Fabrication of TBC-armored rocket combustion chambers by EB-PVD methods and TLP assembling

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Abstract

A thermal barrier coating (TBC) system for rocket chambers made of Cu-based high strength alloys has been developed in a pilot project in line with EB-PVD (electron-beam physical vapor deposition) technology aiming at TBC application on Cu-based walls of real rocket combustion chambers. The TBC system consists of a metallic bond coating compatible with Cu-based material and an yttria partially stabilized zirconia TBC. The TBC overlayer is a distinctive ceramic structure designed for an exceptionally low Young’s modulus to withstand the extreme mismatch stresses between the internally LN-cooled high thermal expansion Cu metal base and the low thermal expansion hot ceramic shell. The TBC system has been qualified under close-to-service conditions on cylindrical LH2-cooled combustion chamber segments, where they have performed superior.

As EB-PVD technology is a line-of-sight process that is rather able to coat internal cavities, a transient liquid phase (TLP) joining technique for fully coated parts has been developed, that allows to assemble complete components out of vapor-accessible fully coated parts. It is capable, e.g. to incorporate sinuous cooling passages in the throat areas of combustion chambers, and/or to assemble oversized parts out of smaller components by maintaining parent metal properties. A manufacturing process is outlined for making internal TBC armored combustion chambers.

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1. Introduction

The inner walls of current rocket combustion chambers have to withstand heat flows in excess of 100 MW/m². The throat areas are the most endangered sections. The useful life of the throat region of cryogenic rocket engines is governed by a distinctive type of fatigue failure named thermo-mechanical ratcheting [1] as is the generally agreed view. To give an example: the European space industry got startled in December 2002 when an Ariane 5 rocket failed shortly after lift-off following a series of anomalies. Experts resumed that the cooling system of the Vulcain 2 main cryogenic engine had got a leakage: some cooling holes in the nozzle part (throat) of the combustion chamber had failed due to thermo-mechanical fatigue. Modifications were suggested to circumvent failures like this in future versions [2].

The rate of ratcheting depends strongly on the severity of thermal loading (both maximum temperature and thermal gradients). Minor benefits may result from improvements of the structural compliance of a system, e.g. by replacing subscale rectangular cooling channels by tubular channels, to prolong the life. As there is a general trend towards increased efficiency of rockets for the sake of better competitive ness, it appears to be more likely, that the subjection of rocket chamber walls to thermo-mechanical loading will increase with time as well. Hence to follow exclusive conservative strategies in rocket chamber construction will not pay in the end. Hence to strike at the root of this ratcheting problem, it would be more meaningful to

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mitigate thermo-mechanical loading of the throat area by substantial precautions as will be addressed below.

The situation is an exceptional but typical challenge for material scientists at first. They will have suggestions how to combat the dilemma of thermo-mechanical fatigue in rocket chamber throats. To this a concrete example of a very recent revolution in materials application on aeroplane and industrial gas turbine layouts will be given: engineers have developed ceramic thermal barrier coatings (TBC) to be deposited on Ni-base superalloy turbine blades to minimize the risk of thermo-mechanical fatigue. They are successfully in use since some 10 years. They are also recommended for the upgrading of elder and/or less advanced gas turbine engines to make them more durable [3]. The advantages of TBCs concern, besides combating thermal–mechanical fatigue and resultant longer lives and longer intervals between inspections and overhauls, less fuel consumption and less pollution. Hence they are increasingly adopted or taken into account for space applications, while shorter durations of space missions but higher thermal loads are encountered.

TBC systems for space applications will of course be different from those used in air transportation. The differences, however, will be of a qualitative and not of a principal nature. Low pressure plasma sprayed and detonation gun deposition coatings have turned out to be less advised than EB-PVD coating structures [1]. Substantial transfer of methodologies should be possible. Design engineers and materials scientists can rely on similar data base and technologies which are currently utilized in aviation industry for planning optimum heat protection systems. They will also be capable for thermal shielding of combustion chambers and their throat sections, with the necessary modifications of the TBC layer system in mind due to different substrate materials and higher heat fluxes. The advise of the experts to modify the throat in the Vulcain engine should therefore be addressed not only to designers but also to material scientists. They may plan ahead viable technological solutions for future scenarios, where more efficient rockets with heavier and more expensive payloads will safely be launched [4,5].

The paper will outline a distinctive approach followed by DLR material scientists and process engineers in a pilot project how to tailor and test a heat protection system particularly for the application on the inner walls of cryogenic rocket combustion chambers and their throat sections. Cu-base high strength age-hardenable substrates are chosen with respect to their high thermal conductivity and mechanical properties with regard to real combustion chambers which have to minimize their parasitic loads. The development of a thermal barrier coating (TBC) system exhibiting outstanding thermo-mechanical fatigue resistant microstructures will be of prime concern. A processing route for the upgrading of small-sized samples and demonstrator models to real components armored by TBC systems will be addressed.

2. Experimental assessments

2.1. Overview

This activity will outline the technology of a production line capable to toughen up present and future rocket engines by means of TBC systems designated for

- linings on the walls of internally LH 2 -cooled combustion chambers to allow superior thrust
- Cu-base substrates with respect to their high thermal conductivity
- high strength age-hardenable Cu alloys to minimize parasitic loads.

They will provide chamber models with

- smooth and erosion-resistant surface finishes to attain optimum aerodynamic flow characteristics
- outstanding erosion resistance to sustain high velocity gas flows
- outstanding tolerance against oxidizing and reducing combustion environments and high temperatures and temperature gradients to endure thermal–mechanical fatigue.

Small-sized combustion chamber demonstrator models (Fig. 1) have been intentionally manufactured in order to allow the up-scaling of experienced processing routes to real parts. Subsequent testing of a segment with LH 2 internal cooling should have close reference to service conditions as well. The materials validation and process procedures are detailed in the following chapters. They encompass the selection of suitable material for machining the combustion chamber models, provision and deposition of metallic bondcoat, likewise of ceramic TBC as top layer, and a joining technique for assemblage of (fully coated) components to final shapes. The last item addresses inter alia the potential incorporation of sinuous cooling passages which are typical for high performance throat areas. A particular joining technique for this task is under development to provide parent material properties in joints.

A high-strength age-hardenable Cu substrate material was selected for the manufacture of low weight combustion chamber segments to become acquainted with a potential chamber alloy right from the beginning of the pilot project. The cylindrical segments had Ø 4 mm cooling channels drilled along the wall, at a distance of 1.5 mm from the hot gas wall surface. They were made watertight—solely in this early design of a model chamber—by galvanoplastic application of a copper coating (an alternative joining technique is presented in the following). Optimum bond coating processes for copper substrate materials were identified. The electron-beam physical vapor deposition (EB-PVD) process was taken for the deposition of metallic bondcoats. EB-PVD is the favorite choice mainly because...
of the superior low roughness finish and the excellent metallic diffusion bonding between Cu substrate and coating. The EB-PVD processing route has been modified to allow the application of coatings at the inner walls in combustion chambers.

Bondcoat development was conducted with reference to minimal interdiffusion and good compatibility between Cu-base substrate and coating on the one hand, and optimal adhesion between ceramic layer and bondcoat tested under thermal-cyclic loading on the other hand. Various MCrAlRE (M: Ni,Co; RE= Ce, Y, Hf) and MCrRE compositions, that were either alumina-forming or chromia-forming oxidizers, were tested, and an optimum alloy solution for EB-PVD on Cu alloys has been identified.

Ceramic TBC top coat manufacture was done by reactive EB-PVD. The attribute ‘reactive’ addresses EB-PVD processing carried out under low pressure gas or gas mixture atmospheres instead under high vacuum, in the present case under oxygen atmosphere in order to maintain stoechiometric oxide compositions on deposition. As partially stabilized zirconia ceramic (YPSZ) is generally agreed to be the most reliable ceramic material commonly used for TBCs, and EB-PVD processing is the optimal processing route to procure stress-tolerant columnar microstructures in this material and smooth surface roughness, an EB-PVD processing route similar to that for metallic bondcoats was set up. Distinctive topcoat development was created to allow the combination of copper and ceramic, as the coefficients of thermal expansion of ceramic and Cu alloys were judged critical. A microstructure with superior tolerance against stresses and thermal gradients has been developed. It proved to be tolerant against any thermal histories. Repeated quenching even from 950 °C in cold water or chilling in LN2 was tolerated without failure.

Any heating of age-hardening Cu alloys beyond 400–500 °C will worsen the mechanical properties. Inferior properties are readily restored by a three-step treatment: (1) solution treatment at high temperatures, (2) immediate chilling to low temperatures, and (3) a final aging treatment. Hence processing steps like those mentioned in the paragraph before are essential to restore parent metal properties in Cu alloys which have been got lost by unfavorable temperature regimes (e.g. during EB-PVD, brazing, diffusion bonding etc.). So fully TBC-coated Cu segments are considered to be assembled to complex shapes via a diffusion-brazing process. A joining technique for Cu parts, although no necessity for laboratory samples and demonstrator models, will be presented in view of technological demands in future. In particular, a TLP (transient liquid phase) diffusion-brazing technology for Cu is in the development stage. It has been applied to parts subjected to a full coating treatment, which have been subsequently assembled to samples and tested.

2.2. Substrate material

The most demanding requirements of high heat-conductive Cu alloys for combustion chambers are:

- Ductility at LH2 temperatures
- High tensile strength close to ~ 500 °C
- Machinability, e.g. drop-forging should be possible
- Thermal fatigue resistance
- Tolerance against hydrogen atmosphere
- Applicability of TBC systems (bondcoat + ceramic topcoat) on the base metal
- Joinability of materials.
The demands led to selecting the commercial Cu base age-hardening alloy CuCrZr, specification number 2.1293. The tensile strength surmounts 350 MPa at room temperature.

The mechanical properties are taken as a baseline from copper data sheets or are otherwise proven by experiments [6]. The application of TBC systems has been successfully accomplished [7]. The ductility of Zr-containing Cu alloys is even said to increase at longer times of creep exposure. The notch ductility is excellent [6]. Drop forging for this alloy is feasible and allows the manufacture of deliberate shapes. The joining technology is addressed in chapter 2.5.

### 2.3. Bond coating

The bond coats, besides protection against oxidation, have to meet the demands of a suitable low thickness (15 μm) and roughness ($R_{\text{a}}$: 1 μm) and perfect adhesion, since any increase in surface roughness and formation of pores and decohesion at interfaces, yields aerodynamic losses and would drastically alter the heat fluxes between substrate and the coated walls.

The optimum solution is

- the development of a ductile MCrAlX coating alloy composition compatible with Cu substrates with regard to low inter-diffusion and good mechanical matching
- auto-formation on same coating of an alumina layer during TBC application for safe TBC bonding and for superior inertness against $O_2$ and $H_2$ attack
- the development of an EB-PVD route to allow coating deposition on the interior of combustion chambers.

The deposition of a MCrAlX composition by EB-PVD is not trivial. The evaporation pool in a vacuum coater contains five or more elements which all have different vapor pressures. So the composition in the liquid pool needs some optimization of the process to get a coating of the ‘right’ composition. Depending mainly on the electron-beam power utilized and on the beam focus the portion of the five elements has to be shifted this way to meet the desired alloy composition in the coating. EB-PVD was accomplished in a 60 kW EB-PVD Leybold equipment in a rotary mode. The axis of this coater with the sample fastened at its tip is favorably inclined to give access of the vapor cloud to the interior of the model combustion chamber to be coated.

### 2.4. Thermal barrier coating

A 150 kW reactive EB-PVD pilot plant (ESPRI, von Ardenne) is exclusively used for the deposition and application of ceramic TBCs. A special e-beam gun is installed which tolerates the evaporation in a low-pressure oxygen atmosphere. A plurality of ceramic structures and compositions has been successfully done there. Referring to coating of the combustion chambers, however, we were faced with two problems. One was the deposition on the interior wall of the model combustion chamber which needs a line-of-sight contact between evaporating ceramic and the candidate deposition area. It was solved in analogy to the prior metallic coating techniques by incorporating an inclined axis for the manipulation of the substrate in a rotary mode.

The other problem addresses a DLR specialty columnar coating type designated ‘crocus structure’ owing to its unique microstructural features [8]. As the thermal expansion of Cu ($20 \times 10^{-6} \text{K}^{-1}$) is considerably larger than for superalloys ($16 \times 10^{-6} \text{K}^{-1}$), and much larger than that of fully dense PYSZ ($11 \times 10^{-6} \text{K}^{-1}$), the Young’s modulus of the ceramic layer must be significantly lower than state-of-the-art EB-PVD PYSZ TBCs to battle mismatch problems. The risk of TBC spallation is due to interface stresses between dissimilar materials on cooling to room temperature or below from processing temperatures; so the coatings may probably be subjected to inferior stress regimes in real service. A unique TBC microstructure like this version will exert a distinctive tolerance against any temperature variations: it will not only withstand severe service conditions but will also sustain extreme heating and quenching procedures to which age-hardening Cu-base substrates may be subjected. The Young’s modulus of the structure is given in Fig. 2 and suggests very low stiffness data even on copper alloys. This microstructure can be preferably made by distinctive control and variation of rotation speed and temperature. The low Young’s modulus of the ceramic layer, compared to state-of-the-art EB-PVD PYSZ TBCs, is given in Fig. 2.

The TBC system after preliminary test campaigns of 14 engine cycles of approximately 1/2–1/4 min is shown in Fig. 3. The scanning electron microscopy micrograph shows the columnar structure of the TBC still staying unaffected by the cyclic test procedure. No densification by sintering at the minute TBC tips can be seen. It suggests the unimpeded
continuance of a low Young’s modulus behavior. The dark fringe at the lower TBC contacting the upper bond coat is a thermally grown oxide (TGO) layer that has well helped to make the TBC adhere by chemical bonding to the bond coat. This layer is mainly formed during the coating procedure and will scarcely grow in service. The TBC armored combustion chamber segment after the test campaign is shown in Fig. 4 exhibiting full integrity of the coating system.

2.5. TLP (transient liquid phase) assembling

A joining process developed in the early 1970s, mainly for assembling superalloy parts, combines the manufacturing ease of brazing and the inherent quality and maintenance of properties of diffusion welds. This process called TLP (transient liquid phase) is a diffusion bonding process which utilizes the ability of a convenient interlayer composition to melt and subsequently re-solidify to accomplish the bond [9]. The interlayer material commonly in thin foil form is placed between the components to be joined. When the entire assembly is heated to a given temperature, the interlayer melts because of its composition. The part is then held to this temperature, at which through diffusional processes the bond region is caused to re-solidify and homogenize in the course of the changing composition in this area. The time at temperature mainly depends on the diffusivity of the components of the interlayer in the metal. The point is that this process enables the manufacture of bonds which exhibit parent metal properties. It has been successfully applied to a wide spectrum of superalloys. The remarkable capabilities of TLP bonding to join various Ni-base materials initiated our R&D effort to explore the versatility of LTP processing also to the class of age-hardening Cu alloys that are a potential cryogenic rocket chamber material.

While boron is a prominent element in Ni-based brazes because of quick off-diffusion along interstitial lattice sites (instant homogenization of brazed areas can be expected) and a favorable melting point depressant for TLP bonding it is of minor use for bonding of Cu-base alloys so far. Alternative bracing alloys have to be provided. A common 28Cu–72Ag brazing alloy is taken as a concrete example to demonstrate the peculiarity of LTP assembling of copper-base pieces compared to soldering. First mechanical properties data of LTP assembled copper alloy parts are given in the next chapter. Heat treatment programs for
optimal restoring the properties after TLP brazing and EB-PVD coating are under way.

3. Testing and results

3.1. Model combustion chamber segment with TBC layer

A test procedure at the P8 test rig (DLR Lampoldshausen) has been designed as standard to reach the highest combustion chamber pressure of 110 bar in three steps, making tests for each step: starting from 45 bar, then rising to 80 bar and finally to 110 bar. Each segment had separate in- and out-flow. The pressure and temperature of the coolant flow at coolant in- and outlet and the coolant mass flow were recorded, and the resultant heat transfer without and with TBCs was obtained. The thermal efficiency determined in sequence always ranged at 25%.

Three runs at 110 bar have been carried out this way on a LH2-cooled segment. No spallation of the coatings was observed (Fig. 4). The surface roughness of the ceramic layer of $R_a = 1.5 \text{ m}$ was maintained.

The test campaign proved the perfect performance as well of the respective single components of Cu-base alloy, bond coat and ceramic top coat as the excellent cooperative presentation of the design in a close-to-service test regime. The TBC system can be recommended to inner wall application in high strength Cu-base combustion chambers.

3.2. TLP diffusion brazing

Various solder materials capable of TLP brazing are in the development stage. They are based on different portions of copper. To demonstrate a peculiarity of the TLP brazing process a special solder low in copper and high in silver will be presented. A 5 \( \mu \text{m} \) thick sputter-deposited 28Cu–72Ag layer on either cylinder face has been held in contact. On vacuum annealing slightly above the melting point of at 780 \( ^\circ\text{C} \) some time some of the liquid solder has diffused into the parent metal parts. It depends on the time at temperature and on the amount of solder if a TLP process has really taken place. If the time or temperature is insufficient some of the solder may have off-diffused into the Cu base metal. But some remnant AgCu phase is still apparent as is demonstrated in Fig. 5. It shows-besides coarse Cr precipitates—an interrupted ‘pearl-chain’ like adhesion zone of smaller islands mainly on locations like grain boundary triple points along the soldered junction. The presence of the remnants makes the difference between soldering and TLP processing. The adhesion strength of the soldered joint will be inferior.

But if the annealing process is held for an optimal time and temperature no remnant AgCu phase will be present any longer. The homogenization-annealing step i. g. can be brought about during EB-PVD processing. Hence no additional solution heat treatment will be necessary provided instant rapid cool-down after coating deposition can be ensured. If it is successfully accomplished parent metal properties in the joining zone can be expected.

![Fig. 5. Adhesion zone after brazing of CuCrZr parts showing remnants of AgCu solder along the junction to demonstrate lacking homogenization treatment at high temperatures for a successful TLP joint. Besides some coarse but insignificant Cr precipitates still originating from former alloy production are dispersed.](image)

![Fig. 6. Tensile-tested CuCrZr sample joint in the center by former TLP processing.](image)

|                        | 0.2% yield strength (MPa) | Ultimate tensile strength (MPa) | Total extension (%) |
|------------------------|---------------------------|---------------------------------|---------------------|
| (1) As-received        | 349                       | 355                             | 16.0                |
| (2) Fully coated condition | 49                       | 211                             | 67.5                |
| (3) TLP processed and fully age-hardened | 265                       | 409                             | 47.9                |
The tensile test on TLP joined samples shows the superior mechanical properties maintained in this area as is suggested by survival of the TLP-affected region after testing, see Fig. 6. The test data are shown in Table 1 and Fig. 7. They demonstrate that the ultimate tensile strength can even be higher in TLP processed material than in the as-received high strength condition. The properties can be tailored towards the demands of the final product within certain limits.

The data represent the very first results for this technique of joining high-strength Cu alloys. It turned out feasible just from the start. Various soldering alloys are in the development stage and need to be qualified, e.g. which heat treatments will result in the respective mechanical properties, and which solder alloy is suited best for a productive TLP manufacturing process.

4. The assembling of thermal barrier coated combustion chambers

The throat area of the combustion chamber needs some of the most advanced technologies with regard to heat protection and internal cooling. Most successful upgrading of rocket combustion chamber performance via TBCs, albeit put as sub-scale combustion chamber segments through their paces in close-to-real-service tests, was obtained via EB-PVD technology [1]. However, it necessitates the development of a particular joining technique for undercut sections common in real parts to assemble them to monolithic products. The incorporation of sinuous cooling passages of circular cross-section, typical for the throat area, depends on adequate joining techniques as well. The choice of an optimal joining technique, which should be commercially available and keeps parent material properties, is facilitated by the unique tolerance of the EB-PVD coatings against high thermal transients and deliberate thermal shocks between LH₂ temperature and beyond 1000 °C. They allow nearly any heat treatment on the condition that their properties are not impaired.

Production engineering of rocket combustion chambers at DLR

A preliminary ‘flow chart’ for the production of real rocket combustion chambers prospected so far is given in Fig. 8. It encompasses the fabrication of components out of age-hardening high-strength Cu alloys and the application of a distinctive TBC system on them, the milling of non-linear grooves for cooling channels that are following the bent conical contours e.g. in the nozzle section, the joining technology needed to get the grooves ‘hidden’ about one mm below the surface within the assembly, and the final heat treatment to obtain perfect mechanical properties all over the part. Some of the processing steps need to be further optimized.

E.g. the positions 3 and 4 within the flow chart can be shifted to an alternative position between 6 and 7, if e.g. oversized components have been provided. They will then be cut to smaller sections for more convenient EB-PVD processing in a common coater. Afterwards the multiple parts will be reassembled via brazing to a final monolithic part. Variations like these to bond previously coated parts is uncritical since the temperature range for TLP is lower by some 400 K than incipient melting of
the coating system. One more advantage of this sequence may be that 'hard-brazing' with the TLP solder and solution-heat treatment can be done in a single processing step. On the other hand smaller parts may be brazed to bigger ones by the sputter-braze technology in the same way, if by doing that a more comfortable processing route can be attained.

5. Conclusions

An advanced EB-PVD TBC system has been successfully designed and assessed on cylindrical LH₂-cooled Cu-based combustion chamber segments. A joining technique has been developed for fully coated parts of the particular Cu alloy that preserves parent metal properties. Both the coating and the joining technologies synergistically contribute to outlining a manufacturing process for the production of low weight high performance combustion chambers.

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