Study on the Compatibility of Carbon / Silicon Carbide Composite Ceramics with Dinitrogen Tetroxide

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Abstract. In this paper, the compatibility of carbon/silicon carbide composite ceramic materials and propellant dinitrogen tetroxide was studied. Referring to similar standards, the test parameters and immersion test scheme were selected. The changes of dinitrogen tetroxide properties and mechanical properties of ceramics before and after the experiment were mainly investigated, which provided theoretical and data basis for the application of this ceramic material in the field of dinitrogen tetroxide.

1. Introduction
Ceramic matrix composites are multiphase materials, also called multiphase composite ceramics or multiphase ceramics, which are reinforced and toughened by introducing second phase materials into ceramic matrix[1]. Ceramic matrix composites are new ceramic materials developed gradually in the 1980s, including fiber(or whisker) toughened (or reinforced) ceramic matrix composites, heterogeneous particle dispersion strengthened multiphase ceramics, in-situ growth ceramic composites, gradient function composite ceramics and nano ceramic composites. Due to its characteristics of high temperature resistance, wear resistance, high temperature creep resistance, low thermal conductivity, low thermal expansion coefficient, chemical corrosion resistance, high strength, high hardness, dielectric and wave transmission, it can be widely used in the case that the organic material base and metal material base cannot meet the performance requirements, and become an ideal high temperature structural material[2]. Silicon carbide ceramic-based conformity materials have attracted the attention of the United States, Japan, Germany and other countries, and have been gradually applied to aerospace fields, such as high thrust-weight ratio engine hot-end components [3].

In view of this, many countries are actively developing the research of ceramic matrix composites, greatly expanding its application fields, and have developed a variety of new preparation technologies[4]. Among them, carbon / silicon carbide ceramic matrix composite is a very important system. There are mainly two types of carbon / silicon carbide ceramic matrix composites, namely carbon fiber / silicon carbide and carbon particle / silicon carbide ceramic matrix composites. Carbon fiber / silicon carbide ceramic matrix composites use carbon fiber to strengthen and toughen silicon carbide ceramics, so as to improve the brittleness of ceramics and realize the necessary properties of high-temperature structural materials, such as oxidation resistance, high temperature resistance and corrosion resistance. Carbon particles / silicon carbide ceramic matrix composites use carbon particles to reduce the hardness of silicon carbide ceramics, realize the machinability of structural ceramics, and have good oxidation resistance, corrosion resistance and self-lubricating[5].
The carbon/silicon composite ceramic material has excellent wear resistance and corrosion resistance. Therefore, carbon/silicon composite ceramic material is considered to replace the enhanced PTFE plastic used in the friction pair of the shield pump for dinitrogen tetroxide. But at present, there is no research on the compatibility of the ceramic material with dinitrogen tetroxide at home and abroad, and there is no scientific and reliable theoretical and data basis.

2. Experimental scheme

2.1. Immersion experiment conditions
There is no correlation between ceramic materials and static immersion corrosion of corrosive liquids in current standards, so the formula for estimating immersion corrosion test time is as follows referring to the Ministry of Space Industry standard QJ1387-88 "Test method for static immersion corrosion of metallic materials in nitro oxidant".

\[ T = \frac{50}{V} \]  

\( T \) - test time, h; \( V \)-year corrosion rate, mm/a.

Referring to the national standards on the compatibility of dinitrogen tetroxide and metal materials, the first-level compatibility requires annual corrosion rate \( V \leq 0.0254 \) mm/a, and the estimated \( T \geq 1968.5 \) h, which is about 82 days. Therefore, the immersion experiment is planned for three months. Considering the possible environment of the ceramic material in practical application, the immersion conditions are as follows:

(1) At room temperature, the ceramic materials were soaked in dinitrogen tetroxide samples that met the index for a specified time;

(2) At room temperature, ceramic materials were immersed in saturated dinitrogen tetroxide vapor for a specified time;

(3) At room temperature, the ceramic material is soaked for a specified time in a sample of 1 % dinitrogen tetroxide with equivalent water content. When the equivalent water content is low, the acid corrosion ability of dinitrogen tetroxide increases with the increase of the equivalent water content. The equivalent water content in dinitrogen tetroxide is generally below 0.40 %. The investigation of acid corrosion resistance of the ceramic material by dinitrogen tetroxide with 1 % equivalent water content meets and exceeds the requirements of practical application, which is a relatively appropriate and desirable experimental condition.

2.2. Testing items

(1) Ceramic testing items
According to relevant national standards, the selection of testing items focuses on the investigation of mechanical properties and surface morphology of ceramics. Testing items of ceramic materials before and after immersion are shown in the table below.

| Number | Testing items                        | Testing reasons                                                   | Reference standard                          |
|--------|--------------------------------------|------------------------------------------------------------------|---------------------------------------------|
| 1      | Corrosion weight loss and size change | Visually reflect the corrosion of materials.                      | GB/T 16534-2009 Test Method for Room Temperature Hardness of Fine Ceramics |
| 2      | Surface microstructure               | Intuitive reflection of surface changes before and after immersion. |                                              |
| 3      | Roughness                            | Roughness changes can directly reflect the surface corrosion.      |                                              |
| 4      | Vickers hardness                     | Hardness is a parameter closely related to the wear behavior of the material. |                                             |
| 5      | Bend strength                        | The brittle fracture strength and                                 | GB 6569-2006 Fine                           |

The investigation of acid corrosion resistance of the ceramic material by dinitrogen tetroxide with 1 % equivalent water content meets and exceeds the requirements of practical application, which is a relatively appropriate and desirable experimental condition.
6 Compressive strength  
This index is related to the friction and wear properties of materials.  

GB/T 8489-2006 Test Method for Compressive Strength of Fine Ceramics  

3. Statistics and analysis of experimental data  

3.1. Experimental data of dinitrogen tetroxide  
There is no obvious difference between the quality test data of dinitrogen tetroxide and blank. Analysis of the reasons, the influence of dinitrogen tetroxide on the ceramic sample is mainly on the surface, the quality of the sample changes little, generally not more than 0.0004 g, the purity of dinitrogen tetroxide detection project, equivalent water and nonvolatile residue has little effect. The pore size of the core filter used in particulate matter is 10 ± 3μm, and the change of roughness shows that the particle size of ceramic particles may be less than the pore size.  

3.2. Experimental data of ceramic samples  
(1) Roughness experimental data analysis  
The sample preparation requires Ra ≤ 0.1μm, so the data (abnormal value) greater than 0.1μm can be considered as surface defects. Six samples were tested under each immersion condition, and five locations were randomly selected for roughness measurement. Thirty sets of data were obtained under each immersion condition.  

The statistical data examined included mean, dispersion (standard variance) and number of outliers. The average value can reflect the overall change level of roughness, the dispersion degree can reflect the change of the distribution range of roughness data, and the number of abnormal values can reflect the change of ceramic surface defects before and after immersion.

![Figure 1. Experimental data of roughness after immersion in gaseous dinitrogen tetroxide](image)
By analyzing the experimental data, the following conclusions can be drawn:

a. Before and after immersion, the average roughness of all samples did not change significantly, but the number of abnormal values increased significantly after immersion.

b. After the sample was immersed in gaseous dinitrogen tetroxide, the roughness increased, the dispersion degree increased significantly, and the number of abnormal values increased significantly.

c. After immersion in liquid dinitrogen tetroxide, the roughness and dispersion of the sample increased slightly, and the number of outliers increased significantly.

d. After the sample was immersed in dinitrogen tetroxide with 1% water, the roughness was significantly reduced, the dispersion was slightly reduced, and the number of abnormal values was slightly reduced.

The reason is speculated that the surface of ceramic material is not uniform, and the compactness is different at different positions during the grinding process. The position with higher density has higher resistance to dinitrogen tetroxide erosion, while the position with lower density has lower resistance to dinitrogen tetroxide erosion, resulting in a significant increase in the roughness of the position with lower density and the number of abnormal value.

(2) Bending strength experimental data analysis
The following conclusions can be drawn from the data:

a. After immersion, the average bending strength of the immersion sample was slightly higher than that of the blank control.

b. The standard deviation of bending strength of soaked samples is slightly lower than that of blank control.

Comprehensive analysis shows that the bending performance of the samples has been improved after immersion under three immersion conditions. It is speculated that the brittleness of the ceramic sample increases after immersion, and the ability to resist bending external force is improved.

(3) Compressive strength experimental data analysis

The following conclusions can be drawn from the data:

a. The compressive strength of the specimens immersed in gaseous dinitrogen tetroxide decreased, and the standard deviation decreased, indicating that the overall compressive performance decreased.

b. After immersion in liquid dinitrogen tetroxide environment, the compression strength of the sample decreased significantly, and the standard deviation decreased significantly, which can be considered that the overall compression performance decreased significantly.

c. The change of compressive properties of the samples soaked with 1 % water and dinitrogen tetroxide is reflected in the discreteness of the data. The compressive properties of some samples are improved, while the compressive properties of some samples are decreased.

It shows that dinitrogen tetroxide has a certain influence on the internal structure of the sample, and the compressive strength changes irregularly.

(4) Vickers hardness experimental data analysis
Analysis of data shows:

a. After immersion under three immersion conditions, the hardness of the samples decreased.

b. After immersion under three immersion conditions, the dispersion degree of hardness of the sample increased significantly.

The reason is speculated as follows:

a. Dinitrogen tetroxide has a certain degree of corrosion on the surface of the sample, reducing its hardness;

b. The corrosion degree of dinitrogen tetroxide on the surface of the sample is affected by the surface density of the sample, and the difference is large, resulting in the increase of hardness dispersion.

(5) Microstructure analysis

In this observation, two different points on each sample were observed by 500 times, 2000 times, 10000 times and 30000 times magnifications, and eight microscopic images were obtained for each sample to analyze the microstructure under different magnifications. Since the gold spraying operation will affect the immersion test, it can only be carried out after the immersion is completed. Therefore, it is impossible to repeat the change of the microstructure at the same position, but it can still roughly find that the defect points on the specimen after immersion increase.

(6) Macroscopic appearance and size change analysis

There was no significant change in the appearance of the sample before and after immersion.

Compared with the blank, the mass change range of the sample is within 0.0004 g, the size change is within 0.002 mm.

4. Conclusion of experimental data analysis

In this paper, when the experimental method is formulated, the reference standard is "Test method for static immersion corrosion of metallic materials in nitro oxidant", and the ceramics are non-metallic materials. Therefore, when evaluating the compatibility of the material, the compatibility standard of dinitrogen tetroxide with metal materials and non-metallic materials is also referred.

(1) Compatibility standard for dinitrogen tetroxide and metal materials

The compatibility of dinitrogen tetroxide with metal materials mainly includes the corrosion rate of the material and whether the propellant is affected. Level 1 compatibility criteria are:

a. Corrosion rate less than 0.0254 mm/a.

b. Propellant is not affected, mass unchanged, not decomposed, insensitive to impact.

According to this standard, the corrosion rate of the ceramic material with dinitrogen tetroxide was calculated.

In three months, namely within 0.25 years, the maximum change of sample size was 0.002 mm, and the corrosion rate was 0.002 mm / 0.25a = 0.008 mm / a, which was first-order compatibility.

(2) Compatibility standard for dinitrogen tetroxide and non-metallic materials
The compatibility of dinitrogen tetroxide with non-metallic materials mainly includes the volume change rate, hardness change rate and whether the propellant is affected.

In the experiment, the volume change rate of the sample was very small, and the propellant was not affected, but the hardness of the sample changed greatly. The micro-hardness of the sample surface after immersion in liquid dinitrogen tetroxide environment was compared with that of the blank, and the change rate was more than 15%, belonging to the fourth-order compatible material.

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Due to my limited knowledge, there might be some mistakes and flaws in this paper, please don't hesitate to correct me.

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