7 AFFORDABLE AND CLEAN ENERGY

● Development of novel mullite-fiber-based ceramic matrix composites with high mechanical properties

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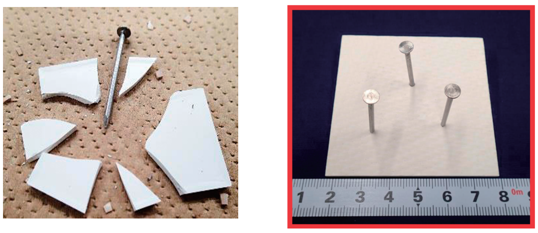
1. Introduction

Ceramic matrix composites (CMCs) are damage-tolerant, stable at high temperatures, and lightweight[1-3], making them viable alternatives to conventional nickel super alloys in thermomechanical, energy, and aerospace applications. For example, CMCs can improve the fuel efficiency and reduce the CO_2 emissions of aircraft gas-turbine engines. The GE9x engine manufactured by GE Aerospace, which employs 65 CMC parts, improves the fuel efficiency by 10% and lowers the CO_2 emissions by 10% from those of a conventional gas-turbine engine[4].

Figure 1 shows the appearances of monolithic ceramics and CMCs after nail-penetration tests. While the monolithic ceramics exhibit fully brittle failure, the CMCs exhibit high damage tolerance, maintaining their shapes through crack deflection along the weak fiber–matrix interface, along with uncollected fiber failure and energy dissipation during fiber pullout[5].

Oxide-based CMCs (Ox/Ox CMCs) composed of oxide fibers and an oxide matrix are cheaper and more resistant to corrosive and oxidative environments than SiC-based CMCs. Therefore, Ox/Ox CMCs are promising candidates for high-temperature applications in various oxidizing environments[6] and have been considered for specialized components of hypersonic vehicles or spacecraft. As Ox/Ox CMCs are also transparent to electromagnetic waves, they can excellently protect the antennas used in data transmission.[7]



Monolithic ceramics CMCs

Fig. 1 Nail penetration test[9]

Practical applications of Ox/Ox CMCs rely on the thermal stability and high-temperature properties of these ceramics. Previously, we developed two Ox/Ox CMCs (TCA-01 and TCM-01) with higher thermal stability than conventional Ox/Ox CMCs[8,9]. TCM-01 in particular exhibited better mechanical properties at high temperatures than single-crystal nickel-based super alloys and conventional Ox/Ox CMCs[10].

This technical report summarizes the mechanical properties of our newly developed TCM-02, which are superior to those of our previous TCM-01. Our purpose in developing this CMCs is to address Sustainable Development Goal 7 (Affordable and Clean Energy) and to contribute to society by providing novel Ox/Ox CMCs.

2. Uniform doping method of oxide fibers

Using our previously developed uniform doping method (UDM)[8,9,10], which improves the thermal stability of oxide fibers, we synthesized Ox/Ox CMCs with high thermal stability. As shown in **Figure 2**, the UDM dopes oxide fibers with grain-growth inhibitors[10], which suppress the grain growth of UDM-treated fibers during thermal exposure.

3. Mechanical properties of TCM-02

TCM-02 is fabricated from UDM-treated mullite fibers and an alumina-based matrix using slurry infiltration and a sintering process. **Figure 3** shows optical images and scanning electron microscope–energy dispersive

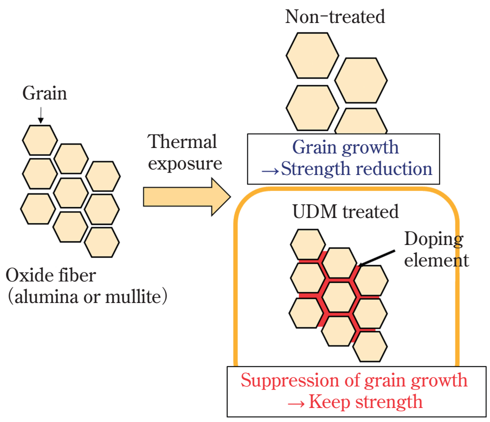


Fig. 2 Concept of uniform doping methods (UDM)[10]

X-ray spectroscopy images of TCM-02. The sample is a 220 mm by 80 mm rectangular plate consisting of twelve woven layers of Ox/Ox CMCs. Its thickness is 2.5 mm. The matrix phase fills the spaces between the woven layers of the pile and within the fiber bundles. TCM-02 has a density of 2.72 g/cm^3 (measured using the Archimedes method) and an approximate fiber volume of 45 volume%.

Table 1 compares the mechanical properties of TCM-02, TCM-01, a commercially available conventional Ox/Ox CMCs based on mullite fibers (N720/A ATK-COIC), and a single-crystal nickel-based super alloy for gas-turbine engines (CMSX-4 Cannon-Muskegon).

The tensile strength of TCM-02 at room temperature exceeds those of TCM-01 (182 MPa)[10] and conventional Ox/Ox CMCs[11].

Figure 4 compares the tensile strengths of the developed Ox/Ox CMCs after processing and after thermal exposure at 1200℃ for 1000 h. The TCM-02 sample fully retained its original tensile strength after thermal exposure[8,9]. In contrast, the conventional Ox/Ox CMCs retained only 88% of its original tensile strength[11,12].

At 1200℃, the tensile strength of TCM-02 (218 MPa) exceeded that of TCM-01 (195 MPa)[10] and exceeded those of the conventional Ox/Ox CMCs and the single-crystal nickel-based super alloy by 30% and 27%, respectively. Moreover, the tensile strength of TCM-02 at 1200℃ did not change significantly at 1250℃. In contrast, the tensile strength of the single-crystal nickel-based super alloy was much lower at 1200℃ (172 MPa) than at 24℃ (942 MPa)[13]. The tensile strength of the conventional Ox/Ox CMCs at 1200℃ was 168 MPa (averaged over the tensile strengths reported in the literature[14–18]).

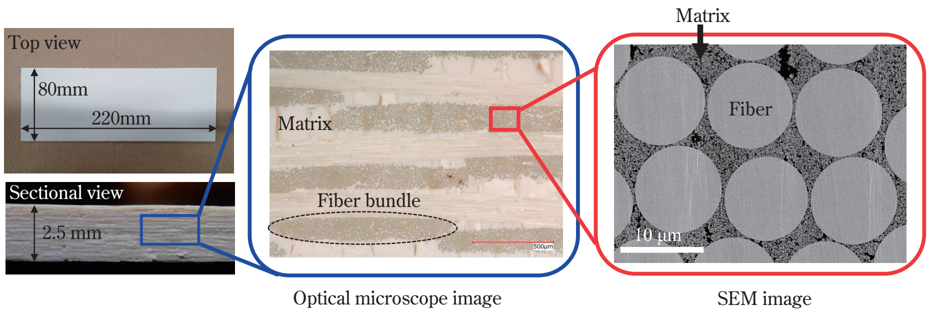


Fig. 3 Optical image and microstructure of TCM-02

Table 1 Mechanical properties of TCM-02

	Tensile strength at R.T. [MPa]	Tensile strength after 1200 ℃ for 1000 h [%]	Tensile strength at 1200 ℃ [MPa]	Creep lifetime at 1200 ℃, 100 MPa [h]
TCM-02	217	224	218	87.7
TCM-01	183[10)]	188[10)]	195	53.8[10)]
Conventional Ox/Ox	169[11)]	149[12)]	168[14-18),※1]	41[15)]
Sigle crystal Ni-based super alloy	942[13)]	—	172	13[19),※2]

※1 Average value of tensile strength in the references
※2 At 1200℃, 80 MPa

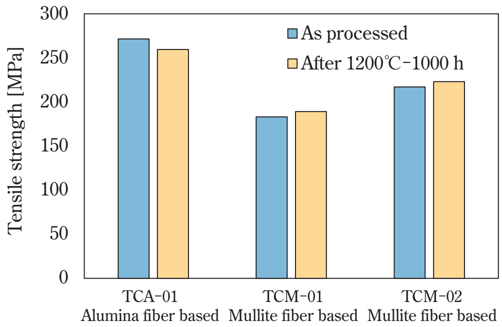


Fig. 4 Tensile strength of developed Ox/Ox as processed and after 1200℃ for 1000h thermal exposure[9]

Moreover, at 1200℃, the creep lifetime of TCM-02 exceeded that of TCM-01 (52.1 h)[10], those of the conventional Ox/Ox CMCs and single-crystal nickel-based super alloy. The time to rupture of TCM-02 at 1200℃ was >100 h at 80 MPa and 87.7 h at 100 MPa. In contrast, the times to rupture of the conventional Ox/Ox CMCs and single-crystal nickel-based super alloy at 1200℃ were 41.0 h at 100 MPa[15] and 13 h at 80 MPa[19], respectively.

Furthermore, the thermal conductivity of TCM-02, calculated from the specific heat, density, and thermal diffusivity following the American Society for Testing and Materials (ASTM) E1461 standard, was only 3.3 W/(m/K).

4. Tensile properties of TCM-02

Based on the ASTM C1275 and ASTM C1359 standard, room and high-temperature (25℃–1250℃) tensile tests were conducted in air using a mechanical test machine (MTS Landmark MTS Systems Corporation; province, country) and a strain gage (MTS System Corporation). The displacement rate was 3.00 mm/min and the temperature was increased at 35℃/min. The strain was calculated from the crosshead displacement. The tensile moduli, tensile strengths, and proportional limits (0.05% offset) were evaluated on dog-bone-shaped specimens (length = 150 mm; gage-section width = 8 mm) over the temperature range. **Table 2** lists the tensile properties and **Figure 5** plots the stress–strain curves from 25℃ to 1250℃, along with the shape and dimensions of the test specimens. **Figure 6** shows the tensile properties of TCM-02 at different temperatures. The tensile modulus, tensile strength, and proportional limit of TCM-02 were not obviously changed at 1250℃ and all tensile properties of TCM-02 was improved from those of TCM-01. Thus, TCM-02 exhibits superior tensile properties at high temperatures (up to 1250℃).

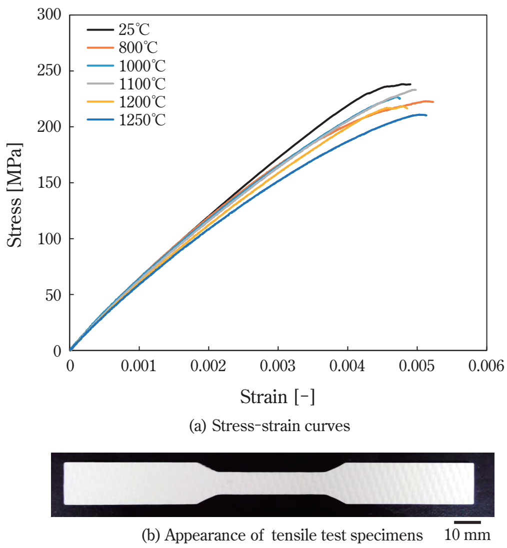


Fig. 5 (a) Stress-strain curves of TCM-02 and (b) appearance of tensile test specimen

Table 2 Tensile properties of TCM-02 at high temperature

Test temperature [℃]	Yong's modulus [GPa]	Proportional limit※1 [MPa]	Tensile strength※2 [MPa]
25	68.9	155	217
800	69.3	153	223
1000	70.7	144	227
1100	69.1	144	233
1200	65.7	145	218
1250	65.0	132	211

※1 0.05% offset method , ※2 following ASTM C 1359

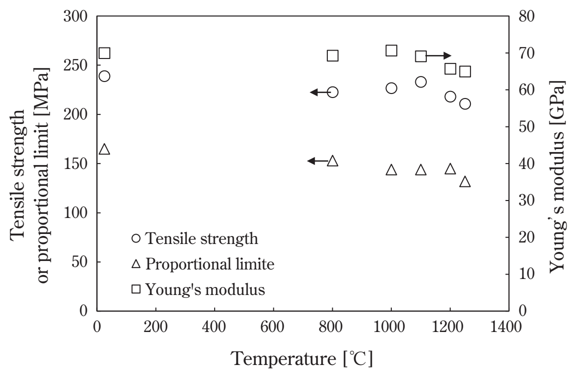


Fig. 6 Tensile properties of TCM-02 at different temperature

5. Fatigue properties of TCM-02 at high temperature

Following the ASTM C1360 standard, high-temperature tension–tension fatigue tests were conducted in air using a mechanical test machine (MTS Landmark 370.10 MTS Systems Corporation) and a strain gage (MTS 632.53F-14 MTS System Corporation). The R ratio (minimum stress divided by the maximum stress) was 0.05 at 1 Hz and the fatigue run-out cycle was 10^5. These tests were conducted on dog-bone-shaped specimens (length = 200 mm; gage-section width = 8 mm) at 1200℃ (temperature ramp rate = 35℃/min). The results are listed in **Table 3**. The maximum stress at run-out at 1200℃ was 140 MPa (64% of the ultimate tensile strength at 1200℃), demonstrating the high fatigue resistance of TCM-02 at high temperatures and in high-stress environments.

6. Creep properties of TCM-02

Following the ASTM C1337 standard, creep tests were conducted in air using a mechanical test machine (MTS Landmark 370.10 MTS Systems Corporation) and a strain gage (MTS 632.53F-14 MTS System Corporation). The specimens were the dog-bone-shaped specimens used in the fatigue test. The test temperatures were 1100℃, 1150℃, and 1200℃ (temperature ramp rate = 35℃/min), and the stress rate was 15 MPa/s. The time of creep run-out was 100 h. The test results are listed in **Table 4**. **Figure 9** shows the relationship between creep stress and time to rupture. At 1100℃ and 1150℃, run-out occurred under a creep stress of 100 MPa. At 1200℃ and 100 MPa creep stress, the creep lifetime of TCM-02 exceeded that of TCM-01[10]. This finding confirms the high creep resistance of TCM-02 at high temperatures and in high-stress environments.

Table 3 Results of fatigue tests of TCM-02

Test temperature [℃]	Maximum stress [MPa]	Cycle to failure [-]
1200	100	＞100000※
1200	125	＞100000※
1200	140	＞100000※

※Run-out

7. Conclusion

This technical report summarized the high-temperature mechanical properties of TCM-02, our newly developed Ox/Ox CMCs. TCM-02 exhibited higher thermal stability than conventional Ox/Ox CMCs in a high-temperature environment (1200℃) for 1000 h. In addition, both the tensile strength and creep lifetime of TCM-02 at 1200℃ were improved from those of TCM-01, single-crystal nickel-based super alloy, and conventional Ox/Ox CMCs. Further increases in mechanical properties and thermal stability can be expected after optimizing the UDM and fabrication processes.

Modern environmental and energy applications impose various demands on materials. For example, high operating temperatures are required to improve the fuel efficiency of turbine engines, and corrosion

Table 4 Results of creep tests of TCM-02

Test temperature [℃]	Stress [MPa]	Time to rupture [h]	Rupture strain [%]
1100	100	＞100※	—
1200	80	＞100※	—
1200	100	87.7	3.04

※ Run-out

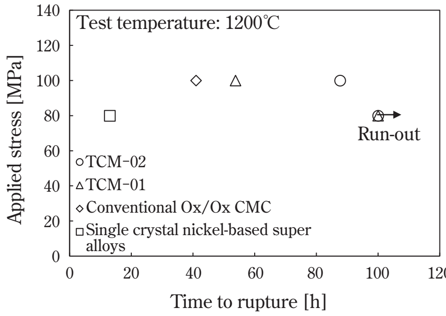


Fig. 9 Creep stress vs time to rupture at 1200℃

resistance is required for hydrogen and ammonia combustion. Our developed Ox/Ox CMCs with excellent thermal stability and high environmental resistance are expected to meet the stringent demands of environmental and energy applications.

Acknowledgments

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References

1）X. Wang et al., *Journal of the European Ceramic Society*, **41**, 4671-4688 (2021)
2）E. Volkmann et al., *Composites Part A*, **68**, 19-28 (2015)
3）T. E. Steyer, *International Journal of Applied Ceramic Technology*, **10**, 389-394 (2013)
4）Ceramic Matrix Composites Market in Aircraft Engines Size, Share, Trend, Forecast, Competitive Analysis, and Growth Opportunity: 2023-2028, Stratview Research (2023)
5）F. W. Zok, *Journal of the American Ceramic Society*, **89**, 3309-3324 (2009)
6）K. Ramachandran et al., *Journal of the European Ceramic Society*, **42**, 1626-1634 (2022)
7）P. Mechnich, *Journal of the Ceramic Society of Japan*, **129**, 32-39 (2021)
8）I. Yamashita et al., Proceeding of Ceramic Matrix Composites II: Science and Technology of Materials, Design, Applications, Performance and Integration (2022)
9）Y. Nawata et al., *TOSOH Research & Technology Review*, **66**, 85-91 (2022)
10）Y. Nawata et al., *TOSOH Research & Technology Review*, **67**, 73-79 (2023)
11）Composite Materials Handbook-17-5A (2017)
12）S. C. Poway, et al., U.S. Pat. 20020197465 (2002)
13）A. Sengupta et al., *Journal of Materials Engineering and Performance*, **3**, 664-672 (1994)
14）M. B. Ruggles-Wrenn et al., *Composites Part A*, **37**, 2029-2040 (2006)
15）M. B. Ruggles-Wrenn et al., *Materials Science and Engineering. Part A*, **37**, 101-110 (2008)
16）M. B. Ruggles-Wrenn et al., *International Journal of Fatigue*, **30**, 502-516 (2008)
17）S. G. Steel, *AFIT Scholar Student Graduate Works*, **3**, 132 (2000)
18）L. B. Harlen, *AFIT Scholar Student Graduate Works*, **3**, 112 (2005)
19）J. B. Wahl et al., Technical report of Cannon-Muskegon (2018)