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APPLICATION AND TESTING OF THERMAL BARRIER COATINGS FOR CRYOGENIC ROCKET ENGINES

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ABSTRACT

The development in thermal barrier coating (TBC) systems for cryogenic liquid rocket combustion chambers is addressed. It resulted in the preference for electron-beam physical vapor deposition techniques (EB-PVD) subsequently used for application of bond coats as well as zirconia TBCs. The high strength potential of age-hardening Cu alloys, e. g. CuCrZr as a well-suited substrate material class, inspired the search for temperature-cycle tolerant coating varieties that allow to follow heating and quenching procedures common for alloy strength optimization through age-hardening routines.

LH_2 cooled sub-scale CuCrZr combustion chambers were coated with developmental TBC systems by in-house EB-PVD procedures. Close to reality rig tests at the Lampoldshausen test facility P8 at pressures of 110 bar and fueled with LO_2/LH_2 confirmed the aptitude of the TBC systems for rocket combustion chamber linings.

1. Introduction

Design engineers of rocket engines are facing a perpetual demand for higher efficiency (= higher specific thrust), reliability, and savings of costs. Great hopes are placed into material scientists who may provide a substantial part to meet these goals. A favorite choice are thermal barrier coatings (TBCs).

Thermal barrier coatings in airfoil and gas turbine combustion chamber applications have proved to be very successful for nearly two decades since their start up in service. Turbine entrance temperatures can now be raised by 150°C, the service intervals can be twice as long, and big efforts are running to utilize safely their full potential to improve the efficiency of turbines by today's about 1% to 4% or more.

TBCs offer potential reductions of both costs and risks for development of liquid rocket engines as well. The focus in TBC system development has to be directed on their reliability and performance with regard to high inner wall surface temperatures and thermal gradients and the different atmospheres compared to gas turbines. Three years ago the German Aerospace Center (DLR) pointed the way to the future and decided to initiate a special TBC research activity for more effective space transportation systems by a joint research activity of the Space Propulsion Institute (DLR Lampoldshausen) and the Institute of Materials Research (DLR Köln). The inherent expertise and European leadership in **E**lectron-**B**eam **P**hysical **V**apor **D**eposition (EB-PVD) technique and close-to-reality testing experience will back up a fast development of TBC linings in cryogenic regenerative cooled combustion chambers [1].

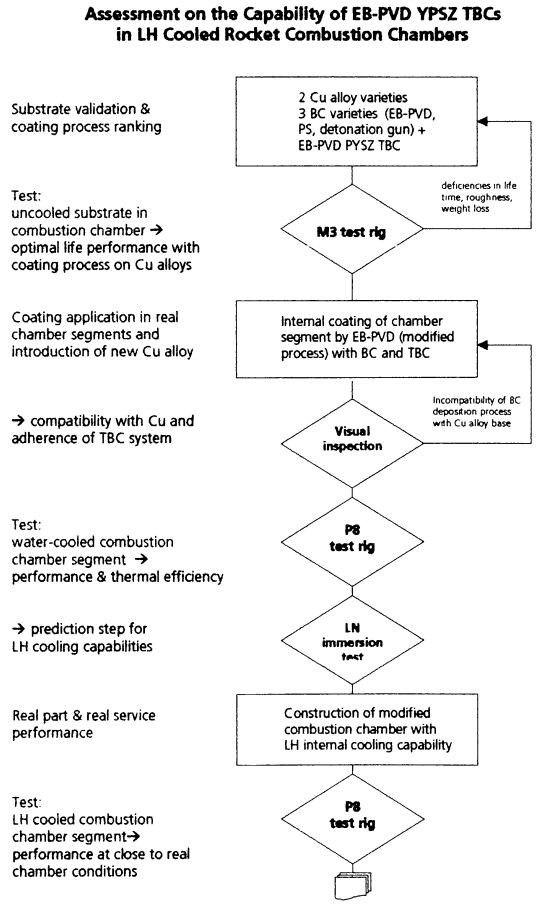

Fig. 1: Flow chart of material and process validations

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2. Experimental Part

2.1 Overall R & D conceptual strategy

The aim of the project is to toughen up present and future rocket combustion chambers in cryogenic rocket engines by means of TBCs

- as linings on the walls of the chambers to allow superior thrust efficiencies
- on Cu-base substrates with respect to their superior thermal conductivity
- on high strength age-hardening Cu alloys to allow maximum weight savings
- with smooth and erosion-resistant surface finishes to attain optimum aerodynamic flow characteristics
- with outstanding tolerance against oxidizing and reducing combustion environments and high temperatures and temperature gradients.

The TBCs will be deposited on the inner walls in small-sized combustion chamber demonstrator models that will allow up-scaling of coating processes in real parts. The progress of this project up to now is detailed in [1] and excerpted in Fig. 1. The materials validation and process procedures are outlined in Fig. 2. Starting with a suitable Cu substrate material small-sized combustion chambers have been manufactured; and going clockwise in Fig. 2 optimum bond coating processes were identified and applied in order to use them for the deposition of bond coatings exclusively developed for Cu alloys.

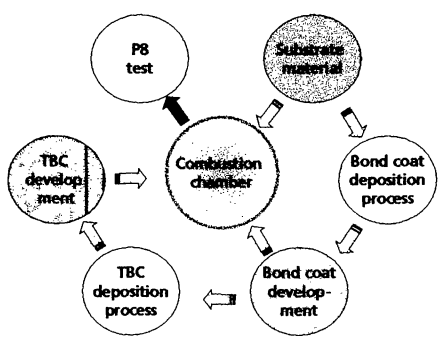

Fig. 2: Materials and process validation and development sequence

Zirconia was identified as the most reliable TBC material. A TBC processing route for zirconia TBCs has been initiated to account for the development of optimum stress and thermal gradient tolerant ceramic coatings. This TBC will not only withstand superior severe service conditions but also the extreme heating and quenching procedures exerted on age-hardening of the Cu-base substrate. Age hardening is essential to restore potential losses in substrate strength by former treatments, and hence the tolerance of TBCs for same treatments is rated as a deciding factor. A consistent strategy

Table 1: Detailed materials/process recommendations

Purpose & applicability	Requirements	Recommended material / processing route
High temperature capability	high $M_{s,}$ resistance against • sintering • oxidation • excess H_2	zirconia
Adhesion on Cu substrate and compliance with Cu alloys, oxidation tolerant	ductile & smooth bond layer	MCrAlX applied by EB-PVD
Low aerodynamic losses along chamber & nozzle walls	plain surface of R_a = 1µm	EB-PVD
Tolerance against • hot spots (1400°C) • cold chills (- 250°C) • thermal gradients (150 000K/mm)	low Young's modulus TBC < 10MPa	zirconia applied by a patent EB-PVD route

for the development of TBC systems will be given. The requirements and recommendations at the beginning of this chapter are given in the preliminary specified materials and processes summarized in Table 1. Developmental details are explained in the following.

2.2 Substrate material

The need for high thermal conductivity/high strength substrate materials led to selecting a representative Cu base age-hardening alloy surmounting 350MPa at room temperature → CuCrZr, specification number 2.1293. A stress-strain diagram for the CuCrZr alloy is given in

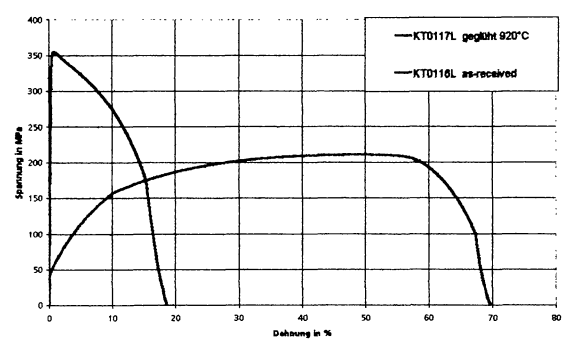

Fig. 3: Stress-strain diagram for CuCrZr alloy 2.1293 in the as-received condition and in a high-temperature annealed state obtained after EB-PVD processing

Fig.3. It shows the stress-strain behavior in the as-received condition and in a high-temperature annealed state that is typical for the after EB-PVD coating cycle state. Both conditions are detailed in Table 2. The low mechanical properties after coating processing of only

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Table 2: RT stress-strain properties of CuCrZr alloy in standard and in "as-coated before age-annealed" state

	Young's modulus [MPa]	0.2% yield strength [MPa]	Tensile strength [MPa]	Total extension [%]
standard (as-received)	116884	349	355	16.0
as-coated before age anneal		49	211	67.5

<50MPa can easily be restored to the as-received standard state by following standard treatment: short 950°C solution treatment, followed by quenching e. g. in water or in cold fluidized bed, and subsequent age-hardening anneal at 425 to 500°C. Sub-scale combustion chamber segments of this alloy , as shown in Fig. 4, were manufactured for coating and testing purposes.

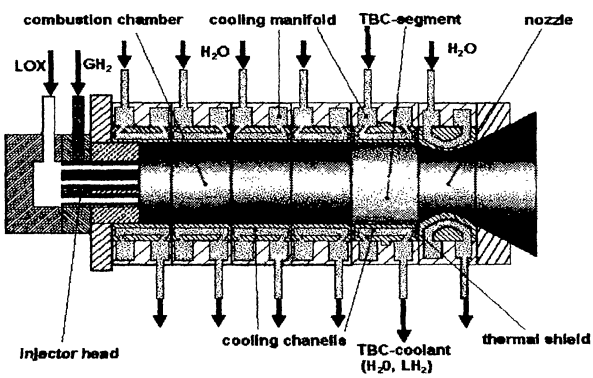

Fig. 4: Sub-scale combustion chamber model B

1.3 Bond coat development

The bond coats, besides protection against oxidation, have to meet the demands of a suitable low thickness and roughness, since any increase in surface roughness, despite aerodynamic losses, would alter drastically the heat fluxes between substrate and the coated wall.

- The coatings have to sustain an extremely high wall heat flux, up to two orders of magnitude as high as for aircraft applications.
- In regeneratively cooled combustion chambers employing LH_2 with a temperature ranging from 30K to 40K as the coolant, an extreme temperature gradient is impressed to the inner lining. This temperature gradient generates a considerable thermal strain within the lining and inducing heavy thermal-mechanical stress into the coating.
- In cryogenic rocket engines employing liquid oxygen (LOX) and LH_2 as the propellants, the coatings are subjected to H_2 rich, high temperature gases and superheated steam.

According to the specific characteristics listed above and in Table 1 the application of TBCs to space vehicles has to meet a number of additional requirements, regarding both materials and techniques of the thermal barrier coating as well as of the bonding layer:

- Employment of a proper material for the bonding layer, suitable for a Cu-alloy substrate.
- Compatibility of same material with oxidizing as well as reducing atmospheres in the combustion chamber percolating the ceramic top layer.
- Application of a TBC technique / material that is capable firstly, to generate the required low thickness and low roughness of the coating and secondly, to sustain the severe environments inside a rocket engine.

The optimum solution to meet all the problems has been

- 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.

2.4 Thermal barrier coating development

A 150kW EB-PVD pilot plant at DLR is exclusively used for the deposition and application of ceramic TBCs

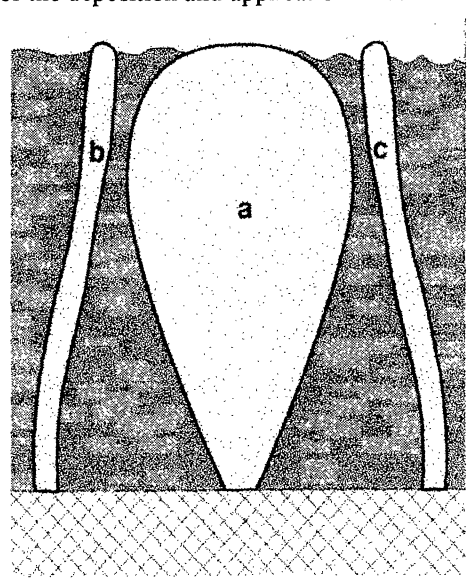

Fig. 5: Scheme of low Young's modulus TBC microstructure showing club-like forms (a) enlarging away from the substrate and sinuous (S-shaped) forms (b, c)

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exhibiting a plurality of structures and compositions. In the connection of the combustion chamber coating task a columnar coating type of zirconia has been designed ("crocus structure") showing unique microstructural features. It shows club-like forms enlarging away from the substrate, while between them other forms show a sinuous (S-shaped) finger-like form. The distinctive attribute of this TBC provide extraordinary low in-plane stresses (substrate dependant!) that prevent sintering and help to preserve all physical properties like low stiffness and low thermal conductivity. They allow deformations and extreme shrinkage of high expansion substrates e. g. copper alloys super-cooled on contacting with LH_2. The Young's moduli at room temperature for the TBC compared to standard TBCs is shown in Fig. 6. It has to be born in mind that the Young's moduli of EB-PVD TBCs are a function of temperature and thermal expansion of the substrate. TBCs on a Cu substrate will be higher at LH_2 temperatures due to the contraction of the copper substrate in contact with LH_2 of course, but will not surpass uncritical 15GPa. So an ideal TBC material for cryogenic rocket engines has been created [2, 3]. This TBC can also be applied on the interior of combustion chambers due to the development of the EB-PVD route just mentioned above.

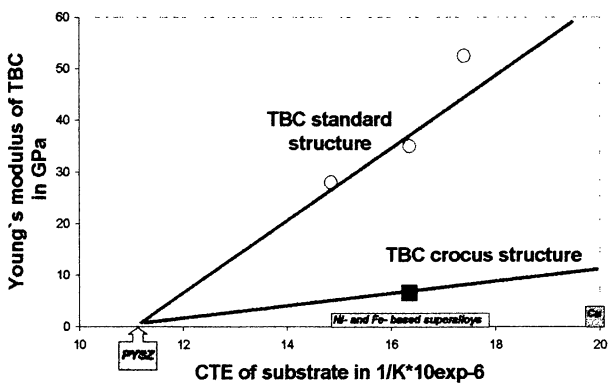

Fig. 6: Young's moduli at room temperature for "crocus-type" TBC compared to standard TBCs giving an in-plane Young's modulus of approximately 10GPa on Cu substrates (extrapolated)

3. Testing

3.1 Testing conditions and efficiency benefits

Two mayor test campaigns in the P8 facility have to be addressed:

1. preliminary tests on a water-cooled sub-scale chamber segments of model B (Fig. 4) using liquid oxygen and GH_2 as fuel to characterize the performance of the TBC systems
2. final tests on a LH_2-cooled sub-scale chamber segment (4th segment from the left in model B) to test potential survival of this element in a "real conditions" at 105 bar.

The next chapter "3.2 Materials performance in preliminary tests" will discuss post-testing materials issues.

The preliminary test campaign at P8 test facility was performed with a chamber with integrated water cooling as just mentioned. It has been coated with a development EB-PVD MCrAlX bond coat and an EB-PVD PYSZ TBC. The EB-PVD process allowed to deposit the appropriate layer thickness of a metallic bond coating (approximately 15µm MCrAlY) as well as of the final ceramic top layer (approximately 15µm PYSZ) throughout the hollow chamber segment.
In this phase of DLR's TBC research the objectives have been as follows:

- optimization of the manufacturing process of combustion chamber segments incorporating TBC
- assessment of the high thermal gradients, high heat load and H_2 rich environment onto:
  -the integrity of the coating surface
  -the adherence of the TBC on the Cu-alloy substrate
- evaluating the thermal efficiency of TBC onto the wall heat transfer compared with uncoated chamber segments
- optimization of thermal efficiency **and** longevity.

The model B combustion chamber consisting of four cylindrical segments and a nozzle segment (Fig. 4) with ∅ 4mm cooling channels drilled along the wall, at a distance of 1.5mm from the hot gas wall surface equals in essence to cooling channel geometries of standard segments. Each segment is equipped with its own cool-

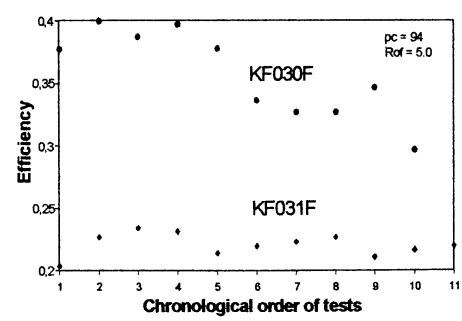

Fig. 7: Cooling efficiency of two segments in comparison showing the effect of progressive TBC process optimization on the "stability" of the cooling performance

ant supply system, composed of a coolant manifold mounted on each segment with separate in- and outflow. The pressure and temperature of the coolant flow at coolant in- and outlet and the coolant mass flow are recorded, and hence the heat transfer is obtained. Com-

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parison of the heat transfer obtained from uncoated and TBC bearing segments bring about the thermal efficiency of the coatings. They turn out to be independent of pressure. Optimized TBCs range between 22 and 28% [1], see also Fig. 7.

3.2 Materials performance in preliminary tests

The TBC system after a test campaign of 14 engine cycles of approximately ½ to ¼ minutes is shown in Fig. 8. The scanning electron microscopy micrograph shows

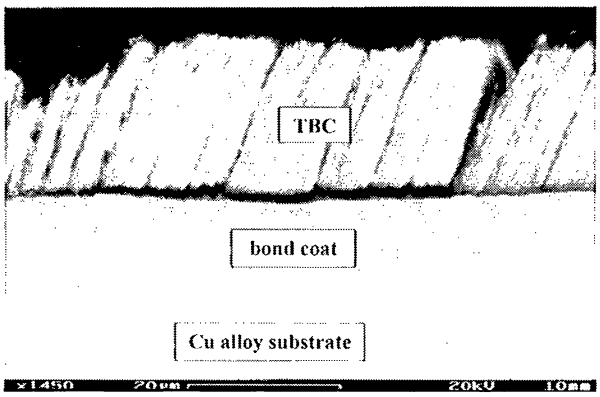

Fig. 8: SEM cross-sectional view of TBC system after testing

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

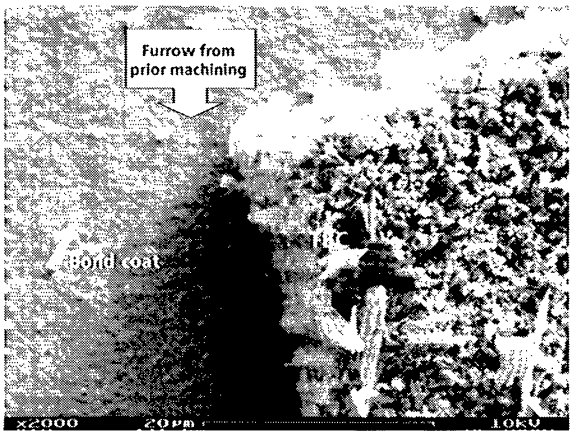

Fig. 9: SEM bird´s-eye view onto the surface of a tested TBC system showing spallated area at the left leaving bond coat with furrow marks from prior machining

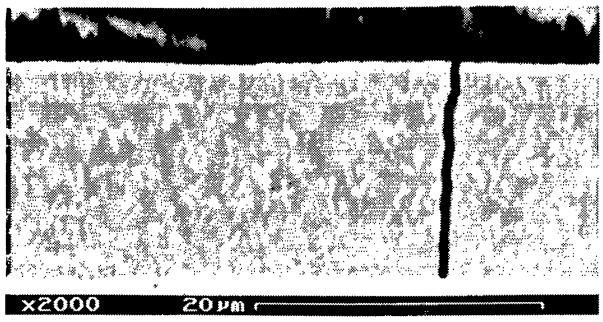

Fig. 10: SEM cross-sectional view as in Fig. 8 but of spalled area after testing showing bright precipitates in the bond coat and thermal-fatigue induced crack due to excessive thermal loading in areas devoid of protective TBC

grow in real service due to relatively low substrate temperatures being effective below a TBC. Oxidation of the developmental alumina-forming bond coat is therefore judged not to be a life-limiting mechanism. A thinner bond coat thickness even <10µm is advisable on future components.

Spallation of the TBC was observed on insufficiently optimized TBC systems. Failure was obviously caused by furrows (see Fig. 9) that induce off-plane stresses in the TBC that promote spallation. In order to avoid this failure mode in future components the inner surfaces have to be machined to an optimum finish before coating deposition to attain really plain surfaces.

Spallated areas show some consequences that will not happen if properly manufactured substrate surfaces and bond coats have been made. Spallated areas can be affected by high cyclic thermal loadings that make the bond coat prone to thermal fatigue cracks that otherwise will not occur. The ductility of the bond coat in the spalled areas seems to be embarrassed by precipitation of a coarse phase (see bright flakes in Fig. 10). They support a tension-induced cracking mode during cool down after a service cycle as is evidenced by preferred crack propagation along this phase and by the perpendicular orientation of the crack through the bond coat.

3.3 Final qualification test (LO_2 / LH_2)

For the final phase of DLR's TBC research the following objectives have been defined:

- providing evidence that the TBC is capable to sustain thermal shocks inducted into the LH_2 cooled copper wall below the TBC system
- determination of the thermal efficiency with LH_2 cooling

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- determination of the operation margins of the coated segment by continuously decreasing the coolant mass flow until the temperature limit of the copper wall or of the coating material is reached.

The test procedure for the current test campaign 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.

The thermal shock durability and overall performance of DLR's TBC systems has been successfully demonstrated even at the highest chamber pressures of 110 bar attainable so far. Three runs at 110bar have been carried out. More cycles are planned to determine the maximum number of cycles until failure. We fear, however, it may prove to be a tedious and time-consuming task with regard to the longevity of the TBCs obtained so far.

Further testing of an identical but TBC-free segment will follow to determine the thermal efficiency of the TBCs versus LH_2 cooling and will be compared to the former values of 23 to 28% efficiency obtained with LN_2 cooling. Determination of the operation margins of coated segments will follow as well by usage of reduced coolant mass flows to determine the temperature limit for a component with special attention to the copper wall and the coating material.

4. Conclusions

EB-PVD coatings have been ranked best against competitive deposition technologies with regard to aerodynamic surface qualification and durability. TBC linings manufactured by EB-PVD processing routes for LH_2 cooled combustion chamber segments have proved successful at 110bar (= maximum pressure obtainable at P8) without damage. It approximately equals to the chamber pressure of 115bar in the VULCAIN 2 engine. Extraordinarily stress-compliant TBC microstructures of PYSZ ceramic have been developed for safer TBC linings to allow any thermal history subjected to fully-coated Cu-based substrates as well for age-hardening purposes as for superior performance during service.

TBC failure, evidenced by TBC spallation and subsequent bond coat embrittlement, originate from furrows introduced by prior insufficient machining of components. They induce off-plane stresses within the ceramic coatings that may promote spallation followed by deleterious temperature attacks on the bond coat. An optimum finish before coating deposition to attain really plain surfaces for safe coating adherence is mandatory.

The longevity of the components during service is not embarrassed by oxidation mechanisms. Hence thin MCrAlX bond coatings even less than 10µm thick applied by EB-PVD are advised. Ceramic top coats may benefit from the unique microstructures ("crocus" structures) obtainable by the optimized EB-PVD processes. They represent a superior potential for sheltering future combustion chamber walls subjected to any hot combustion gas environment at or exceeding 200bar.

5. References

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3. US Patent 6,333,090 B1, see also German Patent DE 197 15 791 C2.

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