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POSSIBILITIES OF SURFACE COATING FOR THERMAL INSULATION

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POSSIBILITIES OF SURFACE COATING FOR THERMAL INSULATION

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1. Introduction

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Surface coatings on materials to reduce corrosion and wear, as well as coatings for electrical insulation, have been state of the art for a long time.

The palette of anti-corrosion coatings ranges from organic coatings through metallic platings of zinc, aluminum, nickel, chromium, duplex or triplex layers based on precious metals, as well as tantalum coatings precipitated from salt bath electrolytes, to ceramics such as enamel coatings in vessel construction.

The technical repertoire of anti-wear and electrical insulation coating materials is less diverse.

For the former purpose, the largest technological use is made essentially of diffusion layers in steels produced by the diffusion of carbon, nitrogen and boron, as well as the galvanically applied hard chromium layers and nickel layers produced chemically by the so-called currentless precipitation method (the hardness of these latter is based on nickel, boron or nickel-phosphorus compounds built into the structure). In addition, in special cases wear problems are solved using hard metal coatings based on Al_2O_3 or zirconium silicate, as well as vapor-deposited or "sputtered" coatings based on SiO_2 or Al_2O_3 -- e.g. in semiconductor technology. By contrast, surface coatings have

*Numbers in the margin indicate pagination in the foreign text.

found only isolated use as thermal insulation, such as zirconium-based coatings used in space technology for rocket drive aggregates or to solve re-entry problems.

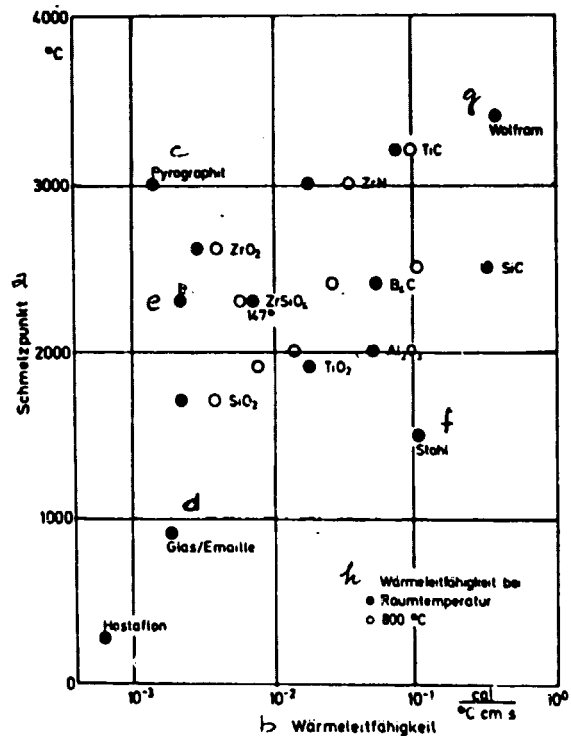
2. Capacity of Surface Coatings as Thermal Insulation

In seeking further possible applications for thermal insulation coatings one first encounters the question of what coating materials can in principle be considered for this purpose, and how much thermal insulation such coatings can actually deliver.

Fig. 1 gives a survey of various materials with their melting temperatures and thermal conductivity. It shows that there are indeed some materials with thermal conductivity values lower than those of the conventional material, steel, by at least an exponent of ten; but few have high melting temperatures, e.g. pyrographite, boron, silicon dioxide, titanium dioxide, zirconium silicate and zirconium dioxide. A further limitation /149

Fig. 1.
Heat conductivity and melting point of various materials

Key:
a. Melting point
b. Heat conductivity
c. Pyrographite
d. Glass/enamel
e. Boron
f. Steel
g. Tungsten
h. Heat conductivity at room temperature/800 °C



for the use of some of these materials results (Table 1) from their faulty oxidation resistance, such as with pyrographite and boron, as well as (in the case of boron and silicon dioxide)

(/158)

Material	Oxydationsbeständig a bis °C	linearer thermischer Ausdehnungskoeffizient b m/m°C x10 ⁶	
SiO ₂		0,4 0,6 1,0	(20 - 500) j (500 - 1000) /2/ (1000 - 1300)
TiO ₂		8,3 10,0 10,2	(20 - 500) (500 - 1000) /2/ (1000 - 1400)
c Bor	900 /1/ i	8,0	/3/
d Pyrographit	i 450 (Graphit) /5/ i	2,5 ^{x)} 1,0 ^{xx)}	(27 - 927) (27 - 927) /4/
e Zirkonsilikat		7,0	(27 - 1027) /2/
f Zirkondioxid (stabilisiert)		10,8 12,2 13,7	(20 - 500) (500 - 1000) /2/ (1000 - 1400)
g Zirkondioxid (monoklin)		7,6	(25 - 1000) /5/
h Stahl (9% Ni, 18% Cr)		16,2	(0 - 100) /3/

Table 1. Summary of some material values for various high-temperature materials and steel

X) at 1800 °C

xx) precipitated at 2100 °C

Key: a. Oxidation-resistant up to ___ °C
b. Linear thermal expansion coefficient
c. Boron
d. Pyrographite
e. Zirconium silicate
f. Zirconium dioxide (stabilized)
g. Zirconium dioxide (monocline)
h. Steel
i. 450 (Graphite)
j. [indicates reference number]

from the relatively large difference between their thermal expansion behavior and that of the base metal used.

Thus zirconium dioxide seems the most promising among the listed materials for thermal insulation purposes, since on the one hand it needs no further oxidation protection and on the other hand it goes through no phase transformation with discontinuous changes in volume, when it is in its cubic form fully stabilized by foreign oxides such as calcium, yttrium or magnesium oxide. Furthermore, in this form it has a linear thermal expansion coefficient of $10 - 11 \cdot 10^{-6} \text{ m/m}^\circ\text{C}$ (range from room temperature up to 1000°C), which is relatively high compared to the other materials with high melting points.

The thermal expansion coefficient of zirconium dioxide in its monocline, unstabilized form is somewhat lower, $7.6 \cdot 10^{-6} \text{ m/m}^\circ\text{C}$ (range from room temperature to 1000°C), but with thermal stresses under 900°C one need anticipate no phase transformation or concomitant discontinuous change in volume.

How can the heating of a material be affected by application of a thermal insulation coating, e.g. of zirconium dioxide; what temperatures occur with and without the coating; and what dimensioning of the coating is necessary?

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An attempt was made to calculate these values (the calculations were performed by Dr. F. Rischbieter and E. Schapeleier of the Battelle Institut eV, Frankfurt/Main), for the use of a pulsating heat source with a given pulse rate of ca. 2500 cycles/min. and a maximum gas temperature of ca. 3000°C . The exact mathematical treatment of this problem is extraordinarily difficult and requires precise knowledge of all boundary conditions, including pressure-time and temperature-time curves in the gas phase to calculate the coefficient of heat transfer $\bar{\alpha}$ as a function of time for the heat transfer from gas phase to reactor

In the case to be examined the heat energy is produced by a chemical combustion reaction in which a part is converted into kinetic energy. From the balance of energy, the kinetics of energy release, the equation of movement and the ideal gas law, the maximum gas temperature, the temperature-time curve and the curve of the heat transfer coefficient over time were estimated.

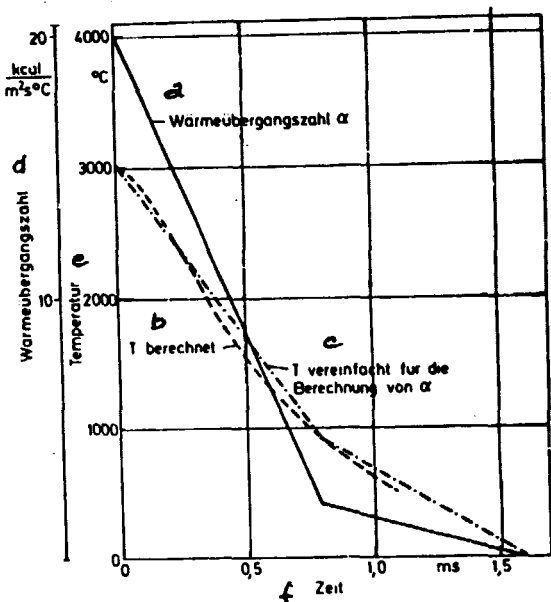
Fig. 2 shows the temperature-time curve and the heat transfer coefficient $\bar{\alpha}$ used as a basis for the further calculations of temperature distribution in the walls of the reaction vessel. This temperature-time curve is to be seen in relation to the totality of a temperature cycle from $24 \cdot 10^{-3}$ sec. The calculation yielded $\bar{\alpha}$ values up to $20 \text{ kcal/m}^2 \cdot \text{sec } ^\circ\text{C}$.

Fig. 2.

Temperature curve in a gas space and calculated coefficient of heat transfer $\bar{\alpha}$ as a function of time.

Key:

- a. Heat transfer coefficient α
- b. T calculated
- c. T simplified for the calculation of α
- d. Heat transfer coefficient
- e. Temperature
- f. Time



To calculate non-stationary temperature distribution in the wall of the reaction vessel the heat conduction problem is treated as monodimensional and cylindrically symmetrical. This simplification is permissible when the whole reaction space including the end surfaces is uniformly coated and the heat release through the end surfaces is negligible compared to that through the cylinder wall.

From the differential equation of non-stationary heat conduction /151

$$\frac{\delta T}{\delta t} = \frac{\lambda}{\rho \cdot c} \cdot \Delta T$$

the material equation

$$Q = \rho \cdot c \cdot T \cdot V$$

and the heat flux equation

$$\frac{dQ}{dt} = \lambda \phi \text{ grad } T dF$$

the temperature distribution was calculated in the reactor wall (which was subdivided into several volume elements) assuming certain boundary conditions for the geometry of the reactor. Also assumed were the heat conductivity coefficients of the various construction materials, the temperature and the heat transfer coefficient on the outside of the reaction vessel. Here

- T = temperature
- t = time
- λ = heat conductivity coefficient
- ρ = density
- c = specific heat
- Q = quantity of heat
- V = volume element

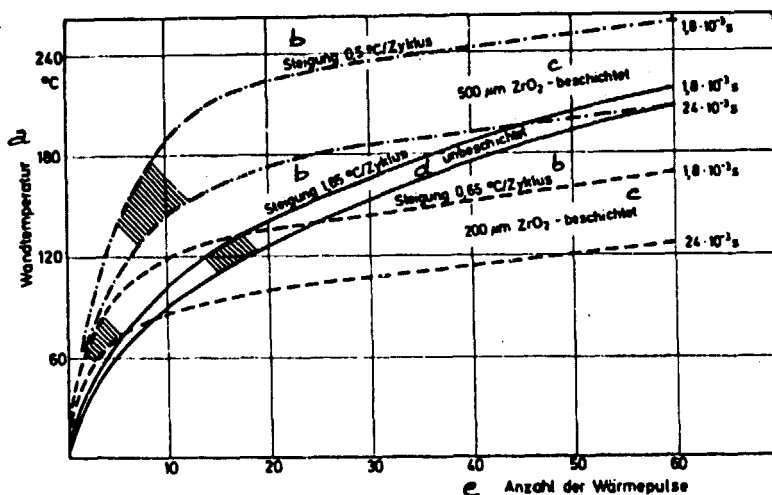


Fig. 3. Wall temperature as a function of the number of thermic pulses.

Key: a. Wall temperature c. Coated e. Number of thermic pulses
 b. Rise ()/Cycle d. Uncoated

Fig. 3 shows schematically the temperature curve thus /152 calculated on the inner chamber wall as a function of the number of thermic pulses for the uncoated reactor, and taking into account thermal insulation of zirconium dioxide layers between 200 and 500 μm thick. The band width between two coordinated curves describes the temperature difference in each case between the time points $1.8 \cdot 10^{-3}$ sec and $24 \cdot 10^{-3}$ sec after the start of the thermic pulsation.

The curves agree on the tendency to reach a quasi-stationary state as the temperature rises sharply after a certain warmup time; in this state the wall temperature rises almost linearly with the number of thermic pulses. The increase tapers off slightly as the thickness of the thermal insulation layer increases, but is some three times greater for the uncoated wall than for the coated reaction space.

For the boundary conditions assumed here, i.e. a limited number of thermal pulses, the calculations showed that a thermal insulation layer 200 μm thick can have more favorable effects on the temperature of the chamber's inner wall than such a layer 500 μm thick. Further calculations showed, of course, that the initial boundary conditions for the temperature-time curve in the gas phase are of decisive importance for the absolute value of the optimum coating thickness.

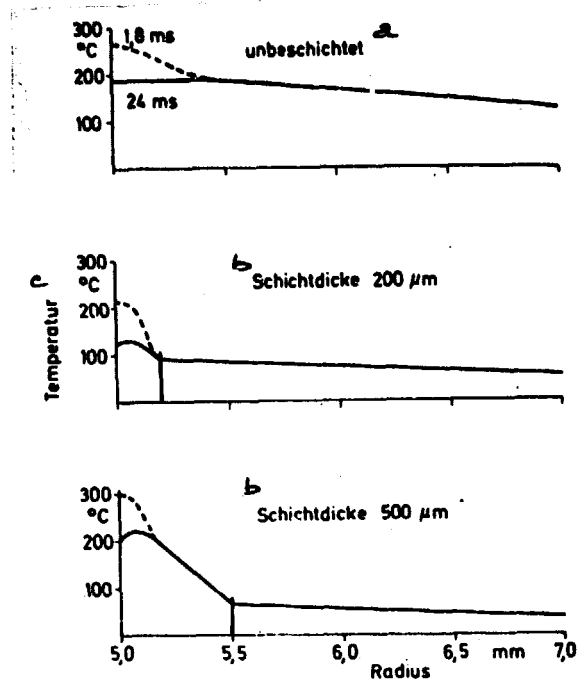
The situation changes, however, to favor the thicker thermal insulation coating as the number of thermal impulses increases.

Fig. 4 gives a look at the processes during a thermic pulse; here the local temperature distribution -- after a given number of thermic pulses -- is represented after 1.8 ms and at /153 the end of a thermic cycle. It develops that the dynamic processes within a thermic cycle are played out in a relatively thin layer, some 150 μm thick in the case of zirconium dioxide and some 500 μm thick in the case of steel. However, if one

observes the temperature in the steel cladding from a distance of 500 μm away from the inner wall of the reactor, one clearly

Fig. 4. Radial temperature curves for the inner wall of the chamber.

Key: a. uncoated
 b. coated _____ thick
 c. temperature



sees the effect of the thickness of the thermal insulation coating, i.e. the temperature appearing there is lower as the thickness of the thermal insulation coating layer increases.

Although the connections shown here are tied to very special boundary conditions, some general conclusions can be drawn for the use of thermal insulation coatings with a pulsating heat source:

-- The dynamic processes with pulsating heat sources occur in a relatively thin layer. This fact is interesting, on the one hand, in view of the thickness of the layer of insulating material to be selected, and on the other hand significant for the thermic stresses occurring due to the temperature gradient in the layer.

-- The thickness of the insulation coating should be opti-

mized; here the optimum coating thickness is determined first by the course of the thermal pulse over time, and second by the requirements made of the coated material (e.g. low temperature on inner wall of the reactor or extensive temperature drop in the construction material).

3. Technical Possibilities for Applying Thermal Insulation Coatings

As has already been explained above, only a few oxide-based materials like titanium dioxide, zirconium dioxide and zirconium silicate, remain for practical use as thermal insulation coatings. What practical possibilities are there for producing such layers?

The technical feasibility of thermal insulation using surface coatings is severely hampered not only from the material side, but also from the side of the process for applying the coatings. As a generally applicable procedure for coating a metallic material with ceramic coatings like titanium dioxide, zirconium dioxide or zirconium silicate, one first thinks of thermic spray processes like flame- and plasma spraying. In these processes the coating materials are used in powder form, for instance, are converted by the flame or plasma into a pyroplastic or melted state, and are sprayed at high velocity onto the cooler substrate. The coatings have a certain residual porosity in the range of 10 - 5% with flame-sprayed and 5 - 2% with plasma-sprayed layers. Such a residual porosity does indeed reduce the general solidity of the material, but is rather to be viewed as favorable in the present case, since both the heat conductivity and the thermoshock resistance of the materials are positively influenced by a certain porous component.

The adherence of the coatings to the substrate in these processes is essentially based on a mechanical interlocking and

can thus be improved by suitable pretreatment of the base, for instance roughening by sandblasting or pickling. Furthermore, the composition of the coating can be varied in a relatively simple manner by using powder mixtures, so that for instance stresses that would occur in a ceramic-metal boundary layer /154 due to the differing thermic expansion of the two materials, can be reduced cermetically by a multilayered construction with intermediate layers.

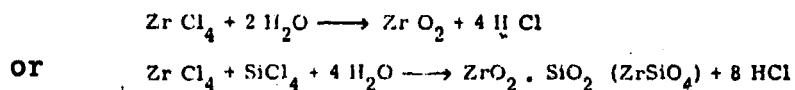
There is furthermore the possibility of increasing the temperature change resistance of the ceramic material by a certain metallic component, while heat conductivity is only slightly increased, as long as the metal component forms no cohesive structure [2].

One limitation of this process, however, lies in the geometry of the parts to be coated. Thus, for instance, drill holes cannot be coated at all beyond a certain depth, and the inner walls of tubes can be coated only when the internal diameter is over ca. 15 cm.

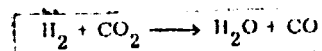
Such a special case is involved in the model for which the initially discussed calculations were performed. One possibility for applying a coating in such cases is gas phase precipitation with the so-called chemical-vapor-deposition (CVD) process.

In contrast to the thermic spray processes, in chemical vapor deposition the compound to be deposited is not present at the start, but rather is generated thermically by a reaction out of the gas phase onto the surface to be coated.

The basic material must here be heated to the temperature at which the gas phase conversion occurs. Thus for instance, coatings of zirconium oxide or zirconium silicate or zirconium oxide-silicone oxide mixtures can be produced at ca. 900°C by the following conversions:



In practice, however, the necessary water vapor is not added to the reaction gas, but generated on the hot substrate surface by a secondary reaction



since the equilibrium of this reaction shifts notably towards the formation of CO and H₂O only at temperatures above 800°C. This procedure is a possibility for suppressing the formation of a powdered reaction product by the undesired homogenous gas phase reaction that plays a decisive role in this system. With this CVD technique it was possible to deposit zirconium dioxide layers with thicknesses up to ca. 70 m (this has already been reported in another place [6]) and zirconium dioxide-silicon dioxide mixtures up to 20 m thick.

The optimum deposit temperatures were around 900°C. Since it was clear that the coated parts would not be heated above this temperature in actual use, the zirconium dioxide in its unstabilized form could be used without fear of additional thermic stresses due to a phase change in the coating material.

However, in the depositing of such coatings on a substrate material with such a sharply different thermic expansion /155 behavior, the adhesion of the layer is of essential significance.

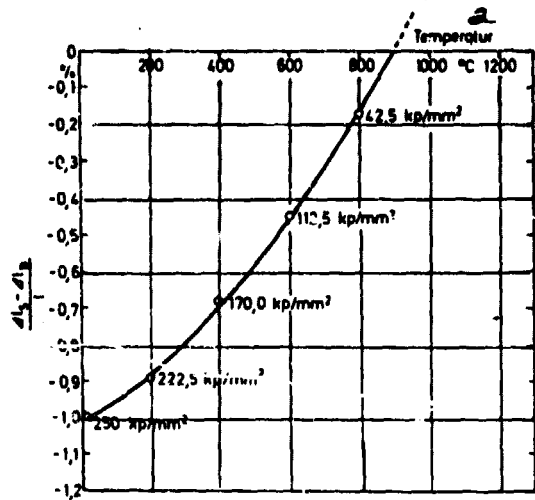
Fig. 5 shows the change in length the coating undergoes under thermic stress because of the base material,

$$\xi = \frac{\Delta l_S - \Delta l_B}{l}$$

calculated from the differing thermic expansion coefficients of coating and base material. Here

Fig. 5. Calculated buckling of the coating material and corresponding pressure stress for the combination of (unstabilized) zirconium dioxide and chromium-nickel steel.

Key: a. Temperature



Δl_S is the change in the length of the coating material when the temperature changes by ΔT

Δl_B is the change in the length of the base material when the temperature changes by ΔT .

At the same time the stresses occurring in the coating are given, calculated from the E modulus of the coating material and the forced change in length ϵ , assuming the applicability of Hooke's Law (here a negative value for the stresses means a pressure stress on the coating).

All these calculations are based on the severely simplified assumption that the coatings are free of stresses at the depositing temperature.

However, they are a valuable aid, since they make it possible first to estimate the order of magnitude and the type of stresses to be assumed by the coating, and second to determine the stresses specific to the procedure.

The CVD process is evaluated especially favorably when the thermic expansion coefficient of the coating material is lower than that of the substrate material, since pressure stresses can be accepted far more extensively by brittle materials than can tensile stresses.

Here the coatings are under tensile stress only when /157
the thermic stress on the piece exceeds the deposition
temperature.

However, in addition to the material characteristics of
the coating material, the material's adhesion to the substrate
is of decisive significance for the stresses which the coating
can accept.

In principle, because of its higher substrate temperatures
and the long coating time, the CVD procedure also offers the
possibility of adhesion by way of interdiffusion or a chemical
reaction, depending on the combination of substances and the
type of conversion. In the case of a zirconium dioxide deposit,
such an adhesion mechanism, however, is not detectable; thus
the combination of zirconium dioxide and steel represents the
weak point in the boundary layer.

To improve the characteristics of this combination there
are the following outstanding possibilities: first the applica-
tion of intermediate layers -- here we have already given certain
starting points -- and second the precipitation of the stabilized
zirconium dioxide phase, which is more suitable in its thermic
expansion behavior.

In summary one should say that according to the calculations
performed for pulsating heat sources, the coating of the construc-
tion material with a relatively thin layer of 200 - 1000 μm can
cause -- at optimum layer thickness -- a temperature drop both
in the construction material and on its surface.

It is essential for technical realization that the thermic
stresses should both be reduced by extensive adaptation of the
coating material to the construction material in their thermic
expansion behavior, and also be shifted as much as possible

towards the pressure stress range by the coating application method.

A further significant aspect is the question of thermoshock resistance of the ceramic material when it is in the form of such coatings. Here the greatest stress in each case is to be anticipated in the starting phase; the temperature switches occurring during a heat pulse, as can be seen in Fig. 3, are only 60 °C, in spite of extreme differences in the gas temperatures. Here extensive experimental studies are necessary for the final evaluation of the technical feasibility of this model, "heat insulation with ceramic coatings."

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