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HIGH TEMPERATURE METALLIZATION, ALUMINA GRAINS AND INTERGRANULAR VOLUME MODELLING

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KEY WORDS: metal-ceramic seals, seal adhesion strength, hight temperture metalization, MoMn metalization, alumina microstructure, Al_2O_3 grain erosion, intergranular volume, ceramic grains, methematical models, grains models, computer models, 3D models

ABSTRACT: It is well known that the alumina microstructure highly influences the quality of the metal - ceramic high vacuum seals. The difference between metallization of fine and coarse grained alumina manifests in different seal adhesion strengths /1/. In the present paper the study of high temperature MoMn metallization of the debased 96% Al_2O_3 is presented. A strong adhesion of metallizing layer on alumina is possible only if enough glass phase is present in bonding layer. In the fine grained alumina sample we could not detect sufficient glass phase in the bonding region between alumina and metallizing layer and the adhesion is expectantly low. The loss of a glass phase in the fine grained alumina can be explained by the comparatively greater intergranular volume that is to be filled with glass phase. During the intergranular glass phase diffusion from metallizing layer in alumina, glass erodes the Al_2O_3 thus producing the new - bigger intergranular volume. The glass phase migration in alumina was observed by tracing the manganese diffusion. In order to simulate the behavior of the intergranular volume in alumina as the function of the average alumina grain size the 3D mathematical model was proposed and evaluated by computer. In the presented model the physical alumina grains are replaced with the modelled grains. The erosion process is modelled and the intergranular volume is calculated for the different erosion depths and different alumina microstructures.

Visokotemperaturna metalizacija, model za izračun zrn keramike in intergranularnega volumna med zrni keramike

KLJUČNE BESEDE: spoji keramika-kovina, trdnost spojev, metalizacija visokotemperaturna, MoMn metalizacija, mikrostruktura keramike korundne, erozija zrn Al_2O_3, prostor med zrni, zrna keramike, modeli matematični, modeli zrn, modeli računalniški, modeli 3D trodimenzionalni

POVZETEK: Iz literature je dobro znan pojav, da mikrostruktura keramike vpliva na lastnosti spoja med keramiko in kovino. Razlika pri metalizaciji grobo in drobno zrnate keramike je v natezni trdnosti spoja /1/. Vakuumsko tesen in trden spoj narejen s 96% Al_2O_3 keramiko nastane le v primeru, kadar je količina steklaste faze v vezni plati med keramiko in metalizacijsko plastjo dovolj velika. Primankljaj taline v vezni plasti drobnozrnate keramike povzroči slabšo trdnost spoja. Ta pojav pojasnjujemo z večjim intergranularnim volumnom med zrni Al_2O_3, ki ga zapolni talina iz vezne plasti. Intergranularni volumen nastane z raztapljanjem zrn Al_2O_3 med difuzijo modificirane taline v keramiko. V delu je predstavljen matematični model za izračun intergranularnega volumna ob upoštevanju različne zrnavosti keramike ter erozije zrn z modificirano talino. Novost predstavljenega modela so tudi zrna, ki so narejena v tridimenzionalnem prostoru.

INTRODUCTION

The metallization process of high alumina ceramics has been the object of many studies. Generally the seals are phenomenologically well understood. The most common metal - ceramic combination are molibden - alumina seals. A typical fabrication process consists of coating a part of alumina surface with MoMn paste. The coated ceramics is fired at a temperature between 1200°C to 1500°C in a moist hydrogen containing atmosphere. During the firing of metallizing paste the intergranular - glass phase from the debased alumina begins to migrate into the porous metallizing layer. The glass phase composition determines the temperature at which seals could be produced /2/. For the glass migration mechanism Twentyman /3/ proposed the twin capillary model in which the direction of the glass phase penetration is a function of capillary pressure between grains in alumina and in metallizing layer.

After firing the sintered coating is plated with thin layer of solderable metal, such as nickel and in the last step join the nickel plated MoMn surface with the metal part by brazing.

Systematic studies of ceramic - metal interfaces have started in the early 1960. The results of this studies were published and cover the topics of thermodynamic reactions, wetting phenomena and the work of adhesion. Chemical reactions between metal and ceramics are considered to be the set of equilibrium thermodynamics reactions. They include redox and dissolution reactions with and without the assistance of a moisture reducing gas. The wetting and contact angle are very significant properties in the metal ceramic seals forming. The glass wets the partially sintered molybdenum and enables adherence between ceramics and MoMn coating. The wettability by solder is also very important in brazing process when nickel plated metallizing layer has to be joined to a solderable metal part.

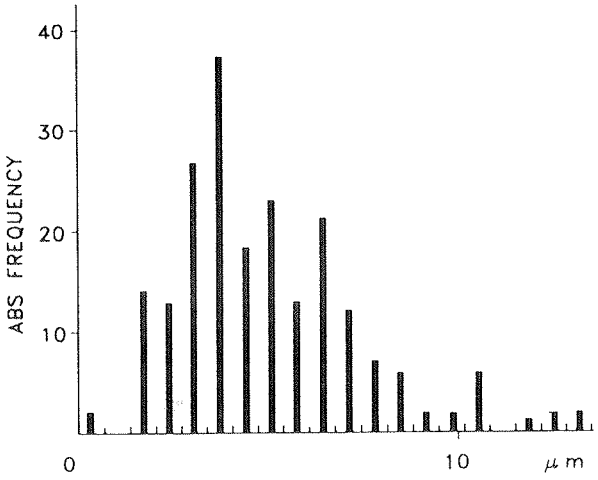
The understanding of physical interaction between metallizing layer and ceramic is not sufficient. The kinetics of metal - ceramic reactions are scarsely documented /4/.

Seal strenght and vacuum tightness are very significant parameters from the commercial point of view.

Floyd /5/ found out that the seal strength depends on the glass phase type present in alumina. The same author also found out that the seal strength increases with metallizing temperature. Floyd and many others reported the empirical relationships between the seal strength and alumina grain size. The present paper proposes the possible answer to these phenomena.

EXPERIMENTAL

The fine (median diameter 4 μm) (Fig.1) and coarse (median diameter 16 μm) (Fig.2) type of debased alumina have been used. The alumina grain size arangement was determined on polished and thermally etched sam-



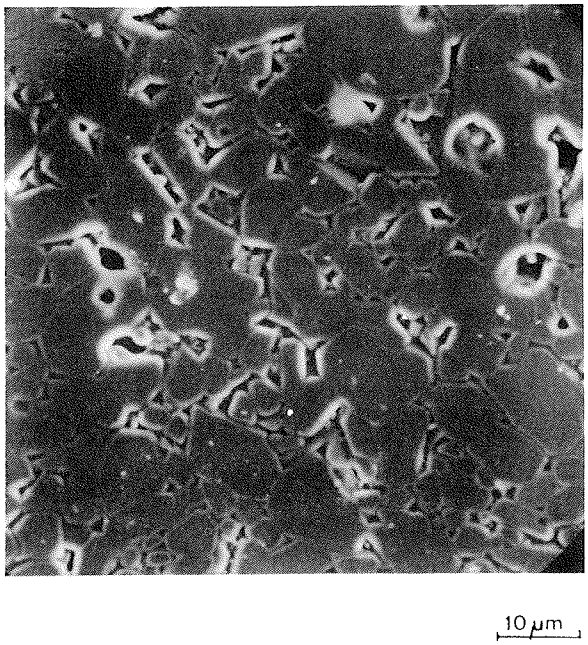
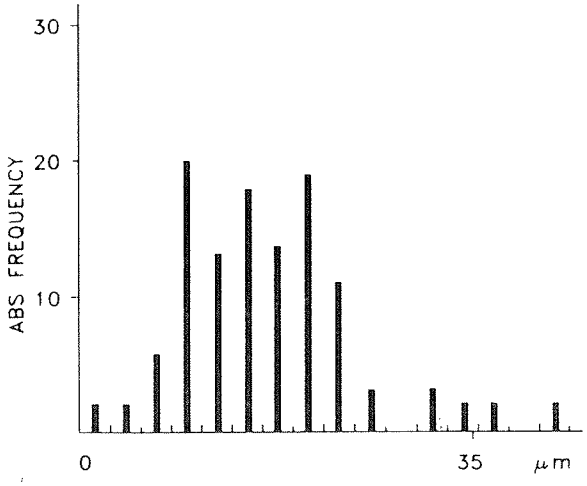


Fig. 1: Microstructure of thermally etched fine grained alumina a.) Corespondent grain size distribution function.



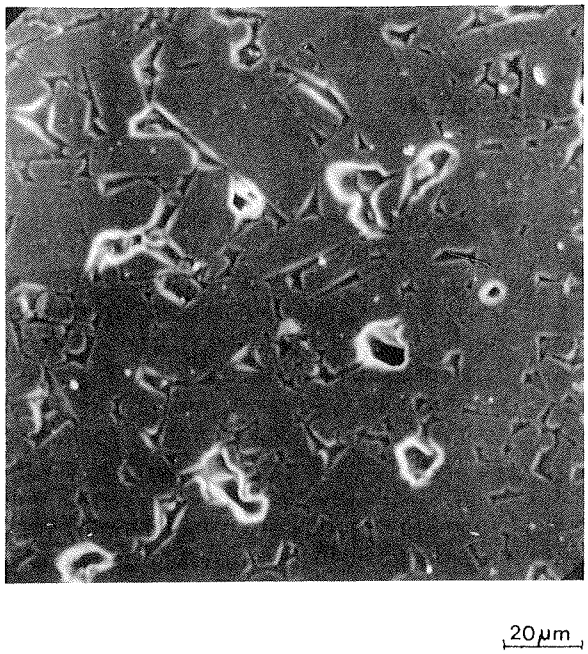


Fig. 2: Microstructure of thermally etched coarse grained alumina a.) Corespondent grain size distribution function.

ples. The MOP CONTRON M-15 device with equivalent spherical diameter method was used for alumina grains size distribution determination (Fig 1a., 2a.). The metallizing paint was produced from 80 wt.% molybdenum powder, 16 wt.% manganese, and 4 wt.% FeSi. The metallizing firings were carried out in 75 %N_2 + 25% H_2 atmosphere at various temperatures. Firing temperatures were in the range from 1250°C to 1450°C, furnace humidity was at a dewpoint at +25°C. The metallized samples were then coated with a thin layer of a nickel oxide paint. The reduction of nickel oxide occured in dry hydrogen at 950°C. The test pieces were brazed with silver-copper eutectic alloy. The brazing process was performed in dry hydrogen.

Depth distribution of manganese in boundary region and in alumina was detected with a WDX microanalyzer by shifting the specimen under stationary electron beam.

RESULTS AND DISCUSSION

Manganese is an additive to high temperature metallizing paste. During firing in wet reduction atmosphere the Mn oxidizes to MnO (ΔG = -137.000 kcal/mol) /6/ and reacts with the glass phase from alumina. The new - modifed glass has the lower melting temperature /4/ and is less viscous. This glass enables the bound formation between alumina and metallizing layer. It fills the porous metal layer and migrates in the debased alumina. The modified glass migration in alumina passes intergranulary. The alumina microstructure determines physical and chemical properties of the seal /7/. The bonding layer in strong and vacuum tight seals consists of a dense metal/glass layer. The effect of alumina microstructure manifests in different adhesion strengths, which are higher at coarse grained alumina, while at the fine grained samples adhesion is low. The reason for the low adhesion strength at fine grained alumina is, that almost the whole glass migrates from the bonding region into alumina, leaving no adhesive substance to keep the Mo cermet layer and alumina together.

The depth diffusion of modified glass was observed by tracing the manganese diffusion. The diffusion process is highly temperature dependent and starts at cca. 1250°C. At 1450°C (30 min) the diffusion depth of modified glass reaches approximately 900 μm.

For fine and coarse grained alumina types at the same coating thickness and at the same metallizing temperature the Mn diffusion depths were approximately the same. Glass diffusion depth is therefore considered to be indipendent on alumina grain size.

During modified glass diffusion into alumina this glass erodes alumina and produces larger intergranular volume (Fig.3). Newly emerged intregranular volume must be filled by the glass phase from ceramic - metallization interface to form strog seals. If there is not enough glass

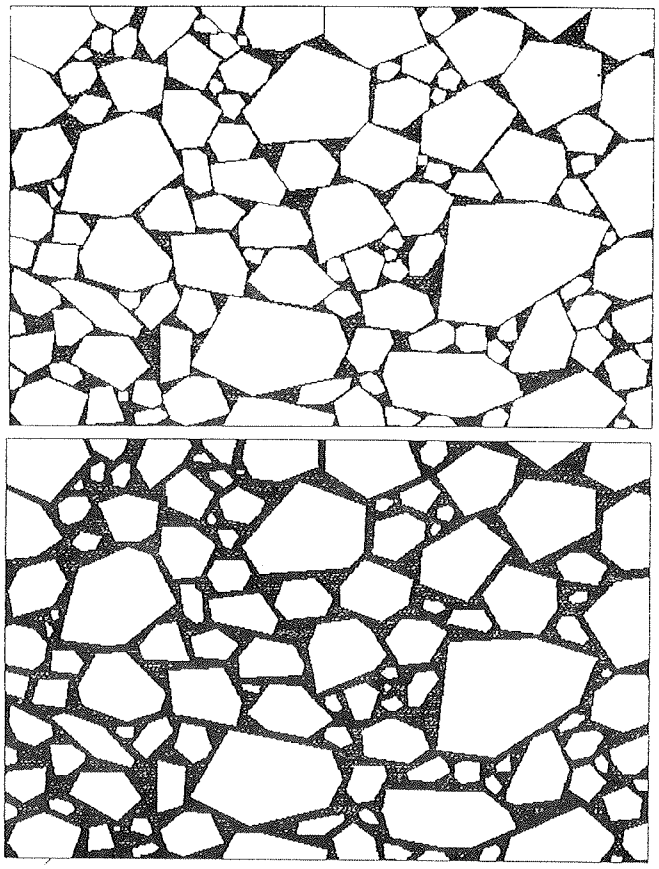


Fig. 3: Computer simulation of alumina microstructure a.) before erosion b.) after erosion.

phase to fill the intergranular volume the seal strength decreases /7/.

The three dimensional computer model explains the behavior of the intergranular volume in alumina as the function of alumina grains size distribution. The model also simulates the effects of alumina grains erosion during the sintering process.

The modelling process undergoes several steps as:

- model alumina grains generation
- tossing generated grains in the unit volume according to the grains size distribution function (distribution function was previously measured on real alumina)
- intergranular volume calculation
- grains erosion

By repeating the last two steps the functional dependence of intergranular volume versus erosion depth (firing time) is calculated.

THE ALUMINA GRAIN MODELLING AND GRAINS VOLUME CALCULATION

The grain is the elementary alumina construction block. The modelled grain shape must be as close as possible to the real alumina grain shape. It must be mathematically easy representable and the grain volume calcula-

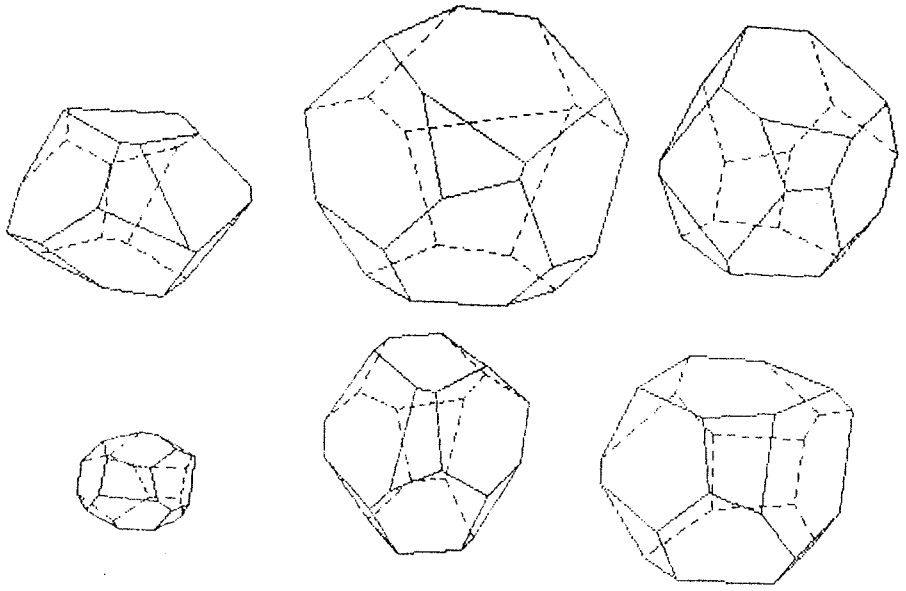


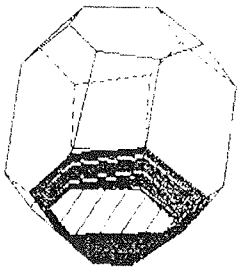
Fig. 4: Randomly generated 3D alumina grains.

tion algorithm must be efficient. The shape that fulfills these conditions is the tetrakaidecaedra /8/. The early studies in alumina moddeling showed us that inproper alumina grain shape selection leads to wrong results /9/. For example the spheras offer very easy and efficient calculations, but the inergranular volume versus grains volume ratio is too high comparable with real alumina. The sphera shape is too far away from real alumina grain shapes.

In order to create the set of different grains the basic shape (tetrakaidecahedra) is modified in process using pseudo random generator. The tetrachaidecahedra is mathematically defined by 14 border planes. For all border planes the planes orthogonal vectors and the vectors starting points coordinates are known.

The deformation is obtained by tilting the planes that define the form for some spatial angle. Of course the spatial angle must be chosen randomly in order to get different "grain" shapes. Border planes tilted for some angle intersect in different edges as they would be in the case of the regular form are thus creating the form of different shape and volume. Fig.4 presents two examples of random generated 3D grains.

Grain volume can be very effectively calculated by the slicing algorithm, where the grain is cut in the number of parallel cuts (Fig.5). For each cut the volume is calculated and the slices volumes sum over the whole grain is the grain volume.



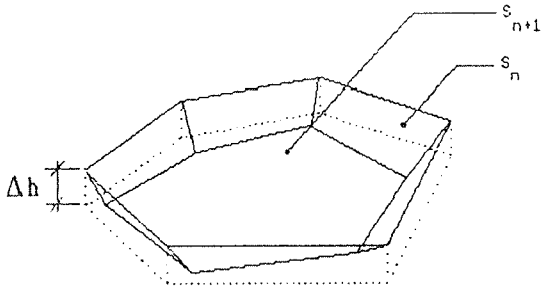


Fig. 5: The volume calculation uses the slicing

THE GRAINS SIZE DISTRIBUTION FUNCTION

The alumina consists of grains where the size distribution can be very accurately measured on the real alumina samples (Fig. 1a, 2a). The grains generation process generates grains of different sizes acording to the experimental distribution function. The intergranular volume is always calculated in the constant (unit) volume. In our case the constant volume is one - 1 mm^3.

For the intergranular volume calculation process it is neccessary to know the exact number of alumina grains in the unit volume.

In present model the average grain size was used for calculation of the number of grains in constant volume. This assumption turned out to be good enough for our work.

When the number of the grains in the unit volume is known, grains are generated according to the given distribution function, the volume is calculated for each grain and at the end the total grains volume is subtracted from the unit volume.

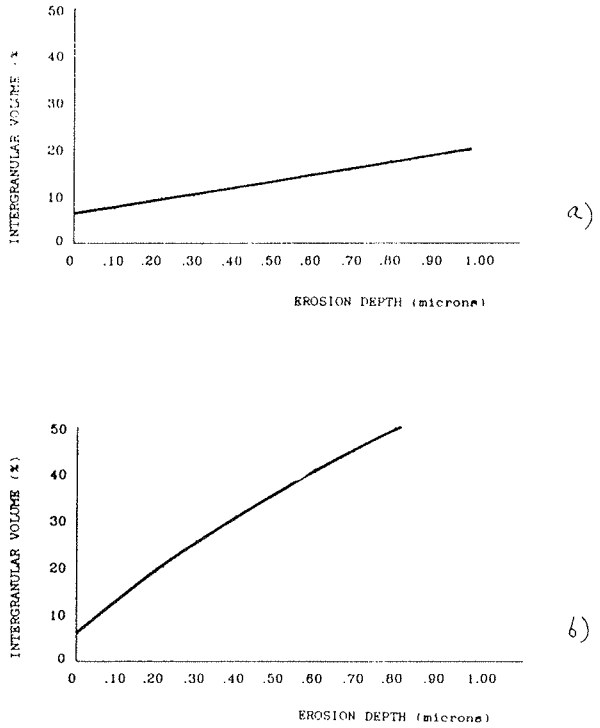


Fig. 6: Functional dependence of intergranular volumes versus erosion depth for a.) coarse grained alumina, b.) fine grained alumina.

THE GRAINS EROSION PROCESS

During intergranular glass phase diffusion the modified glass (containing MnO) erodes the Al_2O_3 grains /10/. The next step in simulation is the grains erosion process. This means that each and every grain is eroded for the same thickness.

Every single grain is eroded for the same depth (0.01 micron) in one computation step. For each step the computer calculates the intergranular volume in the unit volume. Fig. 6a and 6b show the diagrams of percentage of intargranular volume as the function of erosion depth. The given samples represent the erosion process at coarse and fine grained alumina. Those two examples are the proof of the theoretical asumption that the intergranular volume in fine grained alumina increases fast with the erosion depth. This intergranular volume increase is one of the reasons for the glass phase diffiiciency and therefore for the low seal adhesion strength. In fig. 6a and 6b it is necessary to point out the fact that the starting intergranular volume in the unit volume represents almost the same percentage of the total unit volume at both alumina types. The difference in the grains size distribution functions is not so drastic to have any significant influence on the starting intergranular volume. Even if the starting intergranular volumes are almost the same at both alumina types the erosion process simulation shows obvious difference at both alumina.

EXPECTATIONS

The model turned out to be very succesfully designed and the results obtained with this model represent the proof of our theoretical speculation for the cause of a low adhesion strength at fine grained alumina.

The 3D computer simulation was developped in order to make the practically usefull tool in the designing the ceramic metal bonding techniques. The model with simulation should predict the amount of the glass phase needed for the particular alumina type. The simulation must be thoroughly tested with practical experiments.

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