Metallization of ceramic materials based on the kinetic energy of detonation waves

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Abstract. The paper presents an innovatory low-energy detonation-spraying method suitable for the metallization of ceramic materials, in which the energy necessary for joining the metallic coating with the ceramic is delivered in a mechanical way. In the proposed method, the metallic particles, shot from the spraying gun, impinge onto the ceramic substrate with a high velocity, and their kinetic energy is transformed into heat delivered in a specified portion directly to the region of the metal/ceramic joint being formed. The stress distribution and the temperature field at the coating/substrate interface were analyzed also numerically with the aim to optimize the metallization process parameters so as to stimulate the formation of the coating/ceramic joint and, at the same time, to control the region of heat dissipation, the temperature, and the stress state induced in the joint.

Key words: metallization of ceramic, detonation spraying, coatings.

1. Introduction

Industrial applications of ceramics practically always require their joining with metals. With the dynamically developing technique nowadays, the demand for ceramic/metal joints constantly increases and stimulates the investigators to seek new joining methods such that generate lower stress state in the joint and whose fabrication is less expensive [1–5]. The fabrication of ceramic-metal joints belongs to the most difficult goals in this branch of joining engineering. There are two possible methods of their fabrication. One consists of direct bonding the two components in their solid state, but here the range of the materials pairs possible to be joined is considerably limited. In the other method, the ceramic is first covered with a thin metallic layer, which changes the properties of the ceramic surface so as to permit its being wetted by a non-active filler metal. The metallization of the ceramic surface is the crucial stage of the technology of ceramic-metal joints. Conventional methods of metallization of the surface of ceramic materials have been known since the mid-XX century and the joints manufactured by them are of high quality and satisfy the heaviest exploitation requirements. They have however drawbacks of which the most important are that the entire volume of the joined components is heated to a high temperature, the technology is complicated, the process must be conducted in a vacuum- or hydrogen protective atmosphere, the time needed for the formation of the joint is relatively long, and finally the production costs are high. The methods most commonly used in industrial practice are powder metallization, active brazing, and surface coating by the PVD, CVD, and IPD techniques [6, 7].

Irrespective of the joining method employed, there is the risk of a high residual stress state being induced in the ceramic-metal joint which can be decreased by reducing the size of the region where the joint is heated, shortening the heating time, and properly selecting the heating method. The method proposed in the present paper is advantageous in this respect since the heating time is very short and the material is heated only locally within the region where the joint is formed. Moreover, the metal particles, which hit dynamically the ceramic surface remove from it the possible impurities thereby facilitating the formation of the joint. The difficulties in joining ceramic materials with metals are associated with the extremely differing properties of these two materials, such as:

- lack of wettablility of ceramics by metals which results from the differences in their physicochemical properties, and practically, the lack of interactions between these two materials (the bonds in ceramics are ionic, covalent, and mixed, whereas in metals they are metallic),
- no mutual solubility,
- weak diffusion of metals into ceramics,
- different crystallographic lattices,
- substantial difference of the hardness, brittleness and melting temperature,
- and drastic difference in the thermal expansion coefficients $\alpha$ and in thermal conductivity $\lambda$ (properties especially important from the point of view of the residual stress state induced in the joint) [2, 8–10].

The advanced diffusion-based processes suitable for joining ceramic and various other materials with metals must be conducted at high temperatures in vacuum, require additional ex-
When two solid bodies are to be joined, the sum of their free surface energies is greater than the free interfacial surface energy. Assuming that every system tends to achieve the minimum free energy, can be expected that, theoretically, two surfaces brought to contact will join spontaneously. In reality this however does not happen, since:

- It is not possible to bring the two surfaces so close to one another that their atoms, in a sufficient number, will be separated by the distance comparable with the crystalline lattice parameters. The surfaces of metals are not smooth either in the atomic scale or in the micro-scale. Moreover they are covered with oxides, adsorbed vapors and gases, and also with various organic substances.
- Even when we assume that the two surfaces are perfectly smooth, to bring them so close that the joint can form spontaneously requires external energy to be delivered so as to overcome the repulsive forces active between the atoms.

Assuming the thermodynamic approach, the joining process can be illustrated by the curve shown in Fig. 2. Region 1 represents the metastable state with the free enthalpy $G_1$ when, before joining, two surfaces are free. In state 2, the joint has already formed, and the free enthalpy $G_2$ is now lower than $G_1$. The force which drives the transition from state 1 to state 2 is equal to the difference between the two free energies $\Delta G = G_1 - G_2$. The transition from state 1 to state 2 requires overcoming the energy barrier $Q$ i.e. the activation energy must be delivered so that the atoms of the two surfaces can be brought to a distance where they strongly attract each other. In the joining practice, the activation has the thermal character, i.e. an external source delivers heat necessary to increase the temperature to the melting temperature. If the temperature is lower, a pressure must be additionally applied, which facilitates a plastic behavior of the material and speeds up the diffusion.

These phenomena are utilized in the detonation method, described in the present paper, in which the required activation energy is delivered to the system in a mechanic way, namely through the transformation of kinetic energy into heat energy which is dissipated directly within the region of the joint being formed. There are other literature reports describing the use of mechanical energy for enhancing the joining process [19, 20].

The aim of the study was to produce a ceramic/metal joint by spraying pure titanium on an Al$_2$O$_3$ ceramic substrate with the participation of the kinetic energy of detonation waves. During the detonation spraying (D-Gun), the joint is formed when the metallic component reaches locally, in a very short time, a temperature close to its melting temperature and then is very quickly cooled to room temperature. Therefore, the joining process should be considered to be solid-state joining with a substantial share of the kinetic energy of the detonation wave, which drives the particles of the spraying jet. Then, on the impact of these particles onto the substrate, their kinetic energy is transformed into heat energy, which stimulates the formation of a joint at the interface between the two phases.

### 2. Substrate and coating materials

The materials to be joined were corundum ceramic (Al$_2$O$_3$) as the substrate and pure titanium as the coating material. Al$_2$O$_3$ was selected for our experiments because it is very widely used and, among other oxide ceramics, has the uppermost significance in technical applications. Corundum is now the third among the most often used dielectrics (after SiO$_2$ and SiN$_4$). On the other hand, the choice of titanium as the coating material, detonation-sprayed on the ceramic, was based on literature reports [21-24] which describe titanium as the material that actively enhances the wetting of ceramics by metals and facilitates the formation of the joint even when it is only an alloying additive. In view of the strong chemical affinity of titanium to oxygen and aluminum (the basic components of the Al$_2$O$_3$ ceramic), new compounds of the Ti-O and Ti-Al systems are formed. It is known that the reaction products formed at the ceramic/metal interface are rich in titanium, which can dissolve a substantial amount of oxygen to form various oxides. From the thermodynamic point of view, these oxides may form during joining the
detonation-sprayed coating to the substrate. A particularly interesting oxide is TiO$_2$ since it is wetted by liquid copper [21] a property, which may be effectively utilized in the final form of the ceramic-metal joint.

3. Detonation spraying (D-gun) of a Ti coating on ceramic

Thermal spraying, in its various versions, is widely used for modifying or regenerating the surfaces of many products. Using this technique it is possible to produce, on various substrates, coatings composed of a variety of materials such as pure metals and their alloys, pure intermetallic phases and their mixtures, and also metal-ceramic composites including those enriched with intermetallic phases [25]. With ceramic substrates, the best results are achieved by using detonation spraying [26–28].

Detonation spraying is based on the controlled detonation of a mixture of gases, such as an energetic gas (most often acetylene and propane) and oxygen, triggered by an electric discharge between the electrodes of a sparking plug. The detonation of the energetic gas generates a shock wave, which heats up the individual particles of the coating material and accelerates them in the barrel of a special gun to velocities of about 900 m/s [29–32]. Thanks to their high kinetic energy, the hot coating particles shot towards the substrate form on it a coating with a multi-layered, homogeneous, and compact structure. Coatings sprayed by the D-gun method have usually higher hardness and density, and better adhere to the substrate than flame-sprayed or plasma-sprayed coatings [29, 32].

In the D-gun process, the coating is deposited in a discrete (discontinuous) way i.e. when, during each shot (detonation), the hot coating material particles impinge on the substrate, they are fixed to its surface on a certain area about 20–25 mm in diameter forming a layer about 10 µm thick. The frequency of the detonations can be controlled and ranges from 1 to 10 Hz, thanks to which the heat generated in the previous cycle can be dissipated within the substrate before the subsequent layer is deposited.

The detonation method is particularly advantageous in spraying metals on ceramic surfaces, since:

- The temperature at which the metal-ceramic joint forms is here the lowest among all the HVOF methods [29, 30], which is advantageous from the point of view of the residual stress state induced in the joint.
- The process proceeds in a pulsed way.
- The heat delivered to the joint being formed is due to the transformation of the kinetic energy of the coating particles which impinge on the ceramic surface.
- The share of diffusion in the formation of the joint is substantial since it is promoted by the high dislocation density, the impact character of the load imposed, by the detonation wave, on the substrate and the coating being formed, and the high rate of deformation of the material of the growing coating within the interface region.

4. Modelling the physical phenomena that occur during the impact of Ti droplet onto Al$_2$O$_3$ substrate

The models adopted in the present experiments simulated the changes of the geometry of the Ti particles when they were deformed during their impact onto the substrate, and the instantaneous distributions of the temperature and stresses induced at the particle-substrate interface during the impact. In the micro-scale, it can be assumed that the coating is being built of the individual particles, which hit the same area of the substrate one after another. Therefore, the analysis was concerned with what happened when a single metal particle impinged on the ceramic substrate at a certain velocity. The numerical simulation was performed in a dynamic system using the ANSYS Autodyne v.13 software. The models were constructed in a two-dimensional axi-symmetric system. The temperature and stress state prevailing in the region of the joint formation, and the degree of deformation of the metallic particles were modeled. The materials data were assumed according to the materials database of the Autodyne software and the data reported in the literature [33, 34].

Figure 3 shows the adopted model of the particle/substrate system. The average particle diameter 44 µm was assumed to be equal to the average size of the particles used in our experiments (MESH 325). The thickness of the ceramic substrate was 200 µm. The temperature of the particle moving in air after the detonation was adopted, according to the literature reports [31, 35], to be 2773 K and its maximum velocity to be 850 m/s.

![Fig. 3. Schematic representation of the particle/substrate model: a) Ti particle detonation-sprayed on an Al$_2$O$_3$ substrate, b) fragment of the finite element mesh](image)

The finite element mesh (with the element size – 0.5 µm) was constructed in the Euler domain. Its fragment is shown...
in Fig. 3b. Figure 4 shows the results concerning the particle deformation. We can see that, in the successive time moments after the Ti particle impinges onto the ceramic substrate and takes part in the formation of the joint (particle/substrate interface) it is being heavily deformed (becomes flattened), and its edges can be separated from the substrate (Fig. 5). The deformation process lasts for about 50 ns after its collision with the substrate. The final height of the deformed particle is about 12 µm and its diameter is about 113 µm.

Figure 6 shows the distribution of the temperature on a transverse cross-section of the deformed Ti particle at 50 ns after the collision during which the temperature recorded within the contact region was the highest. The red-colored area represents the zone with the highest temperature, which reached 3500K. Figure 7 shows the temperature distributions along the axis of the particle/substrate system recorded at the moment when the temperature was the highest i.e. 50 ns after the collision. The temperature and its gradient are the highest at the Ti/Al$_2$O$_3$ interface and, then, it quickly decreases along the depth of the ceramic substrate. The next figures show the distributions of the reduced stress induced in the ceramic substrate according to the Huber-von Mises hypothesis. The variations of the stress magnitude and distribution with time were analyzed for 50 ns beginning from the moment of the particle impact. Figure 8 shows the time variation of the stresses induced in the ceramic substrate as a result of the impact of a Ti particle. It can be seen that the stresses propagate from the point of the Ti particle impact mainly into the depth of the ceramic substrate but also throughout the expanding contact plane.

Figure 9 shows the distribution of reduced stress in the ceramic from side of the Ti-Al$_2$O$_3$ interface to the opposite surface of the ceramic) according to the Huber-von Misses hypothesis, in the axis of symmetry of the particle/substrate system measured at a time of 50 ns after the particle impingement. The high amplitude of the stress variation versus the distance down through the thickness of the substrate is probably associated with the very short time, which elapses from the particle impingement and with the elastic response of the ceramic substrate.

Figures 10 a,b show the distribution of radial stresses $\sigma_x$ and axial stresses $\sigma_y$, occurred in the ceramic substrate, measured after 50 s after the impingement. The highest stress magnitude is observed at a distance of about 50 µm from the ceramic surface, and the material effort mainly depends on the stress components $\sigma_x$ and $\sigma_y$. The deep oscillations of the stress magnitude visible in the ceramic to a depth of about 150 µm can be attributed to the elastic vibrations induced by the particle impingement. Modeling of the physical phenomena, which occur in dynamic systems is difficult and the results must always be referred to the time instance during the process at which they have been obtained. Presented results indicate that characteristic parameters of the detonation spraying process, i.e. temperature and pressure, are the highest at about 50 ns after the impingement of the Ti particle on the Al$_2$O$_3$ ceramic substrate. These results are significant from the point of view of joining a metallic coating with the ceramic substrate, both in the solid state, using the detonation spraying technique.
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Fig. 8. Distribution of the reduced stress generated in the ceramic substrate mapped during 50 ns after the particle impingement.

Fig. 9. Variation of the reduced stress in the ceramic measured along the axis of symmetry of the particle/substrate system after 50 ns beginning from the particle impact.

Fig. 10. Stress distribution in the ceramic substrate, determined after 50 ns beginning from the particle impingement: a) radial stress $\sigma_x$, b) axial stress $\sigma_y$. 

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5. Microstructure of the Ti coating and Ti-Al$_2$O$_3$ interface

The microstructure was examined on metallographic cross-sections of the joint produced, by the detonation-spraying method, between the Ti coating (obtained from a Ti powder) and the Al$_2$O$_3$ ceramic substrate (Fig. 11). It can be seen that the coating has a uniform thickness (40–50 µm) on the entire area observed, and well adheres to the substrate.

Fig. 11. Microstructure of the coating of the Ti powder detonation-sprayed on an Al$_2$O$_3$ substrate

The surface of the Ti coating is relatively smooth and little rough. The joint between the coating and the substrate is continuous and uncracked. The microstructure of the Ti coating is fine-crystalline without well-marked boundaries between the crystallites.

Figure 12 shows the microstructure of a Ti coating/Al$_2$O$_3$ ceramic substrate joint, and the linear distribution of the elements (Ti, Al, O) on its transverse cross-section. The interface between the Al$_2$O$_3$ substrate and the Ti coating was observed on a cross-section perpendicular to its surface using a scanning electron microscope (SEM). The concentration profiles of Ti and Al indicate a slight mutual penetration between these components. As can be seen, the joint obtained has a very high quality, but no transition layer is visible which means that joint has no diffusive character.

Since no deep diffusion or transition layer were revealed, the joint is most probably formed in a combined way, namely through the mechanical anchoring of the coating particles at the irregularities of the outer surface of the ceramic substrate and through the short-range attraction forces active at a distance of a few atomic diameters.

6. Conclusions

Presented investigations and simulations have shown that the energy delivered to the metallic coating/ceramic substrate system in a mechanical way (transformation of the kinetic energy of the detonation wave into heat energy) plays a very effective role in the metallization of ceramic materials. The specific advantage of this method lies in that it permits delivering a specified portion of energy to a precisely defined place where the coating/substrate interface (joint) is to be formed. An additional advantage is that the high-velocity particles bombarding the ceramic surface remove from it the impurities and adsorbed films thereby increasing the free surface energy of the ceramic. This effect can therefore be considered to be a kind of physical activation, which decreases the energy barrier to be overcome in the joining process.

In the light of our results and in agreement with the respective theory concerning the effects of the temperature, pressure, deformation degree, and time on the formation of a joint, we can conclude that the conditions that prevail during the proposed detonation-spraying process are favorable for the formation of a strong and durable joint between the Ti coating and the ceramic substrate. The transformation of the Ti particle kinetic energy into heat energy results in a high temperature being locally generated at the interface between the Ti particle and the ceramic substrate. This is accompanied by a relatively high pressure and considerable deformation (high density of structural defects) of the coating material. These conditions favor the formation of a high-quality adhesive joint, even though, because of the very short duration of these phenomena, the formation of a diffusion-type transition zone in the joint is little probable.

The most important advantage of the proposed technique over the traditional methods is that the only region heated during the process is the surface of the modified product.
Localization of heat within the region of the formation of the joint markedly shortens the deposition process. Taking into account the results obtained in our experiments and the advantages of the proposed, inexpensive method we believe that it can be successfully used in a variety of industrial applications as an alternative method of metallization of ceramics with titanium.

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REFERENCES


