

Supplementary Information

In situ molten phase assisted self-healing for maintaining fiber's morphology in conversion from melamine diborate to boron nitride.

Chunzhi Wu^a, Bing Wang^{a*}, Nan Wu^b, Cheng Han^a, Xiaoshan Zhang^a, Yingde Wang^{a*}

^a Science and Technology on Advanced Ceramic Fibers and Composites, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, 410073, PR China.

^b Department of Materials Science and Engineering, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, 410073, PR China.

To study structural transformation of H_3BO_3 and $\text{C}_3\text{N}_6\text{H}_6$ separately, they were heated to 150 °C, 200 °C, 400 °C and immediately cooling down to accord with TG procedure. The XRD was used to characterize the H_3BO_3 and $\text{C}_3\text{N}_6\text{H}_6$ and their heated products. As shown in Figure S1a, boric acid (H_3BO_3 , ICSD PDF#73-2158) converted into metaboric acid (including $\alpha\text{-HBO}_2$, ICSD PDF#77-0425 and $\beta\text{-HBO}_2$, ICSD PDF#76-0746) after treated at 150 °C, and in further totally converted into glass boron oxide ($\text{g-B}_2\text{O}_3$, ICSD PDF#06-0297) at 200 °C. The peaks of sassolite (ICSD PDF#30-0199) could be attributed to the moisture absorption of B_2O_3 . In Figure S1b, the crystallinity of melamine became slightly poorer but remained $\text{C}_3\text{N}_6\text{H}_6$ (ICSD PDF#39-1950) molecule stable when heated up to 200 °C and condensed into melem^[1] when up to 400 °C.

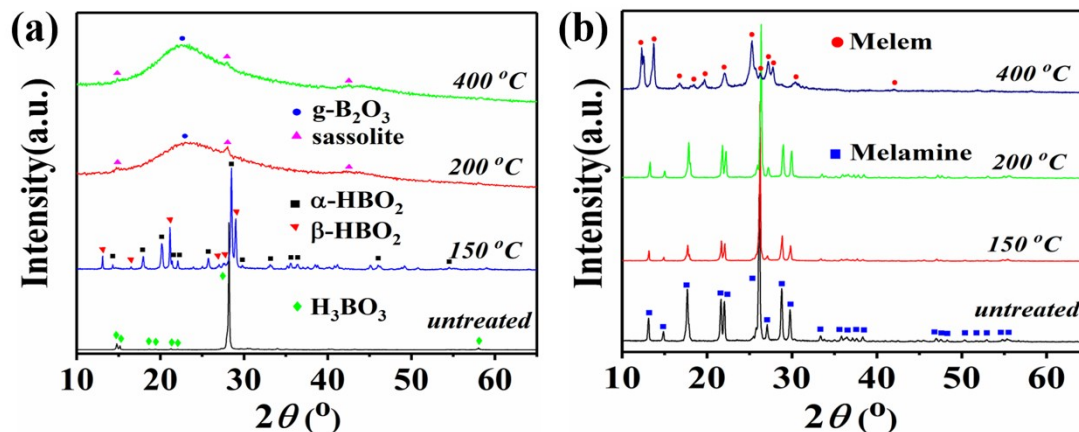


Figure S1 (a) XRD pattern of boric acid and its heating products and (b) melamine and its heating products after treated at 150 °C, 200 °C, 400 °C.

To further confirm the structural evolution, ^{13}C nuclear magnetic resonance (NMR) spectrum was applied. All the ^{13}C NMR spectrum was calibrated according to the septet peaks of DMSO-d_6 solvent. As shown in figure S2, the chemical shift δ of samples were 167.33 ppm ($\text{C}_3\text{N}_6\text{H}_6$ in DMSO-d_6), 165.23 ppm ($\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$ in DMSO-d_6), 164.93 ppm ($\text{M} \cdot 2\text{B}_{150}$ in DMSO-d_6), 164.73 ppm ($\text{M} \cdot 2\text{B}_{200}$ in DMSO-d_6), respectively. It varied from pure melamine to $\text{M} \cdot 2\text{B}$ and to $\text{M} \cdot 2\text{B}_{150}$, which may result from circumstance variation of $\text{C}_3\text{N}_6\text{H}_6$ molecule. And the difference of C NMR spectra between $\text{M} \cdot 2\text{B}_{150}$ and $\text{M} \cdot 2\text{B}_{200}$ reveals the different structure, as depicted in FTIR, seemed to change from the (melamine) C-NH_2 to the C-O-B .

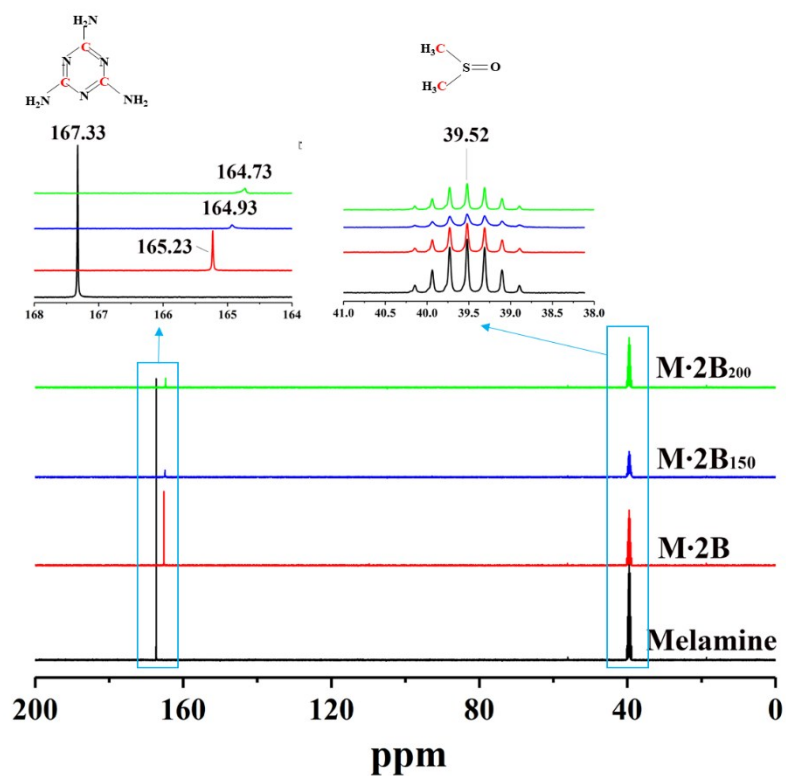


Figure S2 ^{13}C NMR spectra for melamine, $\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$ (M·2B) and its heated products after treated at 200 °C, 400 °C.



Figure S3 Photographs of the heated products of original melamine: remained $\text{C}_3\text{N}_6\text{H}_6$ at 150 °C and 200 °C, condensed into melem at 400 °C.

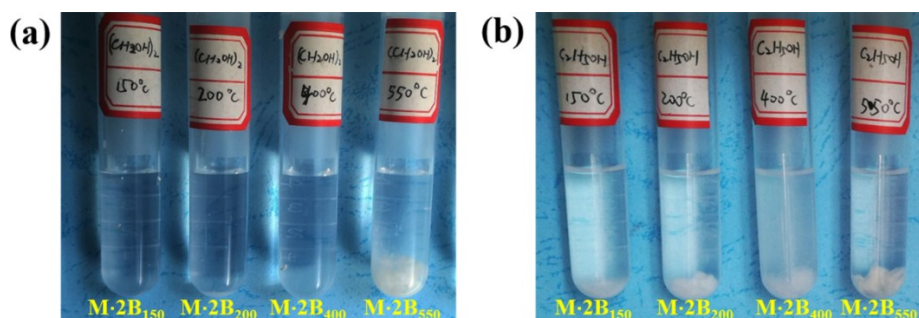


Figure S4 Solubility of the thermal derivatives of M·2B (heated at 150 °C, 200 °C, 400 °C, 550 °C) in solvents after 6 hours (a) ethylene glycol (EG); (b) ethanol (EA).

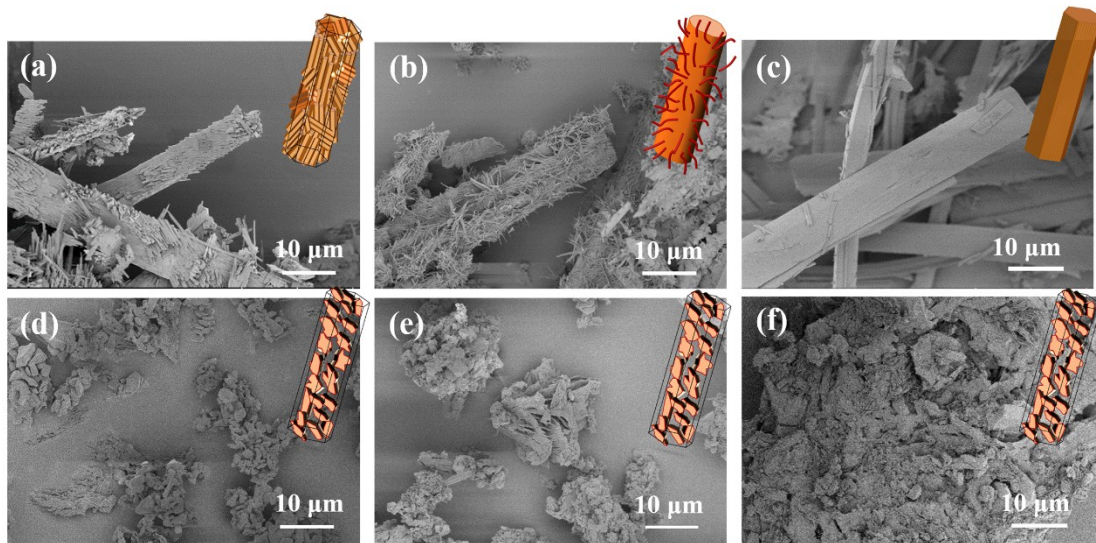


Figure S5 SEM images of the corroded M·2B_T fibers by EA and EG for 1 minute: (a) M·2B₁₅₀, (b) M·2B₂₀₀ (c) M·2B₄₀₀ after immersed in ethanol (EA); (d) M·2B₁₅₀, (e) M·2B₂₀₀, (f) M·2B₄₀₀ after immersed in ethylene glycol (EG). The insets are the corresponding diagram illustration.

Reference

- [1] H.B. Zheng, W. Chen, H. Gao, Y.Y. Wang, H.Y. Guo, S.Q. Guo, Z.L. Tang, J.Y. Zhang, *Journal of Materials Chemistry C* 5 (2017) 10746–10753.