RESIN IMPREGNATING METHOD TO MAKE MULTI-MATRIX  ANTI-ABLATION C/C COMPOSITE

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Introduction

The thermal, chemical, and mechanical environments produced by solid rocket motor (SRM), which has the uncooled nozzle, introduced many material problems in the development of rocket nozzles. Especially the throat material must bear the high temperature, mechanical load, thermal shock, chemical corrosion, and together with the highly requirement of dimensional stability. The materials used as throat including refractory metals, ceramics, graphite and fiber-reinforced plastics and so on, meet the needs of the early stage SRM, but some of them have high density, some can't withstand thermal shock and some can be ablated easily, all of them lead to big inert mass, so as to restrict the progress of the nozzle efficiency. [1][2]

There are some literatures about adding refractory-metal carbide to improve the ablation property of carbon/carbon(C/C) composite, which is widely used as advanced SRM throat for its characteristics of low density, high strength, super anti-ablation and anti-thermal shock properties.

One of the effective methods to improve the anti-ablation property of C/C composite at the temperature above 4000K is to add refractory metal carbide in its carbon matrix. The results indicate that, by the technology of impregnating resin, which containing refractory metal oxide, the C/C composite, which has 5-7% ZrC and the density is 1.90g/cm³, shows excellent anti-ablation property.

Experimental

The reduction-chemical combination method has been used to make metal carbide in the carbon matrix of C/C in this study. The formula is:

\[ \text{MeO} + \text{C} \rightarrow \text{MeC} + \text{CO} \]  (Me---metal)

After the fine grinded refractory metal oxide powder been uniform dispersed in phenolic resin by the technology of ultrasonic vibration, the C/C composite has been made by the carbon felt impregnating the resin above, together with the progress of curing, carbonization, sintering. The final density of the C/C with refractory metal carbide in its carbon matrix is 1.90g/cm³ after several periods of densification. The metal oxide used in this study is ZrO₂ and Ta₂O₅, arc stand-point ablation testing tests the ablation property.

Results and Discussion

The ablation properties of some C/C with different kinds and contents of carbide in its matrix are listed in table 1. In order to compare with the traditional C/C of same substrate, the integral felt C/C and advanced graphite T705 are in table 1 too.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Content of carbide Wt%</th>
<th>Density g/cm³</th>
<th>Linear ablation rate of radial direction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Arc stand-point pressure 2.0MPa</td>
</tr>
<tr>
<td>1# ZrC</td>
<td>7.5</td>
<td>1.946</td>
<td>0.343</td>
</tr>
<tr>
<td>2# ZrC</td>
<td>5.0</td>
<td>1.931</td>
<td>0.23</td>
</tr>
<tr>
<td>3# ZrC</td>
<td>3.0</td>
<td>1.947</td>
<td>0.753</td>
</tr>
<tr>
<td>4# ZrC</td>
<td>0</td>
<td>1.892</td>
<td>0.312</td>
</tr>
<tr>
<td>5# TaC</td>
<td>5.0</td>
<td>1.927</td>
<td>0.158</td>
</tr>
<tr>
<td>T705</td>
<td></td>
<td>1.892</td>
<td>0.347</td>
</tr>
<tr>
<td>Felt C/C</td>
<td></td>
<td>1.74</td>
<td>0.312</td>
</tr>
</tbody>
</table>

The results indicate that, the testing pressure affects the ablation property of C/C very much. The ablation rate of the materials will increase many times (3~8) while the pressure increase one time. Whatever the pressure is 2.0MPa or 4.5MPa, sample 2#, which has 5% ZrC in its matrix, shows much better anti-ablation property than that of sample 4#, which has the same structure with integral felt C/C but no carbide. The ablation rate of sample 2# decreases 26.3% at 2.0MPa, and 36.1% at 4.5MPa than that of the sample 4#. The tendency is same in the compare with practical integral felt C/C production.

The reaction of the ablation procedure of C/C composite with refractory metal carbide in its matrix is analyzed by observing the macro- and microscopic photograph of sample 2# and 4# after-ablation. By observing the samples with carbide in its matrix after arc ablating, the white oxide film can be seen on the ablated surface. This phenomena proves the oxidation of ablation procedure, the formula is:

\[ \text{MeC} + \text{O}_2 \rightarrow \text{MeO} + \text{CO} \]

Figure 1 is the SEM photos of sample 2# and 4# after ablation. Figure 1(a,b) shows that the anti-ablation property of the cross section of carbon fiber is less than any other carbon phase of C/C composite. So what can we do to improve the ablation property of C/C is to improve the property of matrix and to remedy the defects after fiber ablated. From figure 1(c,d), the functions of refractory metal carbide are just as the two points above. While the ablating temperature is higher than the melt
point of metal oxide (ZrO₂, m.p. 2700°C, Ta₂O₅, m.p. 1872 ±10°C), the oxide can form a continuous, fluid liquid film; it can remedy the defects clearly.

There were series of special SRM to test nozzle throat material in America, such as refractory metal, ceramic, graphite and C/C composite. The results demonstrated that the ablation mechanism of throat materials can be classified in three types: melting (or sublimation), oxidation and mechanical abrasion. The ablation properties of different materials exposed to different combustion gas of propellants are related to the properties of materials, thermal and chemical environment. All the refractory metal carbide nozzle throats failed because of the thermal stress and the graphite always failed because of oxidation. TRW Report (1968) refered that fiber reinforced carbide could modify the defects that the block carbide is sensitive to mechanical damage and thermal shock, and the carbon material can be oxidized at high temperature.

In order to improve the anti-ablation property of C/C, different ways must be connected with the different mechanism. As shown in table 1, the C/C with proper content of refractory metal carbide in its matrix has improved its anti-ablation property. The reasons can be concluded as three points:

1) Restraining the oxide reaction: For the existing of oxidation reaction, the carbide will change to oxide at the environment of high temperature and oxygen. The oxide liquid film can restrain the oxygen damaging the material furtherly good as remedying the ablation defects.

2) Improving the anti-abrasion property of matrix: The ceramics, such as refractory metal carbide, has excellent anti-abrasion property. It can improve the ability of C/C withstand mechanical abrasion effectively.

3) Remedying the ablation defects: This has been discussed in detail above.

Conclusions

The resin impregnating method to make multi-matrix anti-ablation C/C composite is realistic. The final density of the C/C with refractory metal carbide in its carbon matrix is 1.90g/cm³ after several periods of densification. The C/C composite, which has 5-7% ZrC, shows excellent anti-ablation property by arc stand point ablation testing. The reasons why the C/C with proper content of refractory metal carbide in its matrix has better anti-ablation property are restraining the oxide reaction, improving the anti-abrasion property of matrix, and remedying the ablation defects.

References

2. Laub B., Thermochemical Ablation of Tantalum Carbide loaded Carbon-carbons, AIAA-80-1476

Figure 1. The SEM photos of sample 2# and 4# after ablation