SOLID SOLUTION FORMATION, PRESSURELESS DENSIFICATION, AND PROPERTIES OF $TA_{0.8}HF_{0.2}C$-BASED COMPOSITES

Buhao Zhang[1], Jie Yin[2], Xuejian Liu[3], and Zhengren Huang[4]

[1] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, zhangbuhao@student.sic.ac.cn
[2] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, jieyin@mail.sic.ac.cn
[3] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, xjliu@mail.sic.ac.cn
[4] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, zhrhuang@mail.sic.ac.cn

Keywords: TaC, HfC, Solid solution, Densification, Pressureless sintering

ABSTRACT

The solid solution formation and densification of $Ta_{0.8}Hf_{0.2}C$-(10, 20, 30vol%)SiC composites with different carbon additions by pressureless sintering at 2200℃ were investigated. Highly densified $Ta_{0.8}Hf_{0.2}C$-based composites were pressureless sintered with homogeneous elemental (Ta, Hf) distributions. High Resolution Transmission Electron Microscopy (HRTEM) indicated that the solid solution formation contributed to the densification progress of $Ta_{0.8}Hf_{0.2}C$ ceramics. $Ta_{0.8}Hf_{0.2}C$-(10, 20, 30vol%)SiC were pressureless densified and the densification mechanism was revealed. The mean grain sizes decreased from 13.6 to 2μm with the increasing SiC content. The mechanical properties, including Vicker's Hardness, elastic modulus, flexural strength and fracture toughness were tailored by the variation of SiC content.

1 INTRODUCTION

Tantalum carbide (TaC) and hafnium carbide (HfC), possessing unique physical and structural properties such as the high melting point (>4000K), high hardness (15-20GPa), and superior thermal and chemical stabilities among the UHTCs, have been attracting a lot of investigation recently. Notablely, TaC and HfC, sharing the same NaCl-type structure (*B1*, space group *Fm3m*), can form a continuous solid solution over the whole range of composition above 1200K. It has been reported that the solid solution $Ta_{0.8}Hf_{0.2}C$ has the highest melting point among all the known inorganic materials and maintains optimized mechanical properties via location stress field created by lattice distortions (Ta:0.1457nm; Hf:0.1585nm). Owing to the strong bonds that exhibit a mixture of covalent and ionic character, the chemically stable $Ta_{0.8}Hf_{0.2}C$ is able to serve in both deficient or rich oxygen concentration high temperature conditions as a versatile material. It is the candidate material for potential ultra-high temperature applications in reusable thermal protection systems (leading edges and nose caps of next-generation hypersonic vehicles), rocket propulsion lining and advanced energy systems (nuclear fusion reactors and concentrating solar powers).

It is worth densifying the low-cost production of complex-shaped components with good mechanical and thermal characteristics by pressureless sintering (PLS) for more applications. Besides, reports on the densification (mechanism) of $Ta_{0.8}Hf_{0.2}C$ were scares, majorly by SPS technique. The driving force provided by SPS is responsible for heating the mixed powders and accommodating the diffusion to densification, pior to solid solution formation. The sequence of emergence of densification and solid solution formation should be reconsidered by PLS.

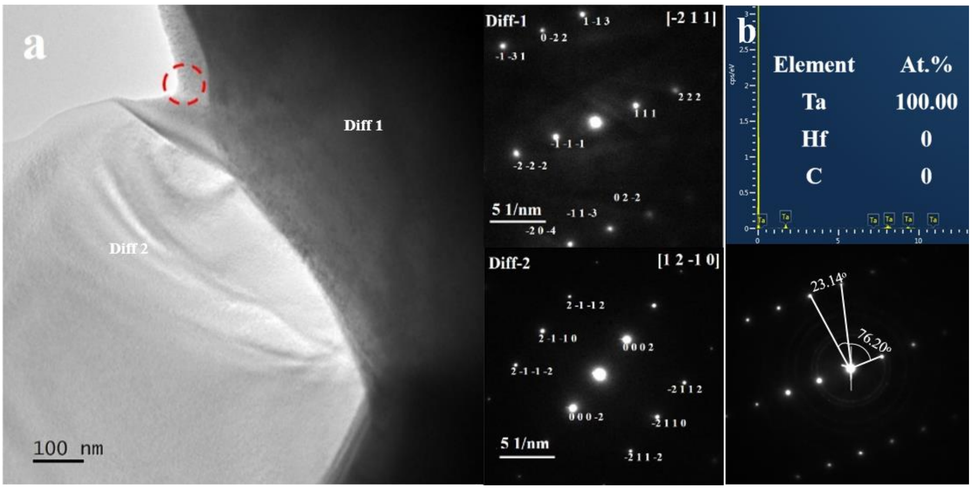

Figure: (a)TEM image of the the THS-III grains inserted with SAED patterns; (b)EDS and SAED taken from red circle in (a);

2 CONCLUSIONS

The $Ta_{0.8}Hf_{0.2}C$ ceramics were firstly pressurelessly densified at 2200°C with series of sub-micron SiC (0, 10, 20, 30)vol% addition. The final lattice parameters of TH was quite consistent with the calculated value by Vegard's Law.

Solid solutioning [1600°C, 2200°C] proceeded during the densification stage. Solid solution (TH) formation decreased the activation energy for diffusion at grain boundaries and contributed to the final densification and grain coarsening. The soaking time at the peak temperature led to elimination of transgranular closed pores.

The grain growth of TH was inhibited by adding sub-micron SiC. An intermediate layer between the SiC and TH matrix was found and characterized to be TaC by EDS and SAED techniques. The HRTEM further illustrates the structure that HfC cubic nanocrystals were embedded in the TaC matrix. The diffusion rate of Hf can be reduced by pinning effect of secondary phase. Such controlling of diffusion along grain boundary inspired a new route to tailor the micro/nanostructure of solid solution.

A gradual reduction of the CTE was found from $7.028\times10^{-6}\,K^{-1}$ to $6.407\times10^{-6}\,K^{-1}$ as the SiC content increased, and room thermal conductivity improvement from the intial 18.616 W/m*K (TH) to 41.507 W/m*K (THS-III) was found. The defects located around HfC nanocrystals in the TaC matrix intermediate layer might play a negative role on the thermal property further improvement. The indentation toughness of THS-III ($4.72 MPa\cdot m^{1/2}$) was 29.3% higher than TH ($3.65\ MPa\cdot m^{1/2}$). The flexural strength, elastic modulus and Vickers hardness decreased with the addition of SiC. The presences of residual carbon and pores played a critical role in influencing the mechanical properties.

ACKNOWLEDGEMENTS

This work was financially supported by the Natural Science Foundation of China (No. 51602325) and State Key Laboratory of Fine Ceramics and Superfine Structure of Shanghai Institute of Ceramics (SKL201602).

REFERENCES

[1] O. Cedillos-Barraza, S. Grasso, N. Al Nasiri, D.D. Jayaseelan, M.J. Reece, and W.E. Lee, Sintering behaviour, solid solution formation and characterisation of TaC, HfC and TaC–HfC fabricated by spark plasma sintering, *Journal of the European Ceramic Society*, **36**, 2016, pp. 1539-1548 (doi:10.1016/j.jeurceramsoc.2016.02.009).

[2] O. Gaballa, B. A.Cook, and A.M. Russell, Reduced-temperature processing and consolidation of ultra-refractory Ta_4HfC_5, *International Journal of Refractory Metals and Hard Materials*, **41**, 2013, pp.293-299(doi.:10.1016/j.ijrmhm.2013.04.018).