氏　　　　　名	久保田 勇希
学位(専攻分野)	博士(工学)
学 位 記 番 号	総研大甲第 1665 号
学位授与の日付	平成26年3月20日
学位授与の要件	物理科学研究科　宇宙科学専攻 学位規則第6条第1項該当
学 位 論 文 題 目	炭素繊維強化フェノール樹脂の昇温過程における劣化と変形
論 文 審 査 委 員	主　査　　准教授　後藤 健 教　授　八田 博志 准教授　山田 哲哉 教　授　向後 保雄　東京理科大学 教　授　松永 三郎　宇宙科学研究所

(別紙様式 2)
(Separate Form 2)

論文内容の要旨
Summary of thesis contents

博士論文題目
炭素繊維強化フェノール樹脂の昇温過程における欠陥の生成と変形
Thermal deformation and damage of carbon fiber reinforced phenolic composites at elevated temperatures

First Chapter

Ablation cooling has been adopted in the severest heating environments, such as re-entry vehicles from space and engine nozzle of solid rocket. The ablator systems protect payloads and the vehicle structures through consumption of ablation materials called ablator. Gases generated by pyrolysis of the ablator thereby insulate it from hot environmental gases. Their associated endothermic decomposition reactions lower the material temperature. The pyrolysis reaction results in carbonization of ablator surface. Sublimation of the carbonized surface contributes to preventing too much elevating payload temperature. Low thermal conductivity of the ablator also lowers the temperature. Carbon-fiber-reinforced phenolic matrix composites have been often applied under severest environments as ablation materials.

To evaluate performance under re-entry environments, the ablator is exposed to extremely high temperatures and high-speed flow in an arc-plasma wind tunnel (AP). Many researchers have predicted recession rates of ablator surfaces based on results of the such tests. The recession rate of an ablator surface is key information for designing the ablator thickness. It has been determined by subtracting the thicknesses of an ablator before and after heating. When an ablator is exposed to a severe environment, it is damaged, and the damage causes large deformation. Therefore, the measurement of recession includes the thermal deformation generated by the cracks of the ablator. The deformation is not negligibly small compared with the recession rate. Therefore, the deformation should be seriously considered in order to estimate the recession precisely. Understanding damage in an ablator is also important for evaluations of material properties of an ablator. For predictions of temperature distribution in and around an ablator and recession, material properties of an ablator, such as thermal conductivity and density, are required. However, these properties sensitively depend on damage in the material. This is another motivation to discuss damaging process of ablators in the present study.

In AP tests, the material is heated unidirectionally and rapidly. Consequently, unsteady rapid-changing temperature distribution with a sharp gradient is induced in an ablator. Under such complex heating conditions, it is difficult to specify the basic mechanisms yielding the expansion deformation and cracking, because observation of the cross-section of material after heating is the only way to assess the damage in AP tests. Therefore, elucidation of the basic mechanisms is crucially important to ascertain deformation behaviour.

(別紙様式 2)
(Separate Form 2)

The cracking pattern of carbon-fiber-reinforced phenolic matrix composite during exposure in static and high temperature environments has been investigated by some researchers. Fischedick and Zhang identified the basic mechanisms under low heating rate conditions using soaking furnace. Herein, these conditions were called as quasi-static heating conditions. The mechanisms identified by them can apply only for the fiber reinforced plastics (FRP) using straight fiber, such as PAN- or pitch-based carbon fiber. However, carbon fiber applied to ablators has special configuration; 3 spun-yarned sub-bundles are bladed into twisted one yarn. This fiber is used for the ablator as the reinforcement because of low density and low thermal conductivity. Since the mechanisms of cracking should depend on the configuration of the fiber, individual research of the basic mechanisms focusing FRP reinforced by kynol-based carbon fiber is necessary in order to understand cracking pattern of ablator.

In this research, the cracking and deformation was observed under quasi-static heating conditions, such as low heating rate and uniform heating. The basic mechanisms under quasi-static conditions were identified from the mechanisms of cracking of the FRP reinforced by PAN-based carbon fiber. Based on the mechanisms clarified under quasi-static condition, cross-sections of an ablator after arc-plasma wind tunnel heating tests were observed to identify causes of thermal expansion deformation.

Second Chapter

1. Introduction

Before arc-plasma wind tunnel tests, ablator materials are quasi-statically heated to ascertain basic mechanisms of thermal deformation and cracking at elevated temperatures in the second chapter. Therefore, objective of this chapter is to provide basic information for discussion of thermal deformation and cracking in re-entry environments.

2. Experiments

2.1 Material

Two types of ablators, kynol-based carbon fiber reinforced plastics (Types 1 and 2), are quasi-statically heated. The materials consist of eight satin-woven fabrics of kynol-based carbon fiber as the reinforcement, and resol-type phenolic resin as the matrix. The kynol carbon fiber is of a spun-yarn type, and has a special microstructure that includes thin short fibers spun into a thin sub-bundle and three sub-bundles braided into a yarn. The principal difference between Types 1 and 2 was porosity. Although the closed porosity of A-1 was higher than that of A-2, A-2 contained more open pores than A-1 did. The total porosity of A-2 was 10.4% higher than that of A-1. The pore sizes differed significantly between Types 1 and 2. The average volume fraction of pores in A-1 was less than that in A-2. In this chapter, thermal cracking behavior of A-1 is in a main focus. Thermal deformation of A-2 was used for addressing the effect of porosity and pore size by comparison with those of A-1.

2.2 Experimental procedures

The deformation during heating up to 1400℃ was measured using Thermo Mechanical

Analyser (TMA). Deformations in the thickness direction of the laminated composites were determined mainly, because samples didn't deform in the directions including the lamination plane.

The deformation mechanisms were clarified through detailed observations of crack formation and deformation processes under quasi-static heating conditions. For these observations, a thermo-optical microscopy (TOM) and X-ray computed tomography (X-ray CT) were used. Using the TOM development of cracks at elevated temperatures was observed under quasi-static heating conditions. The X-ray CT (Fraunhofer; Bayreuth, Germany) was used to observe pores and cracks inside the materials, which were heat-treated at elevated temperatures.

Phenolic resin has high water absorbability, and shows condensation polymerization and breakage of chemical bonds during the pyrolysis reaction. At elevated temperatures, the phenolic matrix composites emit H_2O and pyrolysis gases. In addition to above experiments, measuring porosity and TGA/MS were conducted to determine the effect of gas pressure trapped inside materials on the deformation and crack formation.

3. Results & Conclusion

Major deformation events monitored at around 300°C and 500°C and after 550°C were found to be derived, respectively, from H_2O gas pressure, pyrolysis gas pressure, and cracking by shrinkage of the matrix resin. In the temperatures higher than 550°C, the cracking pattern decided the deformation behaviors. The A-1 material expanded due to cracks generated inside fiber bundles in the direction of fiber axis. On the other hand, the cracks extended from the edge of pore in A-2. As a result, A-2 shrank. Since the reaction progressed actively at a temperature higher than 550°C, the cracking should be caused by the pyrolysis reaction.

Third Chapter

1. Introduction

The third chapter explained the cracking mechanisms of an ablator during active progression of pyrolysis reaction using established cracking mechanisms for PAN-based carbon fiber reinforced phenolic resin. The phenolic resin starts to shrink at 300℃ by pyrolysis reaction. In PAN-based woven-fabric CFRP laminates, two types of cracks, transverse cracks and delaminations were observed under the tensile stress. In contrast, cracking occurred under mismatch strain between the directions of fiver bundle axis and normal to it. However, the basic cracking mechanisms of the ablator were assumed to be the same as those for the woven-fabric CFRP subjected to the tensile stress. Some researchers simulated the pattern of transverse cracks and delaminations during a tensile test of the CFRP. This model was modified to establish a model explaining cracking of ablators, A-1 and A-2 materials.

2. Experiments and Analyses

In addition to A-1 and A-2, three types of PAN fiber reinforced CFRP, B-1, B-2 and B-3, were examined in this chapter. The difference between B-1 and B-2 was location of pores. While small pores were mixed in fiber bundles in B-1, large pores distributed in the matrix of B-2. In contrast, the volume fraction of pores was much fewer in B-3, and laminate thickness of B-3 was thinner than that of the others. The cracks of B-1~3 were simulated using a model estimating transverse cracks and accompanied delaminations in tensile tests. This model simulated the crack density as a function of tensile stress. To validate that the model can simulate the cracking during pyrolysis reaction, experimentally obtained crack densities of B-1~3 were compared with those predicted by the simulation model. After validation of the model by this simulation, the model was used in the initiations of the cracking in A-1 and A-2 during pyrolysis. Observations using TOM and X-ray CT were conducted in the same procedures as the second chapter.

3. Results and Conclusion

The model for tensile tests successfully simulated the crack densities of B-1~3. These results validated that this model can be applied to a simulation of the cracking during pyrolysis reaction.

The simulation indicates that the crack initiation stress in A-1 was lower than that in A-2. Therefore, A-2 released the mismatch strain more easily than A-1. Although only transverse crack released the mismatch strain in A-2, the strain mismatch in A-1 was released not only by transverse crack but also buckling of fiber bundle. This difference is attributable to the difference in pore size embedded in the materials.

Fourth Chapter

1. Introduction

Based on the mechanisms clarified in the third chapter, cross-sections of A-1s after arc-plasma wind tunnel heating were observed to identify causes of thermal expansion deformation during a re-entry from space. In addition, the deformation process during arc-plasma wind tunnel heating was attempted to measure using a laser-based measurement technique. This method was conducted in a corporation study with Institute of Space Center (IRS) of University of Stuttgart.

2. Experiments

The arc-plasma wind tunnel used for this study was PWK 1 of IRS of University of Stuttgart. The tests were conducted at heat fluxes of 2.0 MW/m^2, 6.0 MW/m^2, and 12.0 MW/m^2. These were designated, respectively, as tests A, B, and C. The heating time in each test differed: 60 s in test A, 30 s in test B, and 12 s in test C. The top surface temperature was measured using a pyrometer. Emissivity of material was set to 0.85. The temperature distribution within material was measured by 5 thermocouples.

Thermal deformation of the specimen in the thickness direction was measured from the variations of slit spacing before and after heating. Three alleys of slits were engraved on the side surface of specimens to measure the change of spacing between adjacent slits before and after heating. The original spacing between slits was 3.20–3.69 mm.

In the laser-based technique, sample's surface was scanned by a inclined laser pointer and variation of flashed point was recorded using a conventional video camera to determine displacement of the heating surface during heating. This change was calibrated to the displacement of the top surface.

The thermal stress and temperature distribution during heating was simulated using software of finite element analysis: ABAQUS.

3. Results and Conclusion

In a rapid heating condition, expansion of the thickness becomes greater than that in quasi-static condition because much more delaminations were generated in addition to the cracks appeared in the quasi-static heating conditions. Temperature distributions and thermal stresses inside material calculated using ABAQUS proved that the delaminations were caused by thermal stresses produced by steep temperature gradient inside material during arc-wind heating. The expansion deformation was greatest at the layer closest to the heated surface. Temperature of material generating expansion in an arc wind tunnel test was higher than that in a quasi-static heating test.

Fifth Chapter

This chapter gives general overview of the present study and explains future guide in extensive research. In this study, the deformation- and crack-yielding mechanisms encumbering optimization of an ablation system were clarified. These results should simplify estimating the materials properties such as thermal conductivity and density. The next target is to establish a model estimating the deformation and cracking.

(Separate Form 3)

博士論文の審査結果の要旨

Summary of the results of the doctoral thesis screening

博士論文題目

炭素繊維強化フェノール樹脂の昇温過程における欠陥の生成と変形

Thermal deformation and damage of carbon fiber reinforced phenolic composites at elevated temperatures

アブレーション材料（アブレータ）は宇宙からの再突入環境時に熱防御材として使用される。この時アブレータは、一万度以上の高温ガスの極超音速流に曝される。アブレータ耐熱特性は表面損耗（後退）量や温度分布（搭載機器が保護できる）で評価される。実験的には、アブレータの熱防御性能は、アークプラズマ風洞試験により評価されたものを、解析モデルを使った計算で、再突入環境にまで大幅な外挿をして推定されている。しかしながら、この解析モデルは、高温過程で材料内に発生する損傷や変形の影響を強く受けるにもかかわらず、損傷を含む材料物性を考慮にされておらず、解析モデルの信頼性は高くない。そのため、上記の外挿には経験的な調整定数を導入して実験と解析を合わせる努力がおこなわれている。本研究では正確な評価可能にする解析モデルを確立するために、アークプラズマ風洞環境におけるアブレータの損傷と変形を定量的に把握し、それらの発生機構を明らかにしようとしたものである。

アークプラズマ風洞試験では、試験後の材料しか観察できないため、損傷プロセスを理解することは容易ではない。また、アブレータは複雑なミクロ組織をもつため、損傷や変形の機構を明らかにするのは困難である。出願者は、これらの困難を克服するために、実験が容易な一様温度に近い準静的加熱場と簡素なミクロ組織をもつ材料に着目し、降温時における損傷と変形の進行をそれらのメカニズムに遡って理解し、この損傷過程の理解を基礎に、アークプラズマ風洞試験中に材料の損傷や変形がどのように進むかを初めて明らかにした。

第１章では、本研究の背景と目的を明らかにした。即ち、アブレータ用の主流は炭素繊維強化フェノール複合材料（CFRP）であることを示し。その劣化の変形ついて、既往の研究を紹介し、本研究の位置づけと意義を明らかにした。

第２章では、準静的加熱場におけるアブレーション材料の損傷と変形を観察し、アブレータ内に分散するボイドの大きさによって、別種の亀裂を発生しながら変形することを明らかにした。具体的には、小さなボイドを含む材料では、繊維束が座屈をおこし膨張し、大きなボイドを含む材料では小さな応力でマトリックス中に亀裂を進展させ、この亀裂により応力緩和を起こすことにより座屈を抑制して収縮することを示した。

第３章では、簡素なミクロ組織をもつ CFRP の高温損傷挙動を検討し、この場合には、トランスバースクラックと層間剥離という２種類の亀裂が発生すること及びこれらの損傷の発生過程や亀裂密度が予測可能であることを明らかにした。さらに、アブレータに発生する亀裂がトランスバースクラックに誘導されて起こるもので、アブレータの亀裂発生が予測可能であることを明らかにした。

(Separate Form 3)

第４章では、小さなボイドを含むアブレータに限定してアーク風洞試験後の材料を観察し、アーク風洞試験と準静的加熱場における損傷及び変形の違いを明らかにし、急速加熱場における劣化及び変形要因を特定した。主たる結論は二つで、第一の結論は、アーク風洞試験では、準静的加熱場で発生した損傷に加えて層間剥離を多数発生させるため膨張変形が大きくなることで、第二は、マトリックの炭化反応温度が、準静的加熱場に比べて顕著に高くなることであった。

第５章では､本研究全体で得られた結論を要約すると共に､将来への課題を示唆した。

以上のように、本出願論文は独創的な内容を含むもので、審査委員全員博士論文として推奨すべきとの認識で一致した。

公聴会と合わせて試験を行った。１時間の研究発表後に、審査委員だけでなく聴衆からも多面的な角度から質問を１時間以上ににわたり受け、その回答内容から出願者が博士の学位にふさわしい学力と説明能力を有することを確認した。

出願者は、これまでに国際誌に３報論文掲載させ、１報を受理させ、１報を投稿中としている。この他、12 回におよぶ国際会議での発表や、半年以上にわたるドイツでの実験を経験しており、これらの業績から、出願者は博士の学位に十分な英語の文章作成能力とコミュニケーション能力を有すると判断した。