SPECTRAL EMISSIVITY OF UHTC COATINGS FOR SUPER LIGHT-WEIGHT THERMAL PROTECTION SYSTEMS OF SPACE RE-ENTRY VEHICLES

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ABSTRACT

A test campaign was performed in the GHIBLI arc jet facility in the framework of the European funded LIGHT-TPS project, devoted to research and development of Ultra-High Temperature Ceramic (UHTC) coatings on Ceramic Matrix Composites (CMC) for super light-weight Thermal Protection Systems (TPS) of space re-entry vehicles.

Two UHTC coatings made of different zirconium diboride (ZrB_2) compositions, ZrB_2-3SiC-5WC and ZrB_2-20SiC-10AlN, were tested with the aim of increasing the oxidation resistance of the Carbon/Carbon (C/C) CMC substrates. In particular, four UHTC coated flat disks of 20 mm of diameter were exposed to an hypersonic jet of plasma composed of air and argon for a total duration of 5÷6 minutes, achieving a maximum surface temperature of 1800÷2000°C at stagnation pressures of 23÷25 mbar. The UHTC coating made by ZrB_2-20SiC-10AlN survived the tests forming an oxidized surface layer.

Three different pyrometers have been used to measure the surface temperature in the disk stagnation area. During the tests, one pyrometer was repeatedly switched from dual-color to single-color mode in order to evaluate the experimental emissivity of the surface at different temperatures. At the end, the measured spectral emissivity values at the wavelength λ_e= 1 µm varied between 0.6 and 0.5 for ZrB_2-3SiC-5WC coating in the range 1750÷1800°C and between 0.6 and 0.4 for ZrB_2-20SiC-10AlN one in the range 1700÷2000°C.

1. LIGHT-TPS PROJECT UHTC COATINGS

LIGHT-TPS, Super Light-Weight Thermal Protection System for Space Application [1], is an EU FP7 project aimed to develop a new super-light complex Thermal Protection System (TPS) for various space applications, above all for Reusable Space Systems (RSS), capable of operating within the entire range of working temperatures.

The main challenge of the project was to develop a super-light, corrosion and oxidation resistant TPS by combining the advantages of metallic and ceramic materials in a single system. For these purposes the project combined principle advantages of new metallic and ceramic materials in a single thermal protection system by the combination of metallic and non-metallic materials (e.g. C/SiC and C/C) and construction elements made of UHTC and heat resistant alloys, coated by composites on the basis of UHTC.

LIGHT-TPS systems based on non-metallic structures aim for operation temperatures surpassing 1600°C. Hence, highly refractory ceramics and coatings on its basis for the thermal protection of ceramic composites substructures, C/SiC and C/C, were developed. In addition, the possibility to apply a graded metal-UHTC layer on Nb base substrates for oxidation/erosion protection was explored.

As a reference for the development of UHTCs the project used the heating distribution environment and pressure in the nose cap of the re-entry vehicle X-38, with a similar trajectory to those of Space Shuttle, Buran, Hopper and Hermes.

During the project, alternative atmospheric thermal spray depositions processes were investigated, leading to homogeneous and dense UHTC coatings based on ZrB_2-SiC-WC, ZrB_2-$MoSi_2$ and ZrB_2-20SiC-10AlN. These UHTC compositions were selected on the basis of particular thermo-mechanical properties achieved by the corresponding bulk ceramics [2] [3] [4].

2. LIGHT-TPS PROJECT ACTIVITIES IN GHIBLI

A test campaign was successfully performed in the hypersonic facility GHIBLI for the German Aerospace Center DLR in the framework of the European funded LIGHT-TPS project.

In particular some UHTC coated cylindrical samples were exposed to an hypersonic jet of plasma composed of air and argon, achieving very high surface temperatures.

Two UHTC coatings made of different zirconium diboride (ZrB_2) compositions were tested in GHIBLI with the aim of increasing oxidation resistance of the Carbon/Carbon (C/C) CMC substrates.

In particular, the tests regarded the arc-jet response of two UHTC coatings, ZrB_2-3SiC-5WC (A type sample) and ZrB_2-20SiC-10AlN (B type sample), applied onto a C/C substrate.

3. THE GHIBLI FACILITY

GHIBLI is a hypersonic high enthalpy arc heated continuous facility [5] for the development of experiments on models of little size. It is particularly well suited for TPS material samples characterization.

The hot flow is generated in a 2 MW segmented arc heater. Inside the arc heater column the subsonic plasma flows to the converging–diverging nozzle and it is accelerated to hypersonic speed.

The nozzle has a throat section diameter of ~10 mm, a diverging half angle of 15°, an exit section diameter of ~150 mm and is cooled by demineralized water.

The GHIBLI test chamber is a steel cylinder of 1800 mm inner diameter and 2000 mm length. The plasma jet axis is transversal and displaced respect to the longitudinal axis of the chamber (see Fig. 1).

Fig. 1: GHIBLI Facility

In the test chamber, the interaction between the flow and the model surface occurs, then the plasma is convoyed in the diffuser pick-up. The test chamber walls are not cooled and are equipped of visual ports for the application of optical instruments such as pyrometers, IR cameras, video cameras, spectroscopy and Schlieren systems. Ports are distributed along the test chamber walls for the pressure measurements or electric connections to other devices.

After the flow static pressure is recovered into the diffuser, a heat exchanger cools down the high temperature plasma. A vacuum system provides the proper suction during the facility operation.

4. SAMPLES DESCRIPTION

The samples tested in this investigation were two type A and two type B with a flat disk shape of 20 mm of diameter (see Fig. 2).

Coatings were deposited using a Shrouded Plasma Spray (SPS) system. The SPS system consists of a commercial atmospheric plasma gun (F4MB from Oerlikon Metco) that has been modified to introduce an inert N_2 shroud mantel. Prior to UHTC coating deposition, CMC substrates were ultrasonically cleaned in ethanol, dried and pre-heated with the plasma torch to about 150÷200°C in order to improve the coating adhesion to the substrate. No mechanical pre-treatment has been implemented.

All the samples were installed through their cylindrical tail onto a hollow alumina pipe, part of a dedicated sample holder mounted on board the Model Support System (MSS) of the GHIBLI facility.

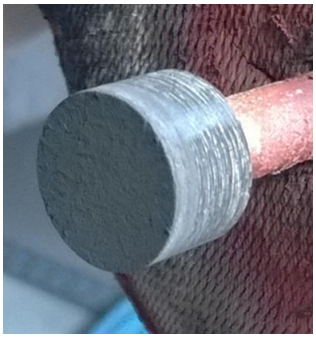

Fig. 2: Pre-test image of sample B2

5. TEST INSTRUMENTATION

Three different pyrometers (see Table 1) have been used to measure the surface temperature in the sample stagnation area (see Fig. 3).

They are the IGAR-12LO (named P300) and the ISQ5 (named P800) of IMPAC manufacturing, and the M77S (named M1000) of MIKRON manufacturing.

The P300 and P800 are dual/single-color (DC/SC) pyrometers, whereas the M1000 operates only in dual-color (DC) mode. The dual-color mode allows to

measure the surface temperature independently from the material surface emissivity, instead the single-color mode requires an emissivity value as input. When the pyrometer P800 was operated in single-color mode, it was set an emissivity of 0.80.

During all the tests the pyrometer P300 has given useful information only during the heating and cooling phases since in steady state conditions the temperature was always out of its measurement range, i.e. higher than 1000°C.

Tab. 1. Pyrometers used in the LIGH-TPS test campaign

Pyrometer	Operative Mode	Range [°C]	Wavelength [µm]
P300	DC/SC	300-1000	1.52-1.64
P800	DC/SC	800-2500	0.9-1.05
M1000	DC	1000-3000	≤ 2

Fig. 3: Pyrometers spot at sample B2 stagnation point

6. TEST PROCEDURE AND CONDITIONS

During each test, the arc-heater was ignited and driven to the planned set point in terms of current level and gas flow rate. The tests have been executed with a mixture of Air and Argon in a mass ratio variable between 3.7 and 3.5, except for sample A2 test where it was variable between 6.0 and 3.7. Once the hypersonic plasma jet was well established, the Probe was injected (see Fig. 4) and the test conditions were qualified in terms of stagnation heat flux and pressure. The facility Probe is a copper hemisphere, 100 mm diameter, water cooled, instrumented with gardon gauge and pressure tap to measure heat flux and pressure at the stagnation point.

Then, the Probe was removed and the sample was injected in the plasma jet such that its stagnation point was at the same axial position of the Probe one.

Finally, the plasma was shutdown and the sample was left in vacuum in order to monitor its temperature via pyrometers during the radiative cooling phase before the test chamber re-pressurization.

Fig. 4. Probe in plasma jet during sample A2 test

In Table 2 and Table 3 the summaries of the test and sample conditions are reported, respectively, including the maximum measured temperature and the test duration from jet center-line achievement to plasma shutdown (dashed data indicate not measured or transient values).

Tab. 2: Test conditions summary

Test	$\dot{q}_S$ [kW/m^2]	P_S [mbar]	m_{Air}/m_{Ar}
A2	1895->-->-	25.0->-->-	6.0->-->3.7
B2	1620->-->-	22.9->-->-	3.7->3.7->3.5
A1	1260	22.8	3.5
B1	1240	22.7	3.7

Tab. 3: Sample conditions summary

Test	T_{max} [°C]	Duration [s]
A2	2123->-->1849	54->268->50
B2	1721->-->1988	109->129->89
A1	1809	302
B1	1949	303

7. TEST RESULTS

Table 4 reports sample A2 test main parameters and Fig. 5 shows sample A2 in plasma jet.

Tab. 4: Sample A2 test data summary

Test ID	P_0 [bar]	m_{Air} [g/s]	m_{Ar} [g/s]
GHI-DLR-141A	1.99	9.10	1.52
GHI-DLR-141B	1.97->1.89	9.10	1.73->2.26
GHI-DLR-141C	1.89	9.10	2.43

Fig. 5. Sample A2 test image

Fig. 6 shows the surface temperature history measured by pyrometers in the sample A2 stagnation area.

It is possible to observe the heating phase due to the injection of the sample in the plasma jet, a first quasi steady state condition (labelled as phase A) where the maximum temperature of 2123°C was achieved.

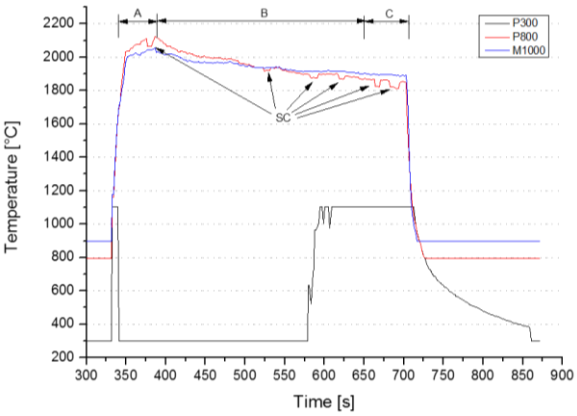

Fig. 6. Temperature measurements by pyrometers during sample A2 test

A series of temperature reductions starting at about 60 s from jet center-line achievement and due to arc heater current decreasing and argon mass flow increasing (phase B), a final temperature decrease starting at about 320 s (phase C) and the radiative cooling phase occurring after plasma shutdown.

Six switches from dual-color to single-color mode SC and back were performed on the P800 pyrometer and the last five ones were considered for spectral emissivity evaluation (see Section 8).

The temperature achieved at the end of the test was of about 1849°C. The sample has been exposed to plasma flow for over 6 minutes from jet center-line achievement to plasma shutdown.

Before the test, the sample A2 mass was of 5.2 g, after the test it was of 2.6 g with a remarkable mass consumption of 2.6 g, one-half of the initial mass (see Fig. 7). The average mass consumption rate was of about 7 mg/s. In this case, the coating detached completely from the substrate which remained exposed to plasma and was consumed.

Fig. 7. Post-test image of sample A2

Table 5 reports the main parameters concerning the sample B2 test.

Tab. 5: Sample B2 test data summary

Test ID	P_0 [bar]	m_{Air} [g/s]	m_{Ar} [g/s]
GHI-DLR-144A	1.88	9.01	2.42
GHI-DLR-144B	1.92	8.88	2.42
GHI-DLR-144C	1.83	8.48	2.42

The initial test conditions, qualified by Probe insertion, were similar to the last ones of sample A2 test (see Table 2).

Fig. 8 shows sample B2 during the test, and Fig. 9 reports the surface temperature history measured by pyrometers in the sample stagnation area.

Fig. 8. Sample B2 test image

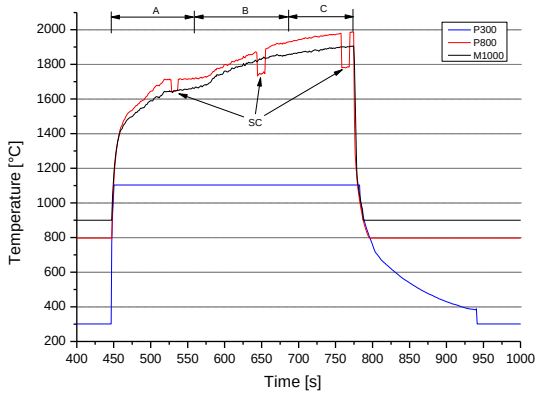

Fig. 9. Temperature measurements by pyrometers during sample B2 test

It is possible to notice the heating phase due to the injection of the sample in the plasma jet, a first quasi steady state condition (phase A), a temperature increase due to arc heater current increase (phase B) with the occurrence of a slope change at about 1730°C, a quasi steady state condition at intermediate arc heater current (phase C) and the radiative cooling phase after plasma shutdown.

Three switches from dual-color to single-color mode were performed on the P800 pyrometer for spectral emissivity evaluation. The slope change in pyrometer P800 trend can be explained by the starting of an oxidation phenomenon and subsequent reduction of emissivity as evaluated in Section 8.

The maximum surface temperature achieved was of about 1988°C. The sample has been exposed to plasma flow for about 5.5 minutes from jet center-line achievement to plasma shutdown.

Before the test, the sample B2 mass was of 5.0 g, after the test it was 3.6 g with a mass consumption of 1.4 g, about 28% of the initial mass. The average mass consumption rate was of about 4.3 mg/s.

Looking at the post-test picture of the sample B2 (see Fig. 10), a thick layer of intense white oxide is clearly visible and, most importantly the UHTC coating remained adherent to the substrate.

Fig. 10. Post-test image of sample B2

Table 6 reports main parameters regarding the sample A1 test.

Tab. 6: Sample A1 test data summary

Test ID	P_0 [bar]	m_{Air} [g/s]	m_{Ar} [g/s]
GHI-DLR-146	1.91	8.97	2.53

The test conditions qualified by Probe insertion were similar to the last ones of sample B2 test (see Table 2).

Fig. 11 shows sample A1 during the test and Fig. 12 reports the surface temperature history measured by pyrometers in the sample stagnation area.

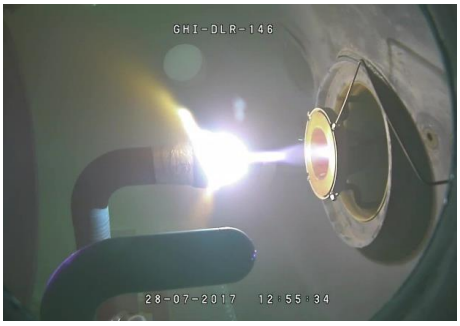

Fig. 11. Sample A1 test image

It is possible to notice the heating phase due to the injection of the sample in the plasma jet, a steady state condition and the radiative cooling phase occurring after plasma shutdown.

Five switches from dual-color to single-color mode SC and back were performed on the P800 pyrometer for spectral emissivity evaluation (see Section 8). The maximum temperature achieved was of about 1809°C.

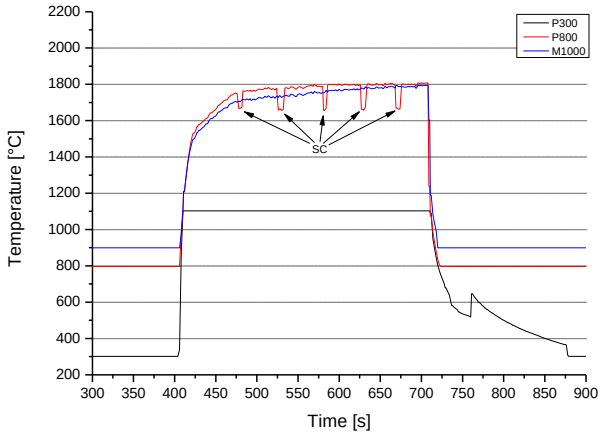

Fig. 12. Temperature measurements by pyrometers during sample A1 test

The sample has been exposed to plasma flow for about 5 minutes from jet center-line achievement to plasma shutdown. During the radiative cooling phase, a disk of oxidized UHTC coating detached from the stagnation region.

Before the test, the sample A1 mass was 5.1 g, after the test it was 3.8 g with a mass consumption of 1.3 g, about 25% of the initial mass (see Fig. 13). The average mass consumption rate was of about 4.3 mg/s, the same of sample B2. In this case, the substrate was protected during the test by UHTC coating which detached during the cooling phase.

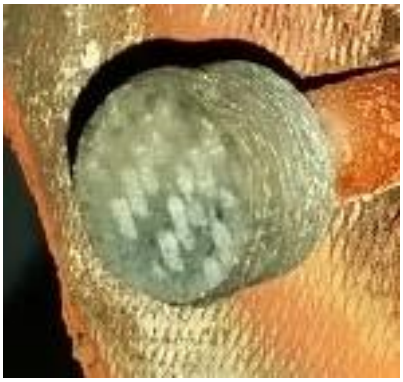

Fig. 13. Post-test image of sample A1

Table 7 reports the sample B1 test main parameters.

Tab. 7: Sample B1 test data summary

Test ID	P_0 [bar]	m_{Air} [g/s]	m_{Ar} [g/s]
GHI-DLR-147	1.89	8.98	2.43

The test conditions qualified by Probe insertion were similar to the ones of sample A1 test (see Table 2). Fig. 14 shows the sample B1 in the plasma jet.

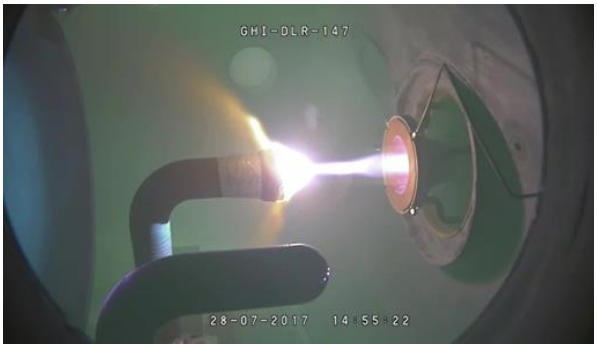

Fig. 14. Sample B1 test image

Fig. 15 shows the surface temperature history measured by pyrometers in the sample stagnation area.

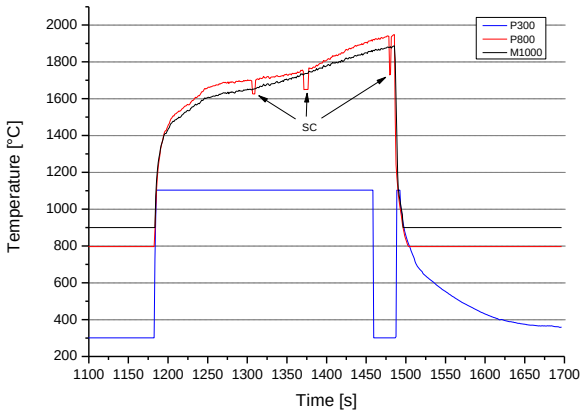

Fig. 15. Temperature measurements by pyrometers during sample B1 test

It is possible to notice the heating phase due to the injection of the sample in the plasma jet, a slope change occurring at about 1730°C, the achievement of a steady state condition and the radiative cooling phase occurring after plasma shutdown. Three switches from dual-color to single-color mode SC and back were performed on the P800 pyrometer for spectral emissivity evaluation. The slope change in pyrometer P800 trend can be explained by the starting of an oxidation phenomenon and subsequent reduction of emissivity as evaluated in Section 8.

The maximum surface temperature achieved was of about 1949°C. The sample has been exposed to plasma flow for about 5 minutes from jet center-line achievement to plasma shutdown.

Before the test, the sample B1 mass was of 4.9 g, after the test it was of 3.8 g with a mass consumption of 1.1 g, about 22% of the initial mass. The average mass consumption rate was of about 3.6 mg/s, about 15% lower than that of the sample B2 test.

Looking at the post-test picture of sample B1 (see Fig. 16) a thick layer of intense white oxide is clearly visible, similarly to that post-test of sample B2 (see Fig. 10). In fact, in both cases, a temperature slope change occurred at about 1730°C and an oxidation process started.

Fig-16. Post-test image of sample B1

At the end, the coating composition ZrB_2-20SiC-10AlN (B type samples) showed a higher adherence to the C/C substrate and stability under selected test conditions, preserving its integrity even though a clear oxidation layer formed.

8. EXPERIMENTAL EVALUATION OF EMISSIVITY

During the tests, the pyrometer identified with the tag P800 was repeatedly switched from dual-color to single-color mode in order to evaluate the experimental emissivity of the sample surface.

Coherently with the calibration function of a pyrometer operating in single-color mode [6], at target temperature held constant it has been experimentally found the following relationship between the emissivity value set on the instrument ε_{SC} and the temperature reading T_{SC} (in Kelvin)

$$\varepsilon_{SC} = \frac{a}{T_{SC}^{N}} \tag{1}$$

where the constant a depends on the construction of the pyrometer and on the target temperature, and N is the N factor

$$N = \frac{C_2}{\lambda_e T} \tag{2}$$

C_2 is the second radiation constant (14388 µmK), λ_e is defined as the effective wavelength of the pyrometer (determined experimentally as 1.00 µm for P800) and T is the true target temperature (in Kelvin).

Since the temperature measured by the pyrometer in single-color mode depends on the emissivity value set on the instrument (for these tests ε_{SC}=0.80), assuming the temperature measured by the pyrometer in dual-color mode T_{DC} as the true target temperature, we can obtain the experimental emissivity ε_{exp} value of the target imposing the following ratio

$$\frac{\varepsilon_{\exp}}{\varepsilon_{SC}} = \left(\frac{T_{SC}}{T_{DC}}\right)^N \qquad (3)$$

that is

$$\varepsilon_{\exp} = \varepsilon_{SC}\left(\frac{T_{SC}}{T_{DC}}\right)^N \qquad (4)$$

The experimental values obtained in this way (see Fig. 17) are indeed the spectral emissivity values at P800 pyrometer λ_e= 1.00 µm and angle of view.

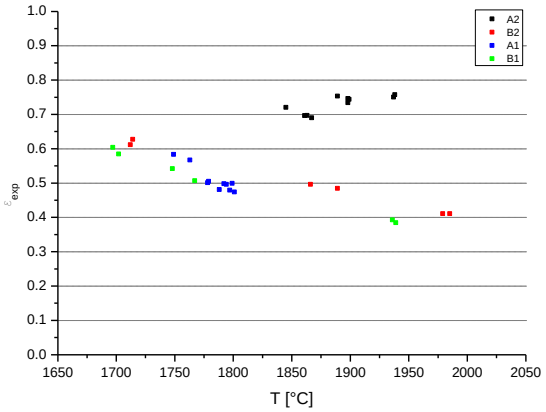

Fig. 17. Experimental spectral emissivity of the samples surface at λ_e= 1.00 µm vs. temperature

The results of this investigation show that the spectral emissivity varied between 0.6 and 0.4 for the ZrB_2-20SiC-10AlN coating (B type samples) in the range of temperature between 1700 and 2000°C, between 0.6 and 0.5 for the ZrB_2-3SiC-5WC coating in the range of temperature between 1750 and 1800°C (sample A1). For C/C substrate of sample A2 the spectral emissivity varied between 0.7 and 0.75 in the range of temperature between 1850 and 1950°C, since the coating detached completely from the substrate which remained exposed to plasma.

9. CONCLUSIONS

A test campaign was carried out in GHIBLI facility in the frame of LIGHT-TPS project on two coatings made of different zirconium diboride (ZrB_2) compositions, with the aim of increasing the oxidation resistance of the Carbon/Carbon (C/C) CMC substrates.

The spectral emissivity of the two coatings was investigated using a pyrometer operating in dual-color and single-color mode (λ_e= 1.00 µm).

The measured spectral emissivity values varied between 0.6 and 0.5 for the ZrB_2-3SiC-5WC coating in the range 1750÷1800°C, between 0.6 and 0.4 for the ZrB_2-20SiC-10AlN one in the range 1700÷2000°C. This last coating successfully survived the plasma jet tests thanks to a good adherence to the substrate.

10. ACKNOWLEDGEMENTS

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