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An overview of the Agency Technology Development Programmes in Materials for Reusable Launch Vehicles

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Abstract

A close scrutiny of Reusable Launch Vehicle (RLV) possibilities as a way to lower the current high cost of launching commercial satellites was initiated more than fifty years ago in Europe. In 1994, the European Space Agency and European industry agreed to forge ahead with a project to assess RLV concepts. In addition, the technology development provisions required to design and build such an advanced launcher were evaluated for the most critical areas - namely aerodynamic, propulsion, heat management, structures and materials. Due to the unique requirements for materials, regarding for instance the reusability, the issue of mass and the harsh environments a RLV will encounter, various material studies were defined in relation with the primary structures, the cryogenic tanks, the elevated temperature components and parts and the Thermal Protection Systems (TPS).

For the FESTIP programme, MAN Technologie was the Prime Contractor and the industrial contractors were: CASA and INTA (Spain), BAM, Dornier and DLR (Germany), Metallwerke Plansee and Forschungszentrum Seibersdorf (Austria), Raufoss Technology (Norway), SONACA (Belgium) and CONTRAVES (Switzerland). In phase 1 of this programme a survey, selection and testing plans for the next phase were established. In the current phase 2, material screening tests were carried out to determine the basic characteristics and to confirm the selection of the different materials and processes that will be further assessed.

An overview of the current status of the following materials will be presented:

Cryogenic tank application
- Aluminium lithium alloys
- CFRP material

Structural materials
- Dispersion strengthened aluminium (DS-Al)
- CFRP material

Materials for elevated temperature applications and TPS
- Oxidation-protected γ-TiAl
- Oxidation-protected and reinforced refractory metals
- CMC materials with oxidation protection
- High temperature materials for sliding application
- High reflective Internal Multiscreen Insulation (IMI)

KEYWORDS: High temperature materials, cryogenic materials, reusable launchers.

INTRODUCTION

The aim of FESTIP (Future European Space Transportation Investigation Programme) was to prepare Europe to undertake developments for future launchers beyond ARIANE 5 and its evolution. Such future launchers would only be developed if they drastically reduced cost for access to space. Therefore it has been assumed that such future launchers will be reusable. Reusable Launch Vehicles (RLVs) represent a real technical challenge. Beside other themes, FESTIP includes a technology development programme for materials.

In order to be feasible and to achieve good payload performance, the dry mass of the reusable launcher must be minimised. A low dry mass requires low density, stiff materials working at high stresses. These materials will be exposed to a wide range of temperatures - from cryogenic up to a large percent of the melting temperature. RLV materials will see service operation in various and severe environmental conditions. Cyclic usage must demonstrate flexibility and reusability.

These issues have not been encountered in quite the same way before. Conventional materials and current processing technologies are generally inadequate to fullfil these requirements, and the development of advanced materials ahead of the design phase of RLVs is extremely important. This FESTIP technical theme has the aim to explore the upgrading of current technologies for RLV materials based on the materials and processes developed with today’s technology.

DEFINITION OF TASKS

The first task was to improve selected advanced materials and coatings based on the combined scientific and technical knowledge of the companies involved in the field of material processing among the European participating countries.
The second task was to assess the mechanical behaviour of these materials using laboratory test methods. To deduce the mechanical and physical characteristics from the properties of the materials in the specific RLV operating conditions, the tests will range from cryogenic up to elevated temperature in various environmental conditions (e.g. air, inert atmosphere, liquid gaseous oxygen and hydrogen). The ability of the materials and their coatings to perform satisfactorily in their chemical service environments must be well demonstrated. The test programme covered the following classes of materials:

- Lightweight metallic and composite materials for the cryogenic fuel tanks, that must intrinsically feature good mechanical properties down to cryogenic temperature and demonstrate chemical compatibility with the liquid cryogens.
- Advanced aluminium alloys and CFRP for the airframe and primary structure.
- Oxidation-resistant ceramic composite materials and high temperature intermetallic materials (with adequate coatings) for RLV skin.
- High temperature ceramic composite materials and refractory alloys for a low maintenance engine, capable for multiple firings.
- High temperature lubricants for application to airframe bearings, actuated control surfaces and air-intake systems.
- Highly reflective internal multiscreen insulations (IMI) for improvement of durable advanced thermal protection systems.

CURRENT RESULTS

Cryogenic tank application

Aluminium-Lithium Alloys

Scope

The conventional aluminium alloys, like the 2219, are widely used in cryogenic environments due to their comparative low cost, good weldability and high toughness.
The recent developments by aluminium suppliers of new aluminium-lithium alloys with high strength and improved fracture toughness at cryogenic temperatures widen the prospects for the usage of these alloys in the spacecraft industry. The potential mass savings of about 8 to 15% using an Al-Li alloy instead of a conventional aluminium alloy may also be considered for structures operating in low temperature environments like the cryogenic tanks.
Based on available literature information, a list of Al-Li alloys and tempers to be suitable for use in a cryogenic environment has been established: 2195-T8R78 from Reynolds, 1460 T1 from VIAM/KUMW, 2090-T83 from Alcoa and 8090-T851 from Alcan

Summary of the results

The 2195-T8R78 from Reynolds was more extensively characterised because it features better static tensile properties at RT and -196°C (in L and 45°) (Fig. 1) and good specific tensile properties at RT, high fracture toughness at -196°C and good properties of the welded joint when compared to others Al-Li alloys.
The fracture toughness was 22 MPa $m^{0.5}$ at RT and 19.5 MPa $m^{0.5}$ at -259°C (in ST-orientation). This reduction of 11% could be linked with the evolution of the ductility of the 2195 with the temperature. The resistance to crack growth propagation of the alloy was higher at -150°C than at +23°C. At a stress level of 400 MPa, the fatigue life of the material is increased from 200.000 cycles at room temperature to 2.000.000 cycles at -150°C. Lower stress levels had the same effect on fatigue life at RT and cryogenic temperature.
2195 sheet featured a high resistance to stress corrosion cracking in L-T orientation, whereas thicker products tested in the S-T orientation showed low resistance to SCC. In both cases, pitting and intergranular corrosion were noticed.
None of the 45° oriented notched specimens exposed either to the liquid oxygen or to the liquid hydrogen failed or cracked during a 200h-constant loading test at 80% of the notched yield strength value. Subsequently, the residual tensile strengths of the LOX- or LH2-exposed specimens were similar to the reference non-exposed specimens.

Comparison between the Al-Li alloy 2195-T8R78 plate with the conventional Al-alloy 2219-T87 plate material used for the current cryogenic tanks fabrication.

Yield and ultimate tensile strengths were much higher for the 2195 than for the 2219 over the temperature range from cryogenic temperatures up to RT (Fig. 2). Young modulus was found higher for the 2219 at cryogenic temperature, but at higher temperature, the Young modulus was higher for the 2195. Elongation at rupture values were similar for both alloys. However, the fracture toughness of the 2195 was roughly half of the one of the 2219 over the whole range of temperature (Fig. 3). Although the joint coefficient values of the welded 2195 were slightly lower than those of the 2219 over the whole range of temperatures (Fig. 4), the welding procedure and parameters established during the programme appeared to give consistent and reliable results which make this particular alloy very interesting for welded structures operating at temperatures down to LH_2 temperature.

CFRP material for tank

Scope

Composite materials have been considered as candidates for cryogenic tanks since the beginning of advanced space transportation system studies.

The selection of a CFRP material to be used in the manufacturing of reusable cryogenic tanks for future space transportation systems must be compliant with the following requirements:

> Light weight, retention of high specific strength and/or stiffness at required temperatures, oxidation resistance, hydrogen embrittlement resistance, compatibility with cryogenic hydrogen or oxygen, thermal cycling and thermal shock resistance, low creep, high fracture toughness and good fatigue properties.

On the other side general considerations have to be regarded such as:

> Availability of manufacturing facilities, quality and inspection procedures, reparability, reproducibility of process and cost.

In the case of the reinforcement, even though there are many different types of carbon fibres, there is a general agreement about which type of fibre is the most adequate for cryogenic tanks.

Intermediate modulus carbon fibre like IM7 or T800 offer an excellent balance between modulus and strength together with a high strain capability. That makes it possible to design a composite able to withstand the loads that will appear during the mission-life in the cryogenic tank.

The various resin systems:

> Tough epoxy, cyanate, polyimide, BMI, thermoplastics and liquid crystal polymers

have been evaluated against the following criteria:

> High and low temperature service, thermal and mechanical cycling resistance, toughness, processability, manufacturing facilities, reparability, availability, general data, cryogenic reference, compatibility with LH_2/LOX, GH_2/GOX.

The most adequate materials according to the a.m. points are cyanate and tough epoxy resins followed by thermoplastics.

Taking into account that no specific requirements have been made for the maximum working temperature, cyanate resins could be suitable candidates that offer a relatively high thermal capability together with a good microcracking resistance and standard manufacturing methods.

The material chosen for the characterisation is the carbon fibre IM7 with the cyanate thermoset matrix 954-2A delivered as a prepreg.

Summary of the results

The material selected was a cyanate ester matrix system with a intermediate modulus carbon reinforcing fibre: the 954.2A/IM7 from Fiberite. The physicochemical properties featured a fibre volume content of 60.2 with a void content of 2%. For the use at cryogenic applications the post curing of the material was deleted due to recommendations of the manufacturer.

Tensile properties at RT were below the expected values with higher ductility and lower strength due to the missing postcuring of the material. Tensile modulus and ultimate tensile elongation were in the scatter of the expected values. Compressive modulus properties agreed with the estimated one, showing low scatter and the strength is approximately 20% lower than the reference value.

The in plane shear properties reached an experimental mean value of 111 MPa determined with very low dispersion. No reference values were available. The interlaminar shear strength reference mean value was of 60 MPa, whereas 87 MPa has been obtained in this investigation. Residual strength properties at RT after thermal cycles produced a reduction of mean value around 9% and fatigue caused a reduction below 6%. Notch effect should be more carefully assessed. A reduction of 30% in strength was determined. Fracture Toughness characterisation in Mode I yielded to a mean value of G_{IC} of 714 J/m^2 and for G_{IIC} of 914 J/m^2.

Regarding compatibility with cryogenic fuels, ILSS tests after immersion showed almost no change in properties. As a preliminary assessment, 95402A/lM7 CFRP could be considered as compatible with LOX and LH_2 under the specific conditions considered in this program. A value of 3,6 x 10^{-9} mbar.l.mm/(cm^2.s.bar) or 3,6 x 10^{-14} m^2/s was determined for the permeability to GH_2. This permeability rate value was much lower than the value requested by the FESTIP-Structures Team by a factor 10^4!. On the basis of the results obtained, reactivity with oxygen is such that the materials can be used safely under a maximum temperature of 60°C and a maximum oxygen pressure of 20 bar.

At 20K, the ILSS was almost a 60% higher than at RT, and the compression strength was around 10 % lower. In plane shear properties showed a slight enhancement on strength with respect to room temperature results. No significant changes were seen in tensile properties (Fig. 5).

Residual strength properties were lowered in comparison with not aged specimen in the same way as for specimen tested at RT but not in the same extend.

A tough epoxy resin was selected as an alternative material (8552/IM7). Tests are on-going.

Structural Materials

Dispersion Strengthened Aluminium

Scope

Dispersion Strengthened Materials made by mechanical alloying (MA) are a promising new class of materials. The Dispersion Strengthened Aluminium (DS-Al), which is one of the most recent development of the MA materials. This material is produced by cryogenic milling in liquid nitrogen, creating a uniform distribution of dispersoids and a fine-grained microstructure. DS-Al derives its strength from the interaction between insoluble particles and dislocations and is based on the formation of small nanoscale aluminium-nitride (AlN) particles formed during the cryornilling process. These particles have significantly better thermal stability than precipitates in conventional alloys.

After extrusion or hot rolling, the grains are not significantly different from that of the hot pressed material, suggesting that the dispersoids are very efficient in pinning the grain boundaries. The uniform distribution of the AlN and small grain size make this material temperature stable with a tensile strength of 100-120 MPa at 450°C. The material exhibits creep properties at elevated temperature which are several orders of magnitude higher than for the conventional aluminium alloys. The threshold value is measured to be around 80 MPa. Further there is indication that a fatigue limit exists for this material.

Summary of the results

After measurement of the physical properties, tensile tests were performed on sheets, extrusions and friction stir welded material. The results at RT (appr. 370 MPa for extrusions and 330 MPa for sheet materials) were reduced to appr. 70 % of that value for 200°C and to appr. 40 % at 400°C. Welded materials showed only appr. 70 % of the tensile strength of the base material. Regarding the short-term creep properties for 0.1% strain value: 100h/150 MPa/200°C and 100h/100 MPa/300°C. Thermal cycling between 150°C and 300°C (100 cycles) did not affect the properties of DS-Al to a large extent. Fatigue tests were also carried out.

Friction stir welded material was conditioned for 100 hours at 400°C under oxygen or hydrogen atmosphere. The tensile strength of the material remained unchanged in comparison to the properties of the base material. However, the elongation showed a large reduction (from appr. 65 % to 15 % after the thermal treatment).

Fracture toughness values of the extruded material showed anisotropy when the T-L and L-T directions are compared. The T-L direction was 40 % reduced compared to the L-T direction (11 MPa $m^{0.5}$). At 300°C the values are reduced to appr. 4 and 5.5 MPa $m^{0.5}$. For sheet material, no anisotropy was found, mean values at RT were 29 MPa $m^{0.5}$ and appr. 10.5 MPa $m^{0.5}$ at 300°C. Salt spraying for 504 hours did not change to a visible extent the static properties from those of the base the material. Even for friction stir welded material, the measured values for conditioned materials are in the scatter of the base material properties. No SCC investigation was performed.

Comparison between DS-Al and other candidate metallic materials for primary skin applications

The specific strength of DS-Al is superior to conventional Al-alloys in the temperature range up to 450°C, but lower than the specific strength of Ti-6Al-4V.

CFRP

A BMI type is under investigation. Results are pending.

Elevated temperature applications materials and TPS

Intermetallics

Scope

Intermetallics is the short and summarizing designation for the intermetallic phases and compounds which result from the combination of various metals and which form a tremendously numerous and manifold class of materials. In particular, intermetallics that are of interest for application at elevated temperatures are compounds of high chemical stability, high melting temperatures, high elastic moduli and with a good resistance to space environment. Several classes of intermetallics are of interest for space applications: titanium aluminides (TiAl, Ti_3Al), nickel and refractory aluminides (NiAl, Ni_3Al, Nb_3Al, Ti_2NbAl, NiAlMo), titanium and refractory silicides (Ti_5Si_3, $NbSi_2$, $TiSi_2$, $MoSi_2$).

Marked improvements in alloy design, processing and properties of titanium aluminides have been achieved during the last few years which brought these intermetallic materials to the dawn of application, whereas nickel aluminides and refractory metal silicides have not yet reached this development stage. Among the titanium aluminides, the γ-TiAl based alloys are considered to have the highest potential for future aerospace applications. In consequence, γ-TiAl based alloys are of special interest as structural materials for hot skins and thermal protection systems and as matrix materials for intermetallic matrix composites (IMCs). Because of their high melting point, high elastic modulus, high specific strength even at elevated temperatures, good oxidation resistance, high resistance to hydrogen absorption and resistance against self-ignition, γ-TiAl based alloys are able to exceed the application temperature of advanced titanium based alloys and also to outperform nickel based superalloys in certain conditions. However for long term applications at temperatures exceeding 700°C, there is a need for a reliable oxidation protective coating. The maximum application temperature for coated/actively cooled components of γ-TiAl based alloys is expected to be around 950°C.

Two alloys have been selected to investigate the development of protective coatings: Ti-47Al-2Cr-0.2Si and Ti-48Al-2Cr-2Nb. Ti-47Al-2CR-0.2Si alloy corresponds to a group of γ-TiAl that exhibit good workability and after a suitable thermomechanical treatment, moderate room temperature ductibility as well as excellent superplastic properties. Ti-48Al-2Cr-2Nb represents the family of γ-TiAl based alloys that was developed to improved high-temperature capabilities, e.g. creep and oxidation resistance, and will be used as reference.

The following coatings were developed and investigated:

- Preoxidation in a SiO_2-pack
- Siliconizing with Ge-or B-additions by pack cementation
- Coating with glass by slurry-fusion-technique
- Chrome-aluminizing by pack cementation
- Nickel-electroplating with subsequent Al-pack cementation
- Coating with a layer of CoNiCrAlY or NiAl by atmospheric plasma spraying with or without a diffusion barrier beneath

Eventually, after preliminary tests, only the last three were selected as the most promising.

Isothermal oxidation tests in static air have been conducted at 700°C, 800 and 950°C for times up to 670 h. In addition, cyclic oxidation tests were carried out between 200°C and 950°C, 100 cycles. Exposure to hydrogen was tested. Inspection and residual strength measurements were performed.

Summary of the results

Three coating systems: Al/Cr by pack cementation, Ni electroplating plus Al pack cementation and CoNiCrAlY by Atmospheric Plasma Spraying (APS), were selected from the larger variety of coating systems investigated originally.

All three oxidation protective systems significantly improved the oxidation resistance of the less oxidation resistant alloy Ti-47Al-2Cr-0.2Si at temperatures up to 950°C. The behaviour can be summarised as follows:

Under isothermal oxidation tests at 950°C for 168 h, all three systems showed fair oxidation protective effects. At 800°C for periods up to 672 h, the systems Ni/Al and CoNiCrAlY were very well protective.

With cyclic oxidation tests between 200°C and 900°C for 100 cycles, the systems Al/Cr and Ni/Al provided good, and CoNiCrAlY fairly good protection.

The mechanical properties of the inherently less oxidation resistant alloy Ti-47Al-2Cr-0.2Si were influenced by the coatings:

- The pack cementation lowered room temperature strength and ductility, but upon subsequent oxidation there was no further degradation.
- The CoNiCrAIY-coating, which is inherently more ductile but less protective, only slightly lowered room temperature strength and ductility, but significant degradation appeared after long oxidation time.

Further optimisation should concentrate on the improvement of the CoNiCrAIY-coating.

Oxidation protection of refractory metals

Scope

Due to their high melting points and their high creep resistance, refractory metals (RM) are candidates for many high temperature aerospace components, in particular for propulsion systems. The use of RM is, however, often limited by inadequate room temperature properties, lack of oxidation resistance at elevated temperatures or difficulties associated with joining or welding. The goal of the present study is to provide technical solutions for the oxidation protection of selected RM alloys and to demonstrate full functionality of oxidation protected refractory metal alloys after iso and cyclic thermal oxidation exposure up to 1600°C in air.

A survey of refractory metals and alloys as well as coating concepts was performed. From each group of materials, one alloy was selected for further investigation.

The following alloys were selected for this research (all compositions are given in wt %):

- Cb752 (Nb10W2.5Zr)
- Ta10W
- TZM (Mo0.5Ti0.08Zr0.03C)
- Mo41Re

Every alloy represents a given class of alloy and is used currently for aerospace applications. They feature outstanding mechanical properties in the intended temperature range and show good processing characteristics.

Five different coating systems were selected:

- Si20Cr20Fe
- Si10B2C
- Al_2O_3 / Si20Cr20Fe / Al_2O_3
- Mullite / Si20Cr20Fe / Al_2O_3
- HfO_2 / Si20Cr20Fe / Al_2O_3

The last three were triplex coating systems on the basis of Si20Cr20Fe combined with oxide diffusion barriers and containment layers (Fig. 6).

The Si20Cr20Fe coating was deposited on all four substrates as a baseline. For each substrate two coating systems were tested. The RM cylindrical samples were coated using APS (Atmospheric Plasma Spraying) process.

Several RM alloys and coatings combinations were tested in isothermal oxidation tests (800°C and 1400°C), cyclic oxidation tests at 800°C and 1300°C, and long isothermal oxidation for 20 h / 1400°C / in air. The residual mechanical properties were evaluated.

Summary of the results

The isothermal oxidation tests at 800°C and 1400°C gave reasonable results only with the monolayer coatings. The multilayers coatings showed premature failure due to spallation of the sandwiched layers. Multilayers coatings were deleted from further research due to this reason.

The number of cyclic oxidation tests cycles to failure at 800°C and 1300°C was above 100 for the combinations: Cb752 / Si20Cr20Fe and TZM/ Si10B2C and limited to 800°C for the Ta10W / Si20Cr20Fe. The other metal / coating combination showed beginning of oxidation of the coated metal after around 20 cycles.

The mechanical properties were in general not critically affected by exposure to air at 1400°C for 20 hours. The yield strength decreased approximately by 4 to 6%. The elongation to rupture of SiBC coated TZM showed a large decrease to appr. 2 % from 32 %. The reason for this embrittlement is unknown and needs further investigation.

The implementation of diffusion barriers in order to de-couple base material and coating as well as the containment concept, i.e. an outer oxide layer to separate the coated refractory metal component from its structural counterparts, should be investigated. Feasibility checks will be required concerning the compatibility of the oxidation-protective coating with the contacting materials (C/C, C/SiC, ceramics).

Dispersion strengthening of niobium alloys

Dispersion strengthening was applied to niobium alloys in order to improve their high temperature behaviour. Based on the niobium alloy C103 (Nb-10Hf-1Ti) the influence of oxide and carbide additions on the properties were investigated. The dispersoids used in the programme were:

HfO2, TiO2

HfC, NbC, TiC

The mechanical properties of the different alloys were tested on cold-rolled and annealed sheets with a thickness of 2 mm and 1 mm, respectively. In the annealed condition the tensile strength in the temperature range from 20°C up to 1500°C was determined. Furthermore the recrystallization behaviour and the creep strength at 1300°C were evaluated. The test results were compared to the I/M C103 alloy.

The DS niobium alloys developed in this program featured no significant tensile strength improvement compared to the C103. The creep strength of the investigated alloys was lower than the literature values for the niobium alloys C103 and Cb 752.

The results indicate that there is still considerable potential to improve the material properties of the investigated alloys:

- For improvement of tensile strength the size and distribution of dispersoids in the starting powder mixture must be improved using complex doping methods like mechanically alloying or chemical doping. Also the sintering parameters must be improved with regard to stabilisation and/or formation of oxides and carbides during sintering. Additionally, optimising the sintering parameters must control the degassing behaviour, possibly by usage of controlled sintering atmospheres.
- For long-term applications, optimisation of the size and distribution of dispersoids can improve the creep strength on one side. On the other side the effect of heat-treatments and ageing cycles on creep properties must be investigated to fully exploit the potential of DS niobium alloys.

Reinforcements of refractory metals

Refractory metal alloys are candidate materials for hot skin and propulsion applications of RLV, but the high density of the material results in low specific properties. Besides solution-, dispersion- and precipitation strengthening, one promising approach to overcome this problem and to increase the specific strength and the creep rupture strength of refractory metal alloys is to make use of reinforcements.

Several reinforcement possibilities were assessed during the programme: reinforcement using long and short fibres and sheet co-lamination

Long fibres reinforced niobium

Niobium sheets were stacked with W26Re wires and HIPed. The wire distribution in the Nb matrix was very uniform with diffusional bonding at the interface fibre/matrix. The yield strength of the composite was enhanced by factors of about 4 at RT and about 6.4 at 1300°C. Thus, even taking in account the higher density of the composite (10.6 g/cm^3 in comparison to 8.5 g/cm^3 for Nb), the specific strength exceeds by far the one of the niobium. The fracture elongation at RT is decreased to about 27 %. At 1300°C, no significant decrease of fracture elongation for the reinforced samples was found. The steady state creep rate was derived from the elongation-time curve after 5 hours of creep testing to about 8.5. 10^{-7} s^{-1}.

Short fibres reinforced niobium

Nb powder was blended to short fibres of Al_2O_3,CIPed, HIPed and rolled. The fibre distribution in the samples was uniform and the voids content was low. The RT yield strength of the reinforced samples was higher by a factor ca. 2.5 at RT and by a factor of 4.5 at 1300°C. The fracture elongation was lowered by a factor of 6.5 at 1300°C. The creep rate was reduced at 1300°C by approximately 23% in comparison to standard niobium.

Niobium laminates reinforcement

Nb sheets were PVD coated with a few µm of ZrO_2, stacked, canned, HIPed and some were eventually rolled. Mechanical properties of laminated samples were depending to a large extent from the HIPing conditions and the thickness of the reinforcing ZrO_2 layer. The yield strength was enhanced by the reinforcement by a factor of up to 3. The rolled variants exhibited strength values that are lowered by 10-20% compared to those of the HIP-compacted laminates, as well as a somewhat lower elongation. The steady-state-creep rate at 1300°C was reduced by a factor of about 60 by means of lamination. The improvement for the rolled variants was only a factor of 20 to 40.

A next step in the investigation will be the replacement of the Nb matrix material with alloys like the C103 or the Cb752, and to check the suitability of the oxidation protection systems developed in this programme with the Nb.

Oxidation protection of CMC materials

Scope

The realisation of Reusable Launch Vehicles will require thin-wall structural elements that will be heavily loaded under high temperature and different environmental and pressure conditions. In order to realise low masses for these parts, only materials with low density and high specific strength are acceptable.

As far as a temperature range of 1200°C is exceeded, C/C and C/SiC materials become candidates for this application. In the slightly lower temperature range, SiC/SiC may also be an interesting alternative.

For the manufacturing of the fibre-reinforced silicon carbide, four main processing families can be identified:

- gas infiltration process
- liquid phase infiltration/prepreg technology
- liquid silicon impregnation process
- solid state hot processing/sintering

The various production routes applied for CMC show very specific features. Therefore it depends very much on factors like:

parts complexity design
max. temperature and thermal load
degree of reusability/service intervals
mechanical properties
environmental conditions
preferred kind of material and production route

In this programme, the CMC will be processed according to the following routes:

LSI - liquid silicon infiltration
LPI - liquid polymer infiltration
LPI/CVI - liquid polymer/chemical vapour infiltration

and will be manufactured by DLR, DASA and MAN.

The application of C/SiC in oxidising atmosphere is restricted to temperatures lower than 500°C. At higher temperatures degradation of the mechanical properties occurs by the oxidation of the carbon fibres and of the fibres/matrix interface. To solve out this point, a surface multicomponent oxidation protection was already developed. However the concept of a surface thermoviscous coating is not suited for applications with contact surfaces and/or submitted to a high pressure/velocity gas flow. In such conditions, the thermoviscous coating of the outer glass-layer flows through the natural micro cracks of the matrix, opened under mechanical loads, and oxygen comes into contact with the carbon fibre matrix interfaces and damages them.

Based on a LPI matrix and CVI densified C/SiC material, two concepts of coatings were investigated (Fig. 7):

- The internal protection with inner sealing of the C/SiC pores by infiltration of thermoviscous material, the application of an interlayer between substrate and outer coating and finally the cover layer, consisting from CVD deposited SiC
- The sandwich coating concept with the deposition of a primary CVD SiC coating, the application of an intermediate layer, consisting of glassy components with refractory components and oxygen getters and the cover layer again by applying a CVD SiC coating process.

The tests performed to evaluate the efficiency of the coatings focused mainly on mechanical tests in the temperature range from 700°C to 1500°C:

Static ageing in air (40 h at 700°C to 1300°C) and determination of the residual bending strength at RT and -196°C
ILSS at RT hot bending strength at 1500°C
Thermal cycling in air from RT to 1000°C (50 x 30 minutes dwell time) and from 800°C to 1300°C (25 x 60 minutes dwell time) and determination of the residual tensile strength
Bending creep (20h with 150 MPa from 700°C to 1500°C)
Long term stability (100 h) in hydrogen at 700°C and 1400°C
Environmental tests in the M3 combustion chamber, the fast flow reactor and the plasma wind tunnel (see next paragraph)

Summary of the results

The concept of internal oxidation protection was stopped after the first mechanical tests. The material used to fill the pores destroyed the structures and the materials of the composite, resulting in very poor mechanical properties. The work was then focused on the sandwich coatings.

The mass loss for all testing conditions was very low excepted for the testing at 700°C. This temperature was too low for self healing effect of the viscous glass. All mechanical tests performed after ageing at this

temperature showed a dramatic reduction of the properties of the material.
Mechanical properties, after ageing at higher temperatures were reduced to appr. 10 to 20% compared with the not aged materials, showing the very good performance of the coatings at these temperatures.
Ageing under mechanical stress showed residual bending strength reduced to appr. 400 MPa from appr. 770 MPa, after 20 hours of exposure at 1000°C and 1500°C as well.
Ageing in hydrogen atmosphere showed no change in mass and in the bending strength of the specimen. After exposure at temperatures of 1400°C, a mass loss of appr. 16% was measured. The bending strength reduced to 50% of the previous strength.
Hence, the effectiveness of the oxidation protection in the low temperature range ($\leq$ 750°C) must still be improved.

Behaviour of CMC and C/C materials in propulsion and re-entry environments

Scope

The Vulcain engine thrust chamber is qualified for 20 missions and 6000 seconds total run time. The target for reusable launcher engines is 50 missions at roughly 500 seconds burn time each. In general, various tough requirements are imposed to materials used in the propulsion area. The materials in the nozzle have to withstand high temperatures, high gas velocities and have to be inert against hot gases. These gases are partly dissociated meaning that they are very reactive against the nozzle wall materials. In some parts of the nozzle compartment, a reducing atmosphere (fuel rich) exists, while other segment have to withstand an oxidising (oxygen rich) environment. The cryo engine needs large LOX/LH2 plug nozzle parts. The lightweight hot skin structures required around the exhaust area of the propulsion system are exposed to high thermal loads. Similarly, the intake area of airbreathers is also heavily thermally stressed due to the kinetic heating.
Current materials for the realisation of such structural parts are C/SiC and C/C. However suitable oxidation protection layers have to be applied to sustain the long term oxidative environment.
The programme investigated the principal properties and reusability of CMC under the relevant combustion and re-entry conditions. Substrate materials LSI C/C-SiC (DLR), CVI C/SiC (MAN), LPI C/SiC (DASA, MAN) and C/C as reference were evaluated as coated and uncoated.

The samples were tested in the following facilities:

- Fast flow reactor (FRP), exposing specimens to a well defined concentration of high reactive particles (e.g. radicals)
- M3 combustion chamber, simulating realistic hydrogen-oxygen combustion conditions: pressure, chemical environment, mass flow rate and temperature.
- Plasma wind tunnel (PWK) where the samples were tested under hydrogen-oxygen combustion conditions in a low pressure environment as well as with re-entry environmental conditions.

The testing conditions were as follows:

Fast Flow Reactor:

Temperature:	1000-1100°C
Pressure:	10^{-5} MPa
Duration:	2 - 3 hours
Environment:	H_2O, H_2, OH, H

M3 Combustor:

Temperature:	1600-2000°C
Pressure:	0.2-0.4 MPa
Duration:	10-15 seconds
Environment:	H_2/O_2- mixtures

Plasma Wind Tunnel (propulsion environment):

Temperature:	1600-l 800°C
Pressure:	1-7. 10^{-3} MPa
Duration:	appr. 5 minutes
Environment:	H_2, H_2/O_2-mixtures, H_2/air

Plasma Wind Tunnel (re-entry environment):

Temperature:	1300-1400°C
Pressure:	5. 10^{-4} MPa
Duration:	20 - 25 minutes
Environment:	air plasma

Summary of the results

Fast Flow Reactor: the reaction products were detected on-line by a mass spectrometer. For all the samples, the tests featured a catalytic recombination of OH on coated surfaces giving O_2 and H_2; a corrosion of SiC by H_2O and H_2, yielding to CH_4+Si, and a reaction of C with the OH radicals, producing CO.
M3 Combustor Test Bench: the specific mass change of the samples tested was quite low for nearly all the samples. Coated samples seemed to get a lower thermoshock resistance compared to the non-coated samples.
Plasma Wind Tunnel (propulsion environment): corrosion of SiC as previously noted for the FFR tests.
Plasma Wind Tunnel (re-entry environment): all coated samples showed a low specific mass loss. Adequate oxidation protection for all coated samples at 1300°C / 20 mn was observed.

The tests performed showed no restriction for using C/SiC materials at temperatures above 1600°C in oxidative atmosphere. However, for reusable vehicles the carbon fibres have to be protected from oxidation and from chemical environments like the hydrogen-oxygen combustion flow coming from the propulsion gases (Fig. 8). The silicon carbide matrix is damaged by hydrogen. The coatings have to be adapted to these special propulsion environments.

High temperature materials for sliding applications

Scope

Lubricant materials might be used in reusable launch vehicles for special applications in the propulsion system like bypass duct or movable hot structures (e.g. body flaps). Currently, these critical parts - specifically sleeve and roller bearings, hinge joints - are designed in such a way that they are located in a cold area, because the operating temperatures of such critical components are far below the surface temperatures of the hot structures. Today the realisation of hypersonic engines and lifting bodies requires hinge joints (e.g. for air-intakes or body-flaps) which must be operated at temperatures up to 1600°C in air with a compact and light design.

Conventional liquid lubricants are unsuitable for use above approx. 200°C and solid lubricants and solid lubricant coatings cannot be used above 1000°C. Consequently, suitable substrates, lubrication mechanisms and coatings have to be developed in order to fulfil these extreme requirements.

Mainly, four main dry lubricant mechanisms have been assessed with respect to suitable material combinations:

- Tribo-oxidative formation of lubricous oxides
- Incorporation of intrinsic solid lubricants in a matrix
- Transfer film formation
- Vapour phase lubrication

For a first selection of materials usable as high temperature lubricants, a screening test was performed using different material combinations of coating materials on C/SiC base material. The high number of promising coating combinations selected theoretically has been reduced by simple and quick tests, in which only the adhesion-behaviour of the coating combinations under load (thermal and mechanical, but no sliding) has been investigated. The following four tribo-coating combinations showed promising results:

- SiC - SiC
- SiC - hex. BN
- SiC - (C+$AlPO_4$)
- SiC - ZrO_2

A complete hinge joint prototype has been designed, manufactured and tested successfully up to 1600°C in air and under mechanical loads to show up feasibility and functionality, whereas all components of the hinge joint have been manufactured of C/SiC material that was coated by a CVD-SiC layer.

Suitable measurement equipment has been developed in the frame of the FESTIP programme. This facility is able to measure wear and friction of selected material combinations in sliding contact in rotation up to 1600°C in air.

Summary of the results

So far, the following coating have been tested up to 1400°C in air:

Combination SiC-SiC: The wear scars and tracks exhibited tribo-oxidation accompanied with a strong wear particle adhesion. The coefficient of friction was within the targeted range, but the wear rate was at least two orders of magnitude too high.

Combination SiC-hex. BN: Hexagonal boron nitride forms B_2O_3 by oxidation, which evaporates and condenses in colder regions of the test rig. The wear coefficient of the stationary BN-sample was unexpectedly high. However, the coefficient of friction of the hex. BN-SiC couple is attractive.

Combination (C+$AlPO_4$)-SiC: The carbon impregnated with $AlPO_4$ is unsuitable for the application as hot hinge joint, due to the evaporation of the $AlPO_4$ around 1200°C - 1350°C, and indeed cannot protect the carbon against oxidation anymore.

Combination ZrO_2-SiC: A stationary SiC sample (bearing shell) mated with a rotating ZrO_2 sample (bearing shaft) exhibited no detectable wear during this test. The coefficient of friction was overall low for this couple, result which maybe correlated with the adhesion tests performed by DLR. However, some problems with the adhesion of the ZrO_2 on the SiC base materials were found.

All coating combinations have low coefficients of friction and the hinge joint manufactured with the last combination would not fail by adhesion (welding of coating layers together)

Tests up to 1600°C are in progress.

High reflective Internal Multilayers Insulation screens

Scope

The development work for the highly reflective IMI screens started with the HERMES program. Together with the C/SiC shingle, IMI was the main insulation and part of the Rigid External Insulation concept, considered for the spaceplane lower surfaces and the cabin area.

The development of the IMI insulation elements, i.e.:

- the reflective and high temperature resistant screens
- the ceramic fibre felts, to stack the screens together and
- the ceramic fabric bag for the assembly

was finished and the assembly was tested under realistic thermal and vibro-acoustic conditions

However, the internal multiscreen reflective foils for the FESTIP will be used at a more elevated temperature range and during a longer exposure time compared with the HERMES programme component requirements. Depending on the application temperature for the screens, gold and platinum were used for the noble metal reflective coating. For thermal stabilisation of the reflective coatings, intermediate and cover layers on the basis of oxides were used. This allowed the long-term application of those screens on gold-basis up to 1000°C and for screens with platinum coatings up to 1300°C. However, this type of a very thin platinum coating was optimised with respect to a short-term application and extremely low mass requirements. Therefore the main task of this programme will be the improvement towards higher temperatures and longer exposure time of a reusable coating.

The activities to reach this target were as follows:

- Increase of the reflective noble metal coating thickness,
- Development of improved intermediate and cover layers for the platinum-based noble metal coating, i.e. Pt coated with various types of intermediate layers and Pt-alloys,
- Variation of the evaporation temperatures (PVD process) for noble metal covers and intermediate layers.

Various physical and thermal tests were carried out to assess the improved IMI.

Summary of the results

The new IMI featured:

- Increase of the noble metal layer thickness,
- Intermediate and cover layers of Zr, Ti, Ta and Al oxides
- Pt-alloys usage like Pt/Rh, Pt/Ir and Pt /Au
- Optimisation of the PVD coating parameters

Eventually, an IMI able to sustain 1700°C during 17 mn in air, with an emissivity lower than 0.45, was successfully tested. It consisted of 1000 nm Pt screens with an Al_2O_3 covers weighting 86g/cm^2.

CONCLUSION

This presentation is a summary of the various studies dedicated to RLV machines and undertaken since four years in the field of materials by a leading team of European industries under the leadership of ESA. A preliminary answer to the question "Does the material technology to build a RLV already exist, and if not, is it within reach?" is given. The FESTIP programme is now running up to the beginning of 2000 and will find a continuation in the FLTP programme.

Acknowledgement

The paper reflects the varied fields of expertise of the colleagues from European industry and research institutes that fruitfully contributed to this programme and to whom the authors are thankful. This programme was funded under ESA contract No. 11483/95/NL/FG.

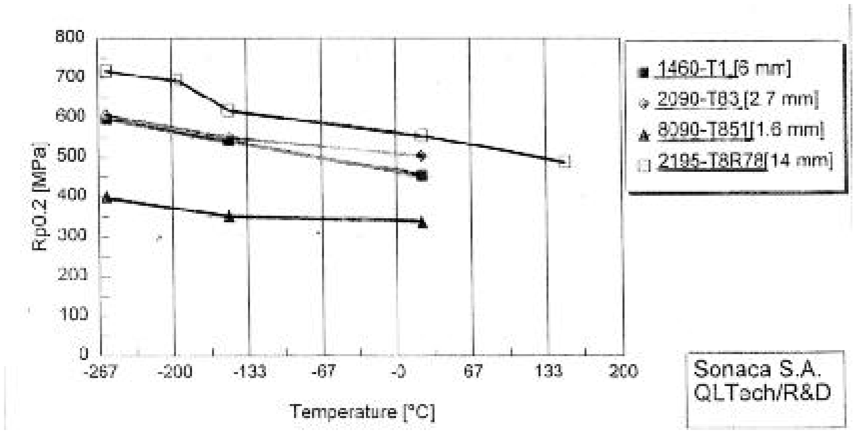

Fig. 1 – Average specific tensile yield strength values of various Al-Li alloys

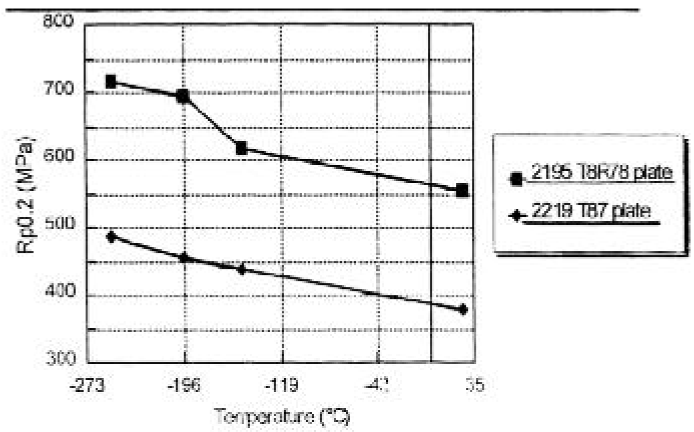

Fig. 2 – Comparison between Al-Li 2195 and conventional Al 2219.
Average yield strength values L and T

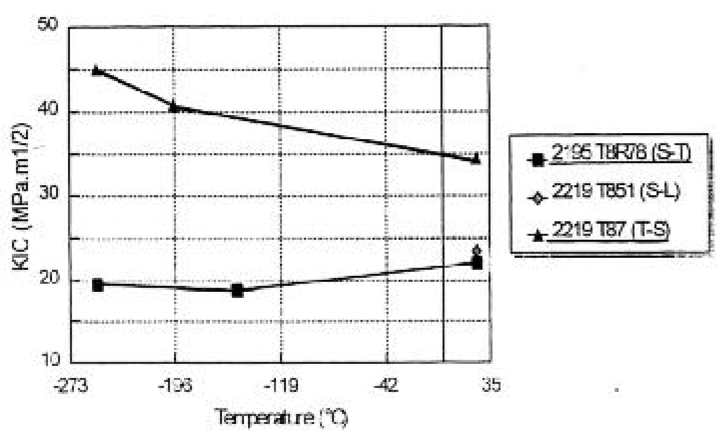

Fig. 3 - Comparison between Al-Li 2195 and conventional Al 2219.
Fracture toughness values

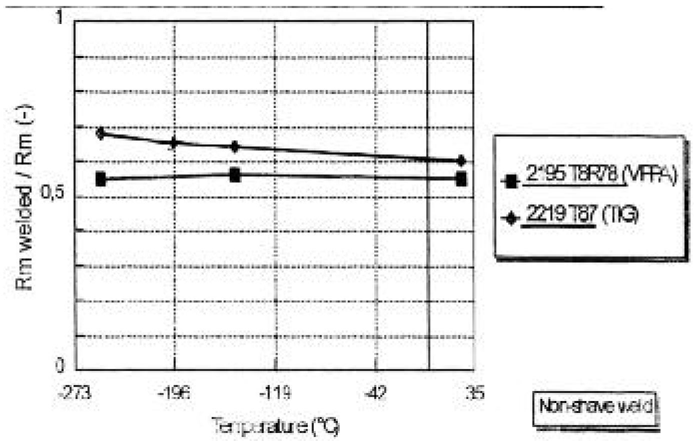

Fig. 4 - Comparison between Al-Li 2195 and conventional Al 2219.
Joint coefficient values

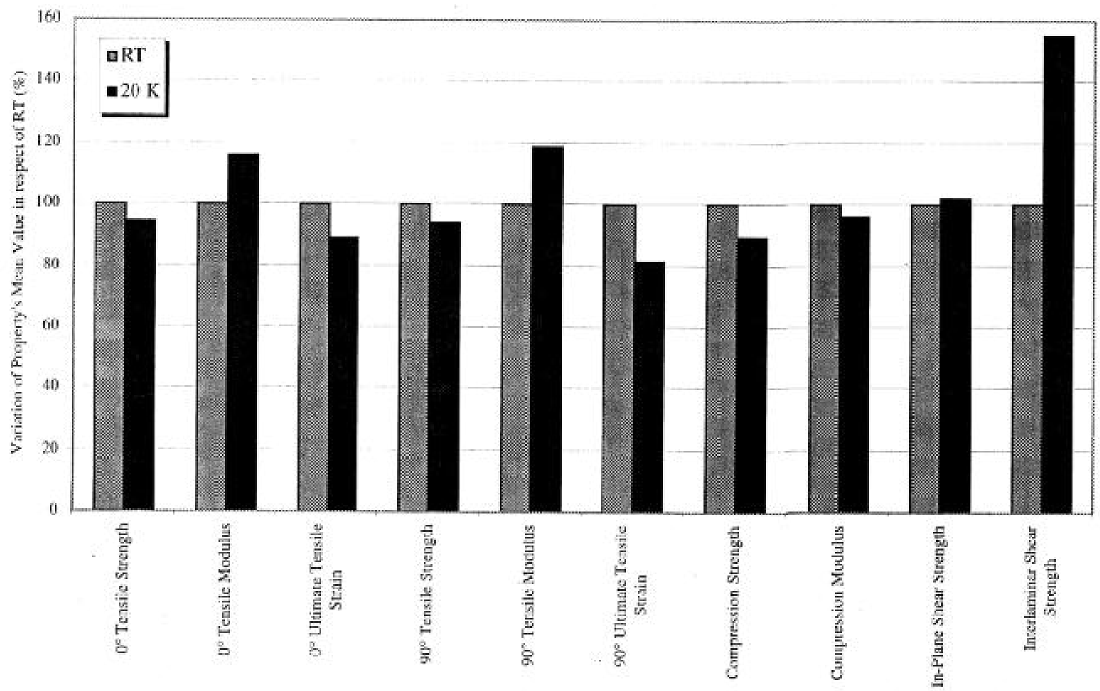

Fig. 5 – CFRP 954-2 / IM 7 UD - Comparison of mechanical properties at 20K and RT

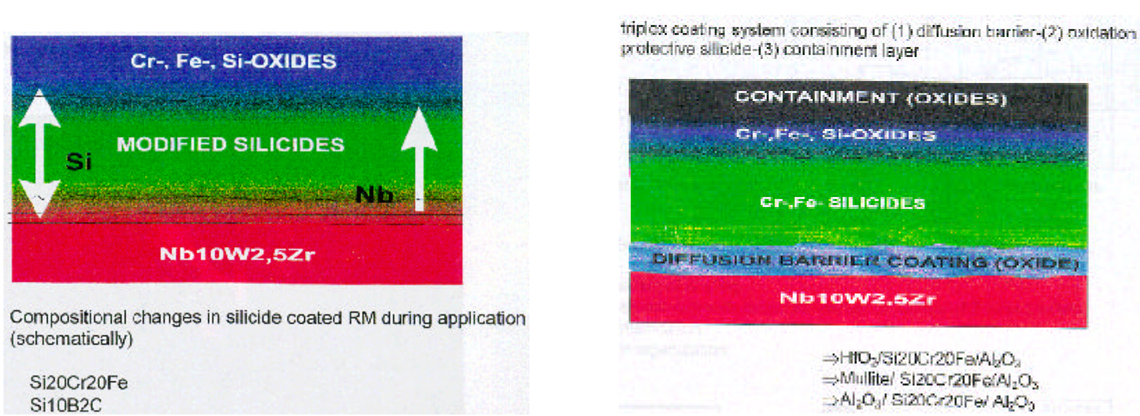

Fig. 6 – Monolayer coating (left) – Composition variation after high temperature exposure in air
Multilayers coating (right) – Composition variation after high temperature exposure in air

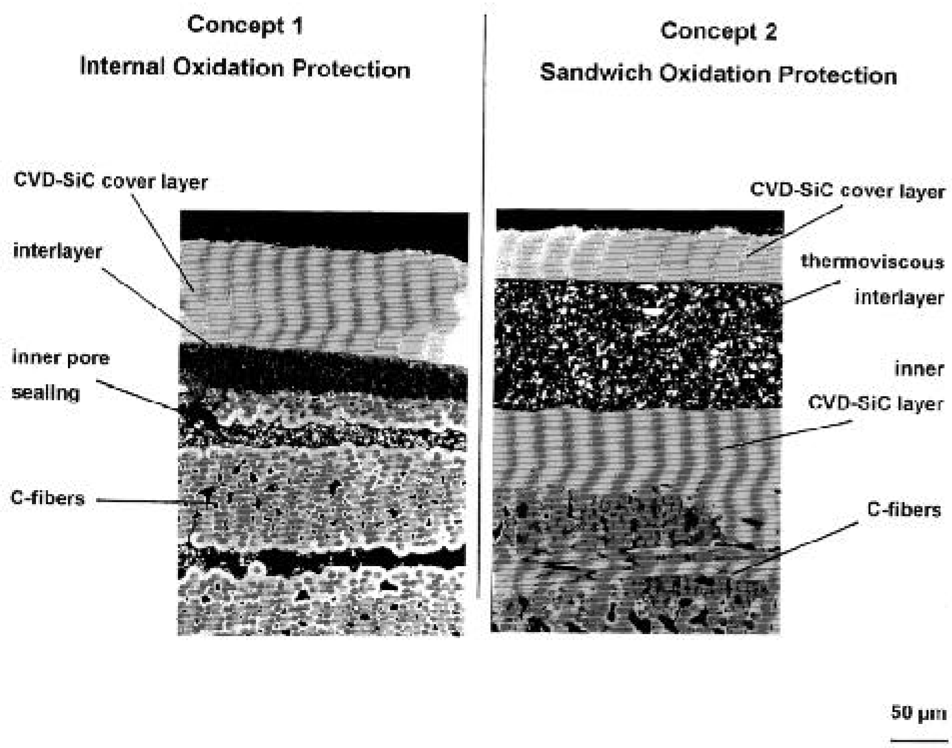

Fig. 7 – Oxidation protection systems developed. The left one was not promising as expected.

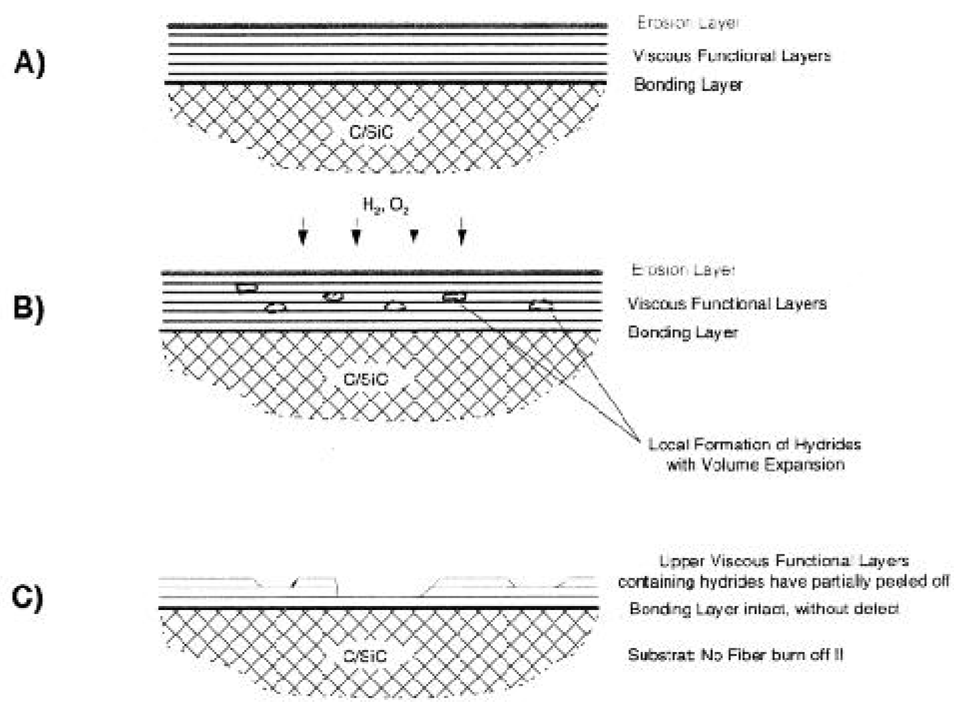

Fig. 8 – Tentative interpretation of the degradation of a multilayers CMC coating.