibenzene metal halides such as dimesitylene di-iodide.

When the metal is deposited from halide vapor by hydrogen reduction, first the hydrogen is passed over or through the solid or liquid metal halide, which is heated in its container to such a temperature that the resultant gas mixture contains from 1 to 30%, by total volume, of metal halide vapor. Next the gas mixture is passed through the coating chamber into contact with the heated specimen. Then the metal halide vapor is reacted at the surface of the heated specimen in order to deposit its metal as an adherent coating. Finally the spent gas is passed out of the chamber. Generally the thermal decomposition process is carried out in analogous fashion, an inert carrier gas, such as argon or helium, being substituted for the hydrogen when the system is at atmospheric pressure. When the system is at reduced pressure, the carrier gas may be omitted entirely. In a somewhat complicated variation of the reduction type of coating reaction, the specimen, first is coated, for example, by evaporation in vacuum, with a reactive metal such as magnesium, aluminum or calcium. Then this reactive metal serves to displace the metal in the vapor in such a way as to be replaced itself on the specimen.

Bonding of the coated face of the fibrous stratum to a contiguous face of the metallic support stratum may be effected in any of a variety of ways involving interdiffusion of the two faces. In one procedure, the coated face of the fibrous stratum and the contiguous face of the metallic stratum are welded together by the application of sufficient heat to raise the contiguous surfaces to their melting points. In another procedure, the contiguous faces are brazed or soldered together with the aid of an intermediate flux, such as a stainless steel or silver flux, that is capable of wetting both faces when fluid. The contiguous face of the metallic stratum, in one pro-

cedure, is provided with a coat by vapor deposition in the same way as the fibrous stratum.

Example I

The composite structure illustrated in the drawing is fabricated first by vapor depositing, on the opposite faces of an inorganic fibrous layer 20, coats 22 and 24 of a refractory metal, such as chromium. Next a second coat 26 of a metal, such as beryllium, is vapor deposited upon coat 22 and oxidized in order to produce a metal oxide such as beryllium oxide. An auxiliary coat 28 of a metal, such as nickel, is vapor deposited upon a layer of a refractory metal support 30, such as beryllium. Then coat 28 is bonded at welding temperature to coat 24. Coat 26 provides an erosion and corrosion resistant surface of extremely high emissivity. The discontinuity in the thermal gradient between coats 26 and 22 provides radiation reflectivity as well as a bond of minor weight and thickness. Fibrous layer 24 provides an insulating barrier of remarkably steep temperature gradient. Metal coat 28 provides a bond of minor thickness and weight. And refractory metal layer 30 provides a dimensionally stable support. The thickness of each of layers 26, 22, 24 and 28 approximates 25 microns. The thickness of fibrous layer 20 approximates 80 mils and the thickness of metal layer 30 approximates 60 mils.

Example II

A process for producing the foregoing product is as follows. A strip of ceramic fiber 2" x 1/2" x 80 mils is coated on its opposite faces with chromium by raising the temperature of the strip to 450° C. and passing in contact therewith chromium di-cumene at a temperature of 100° C. and a pressure of 30 mm. Hg for a period of 30 min. During this time, a sufficient movement of the vapor is continued in order to ensure that the vapor in contact with the faces of the fibrous strip is fresh. Next beryllium is coated on one of the chromium coats by deposition in a vacuum of 10⁻⁵ mm. Hg or better from a molten beryllium source. The resulting beryllium coat then is oxidized by first immersing in 50% nitric acid and then firing at 1000° C. in an oxygen atmosphere. Then a strip of beryllium 2" x 1/2" x 60 mils is coated on one of its faces with nickel by electrodeposition. Finally, the free coated face of the fibrous strip and the coated face of the beryllium strip are pressed together and subjected to a bonding temperature of 1000° C. in a high vacuum of 10⁻⁵ mm. Hg or better. The resulting structure is capable of undergoing an application of a temperature of 2500° F. to its beryllium oxide face and providing a temperature gradient which is sufficiently steep to maintain its beryllium face at 1200° F. or lower, in which condition the beryllium strip retains many of its desirable mechanical characteristics.

The illustrated process thus results in a product possessing an extraordinary combination of characteristics including high corrosion and erosion resistance, light weight, extreme thinness thermal shock resistance, and remarkable resistance to high thermal flux and high thermal gradient.

Since certain changes may be made in the above process and product without departing from the scope of the invention herein involved, it is intended that all matter

in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A heat insulating sheet product comprising, in bonded sequence, a metal support, a vapor deposited metal coat, an inorganic fibrous layer, a refractory metal coat and a refractory metal oxide coat, said metal of said metal support, said vapor deposited metal coat, said refractory metal coat and said refractory metal oxide coat having melting points each in excess of 1000° C., said vapor deposited metal coat ranging in thickness from 0.1 micron to .001 inch, said inorganic fibrous layer ranging in thickness from 10 to 300 mils and said metal support ranging in thickness from 10 to 300 mils.

2. A heat insulating sheet product comprising, in bonded sequence, a layer of beryllium, a coat of nickel, a coat of chromium, a layer of ceramic fiber, a coat of chromium, and a coat of beryllium oxide, the coats of beryllium oxide, chromium and nickel approximately 25 microns in thickness, said layer of ceramic fiber approximately 80 mils in thickness and said layer of beryllium approximately 60 mils in thickness.

3. A process for producing a heat insulating sheet product, said process comprising the steps of heating a ceramic fiber layer approximately 80 mils thick to a temperature of approximately 450° C., subjecting said ceramic fiber layer to chromium di-cumene until chromium coats from 0.1 micron to .001 inch thick are deposited on opposite faces of said ceramic fiber layer, depositing a coat of beryllium on one of said chromium coats by vacuum deposition, oxidizing said coat of beryllium by immersion in nitric acid and firing at approximately 1000° C. in an oxygen atmosphere, coating a layer of beryllium approximately 60 mils thick on one of its faces with nickel, and diffusion bonding the nickel coated face of said beryllium layer to the other of said chromium coats at a temperature of approximately 1000° C.

4. A process of producing a heat insulating sheet product, said process comprising the steps of vapor depositing, upon a fibrous refractory stratum, a thin metallic coat, and diffusion bonding said metallic coat to a metallic support stratum, said metallic coat ranging in thickness from 0.1 micron to .001 inch, said fibrous refractory stratum ranging in thickness from 10 to 300 mils and said metallic support stratum ranging in thickness from 10 to 300 mils.

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