

9-18-2017

# Feasibility research of gaining “refractory high entropy carbides” through in situ carburization of refractory high entropy alloys

Yuanlin Ai

*National University of Defense Technology, 495586680@qq.com*

Shuxin Bai

*National University of Defense Technology*

Li'an Zhu

*National University of Defense Technology*

Yicong Ye

*National University of Defense Technology*

Follow this and additional works at: [http://dc.engconfintl.org/uhtc\\_iv](http://dc.engconfintl.org/uhtc_iv)



Part of the [Engineering Commons](#)

## Recommended Citation

Yuanlin Ai, Shuxin Bai, Li'an Zhu, and Yicong Ye, "Feasibility research of gaining “refractory high entropy carbides” through in situ carburization of refractory high entropy alloys" in "Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications IV", Jon Binner, The University of Birmingham, Edgbaston, United Kingdom Bill Lee, Imperial College, London, United Kingdom Eds, ECI Symposium Series, (2017). [http://dc.engconfintl.org/uhtc\\_iv/53](http://dc.engconfintl.org/uhtc_iv/53)

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications IV by an authorized administrator of ECI Digital Archives. For more information, please contact [franco@bepress.com](mailto:franco@bepress.com).



**国防科技大学**

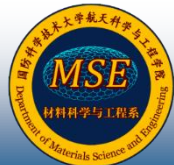
National University of Defense Technology



# **Feasibility Research of Gaining “Refractory High Entropy Carbides” Through In Situ Carburization of Refractory High Entropy Alloys**

**Lian Zhu, Yuanlin Ai, Shuxin Bai**

**National University of Defense Technology, China**



# Outline

1

**Introduction**

2

**Experimental**

3

**Results and discussion**

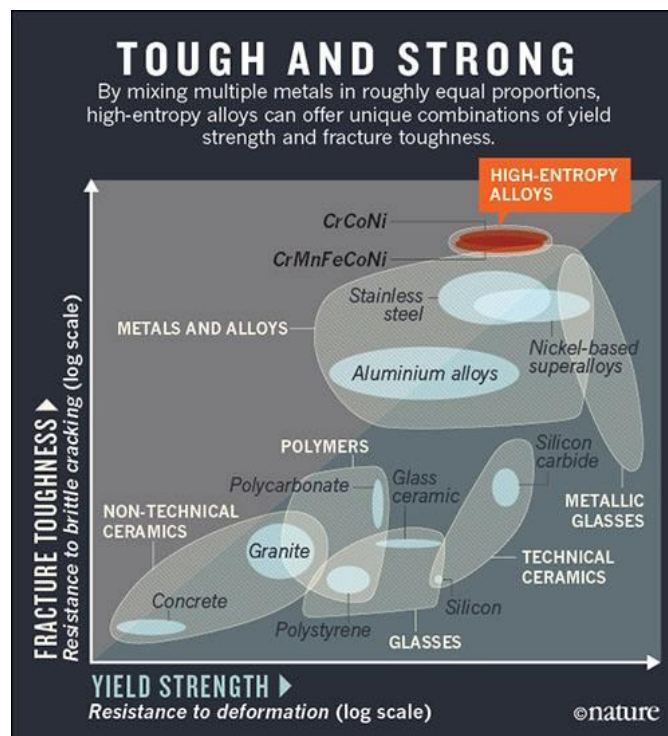
4

**Conclusions**

# 1. Introduction

## ● High-entropy alloys (HEAs)

- First proposed by Yeh in 2004
- Excellent comprehensive properties
- 4 core effects



Gludovatz, B. *et al. Nature Commun.* **7**, 10602 (2016)

# 1. Introduction

- **High-entropy ultra-high temperature ceramics (HEUHTCs) ?**
  - Entropy stabilized material?
  - Excellent comprehensive properties?

High entropy alloy → High entropy carbide ceramic

HfZrTiTa → (Hf,Zr,Ti,Ta)C

SCIENTIFIC REPORTS

OPEN High-Entropy Metal Diborides: A New Class of High-Entropy Metal Alloys and Ultra-high Temperature Ceramics

Joshua Gild<sup>1</sup>, Yuanyao Zhang<sup>2</sup>, Tyler Harrington<sup>1</sup>, Sicong Jiang<sup>1</sup>, Tao Hu<sup>1</sup>, Matthew C. Quinn<sup>1</sup>, William M. Mellor<sup>1</sup>, Naizhe Zhou<sup>1</sup>, Kenneth Vecchio<sup>1,2</sup> & Jian Luo<sup>1,2</sup>

Seven equimolar, five-component, metal diborides were fabricated via high-energy ball milling and spark plasma sintering. Six of them, including  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$ ,  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Mo_{0.2}Ti_{0.2})B_2$ ,  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2}Ta_{0.2})B_2$ ,  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2}Ta_{0.2}Ta_{0.2})B_2$ ,  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2}Ta_{0.2}Ta_{0.2})B_2$ , and  $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2}Ta_{0.2}Ta_{0.2})B_2$ , possess virtually one solid-solution boride phase of the hexagonal  $AB_2$  structure. Revised Hume-Rothery size-difference factors are used to rationalize the formation of high-entropy solid solutions in these metal diborides. Greater than 92% of the theoretical densities have been generally achieved with large uniform compositions from nanoscale to microscale. Aberration-contrast electron transmission electron microscopy (AC-TEM) with high-angle annular dark-field (HAADF) electron spectroscopy (EDS) and energy-dispersive X-ray (EDX) mapping, has been used to confirm the formation of a single phase. These metal diborides represent a new type of ultra-high temperature ceramics (UHTCs) as well as a new class of high-entropy materials that not only exemplify the first high-entropy non-oxide ceramic (boride) fabricated but also possess unique non-cubic (hexagonal) and layered (quasi-2D) high-entropy crystal structure that makes them suitable for high-temperature applications. The excellent mechanical properties and oxidation resistance of these high-entropy metal diborides are greatly enhanced by carburization and the oxidation resistance of these high-entropy metal diborides made by identical fabrication processing.

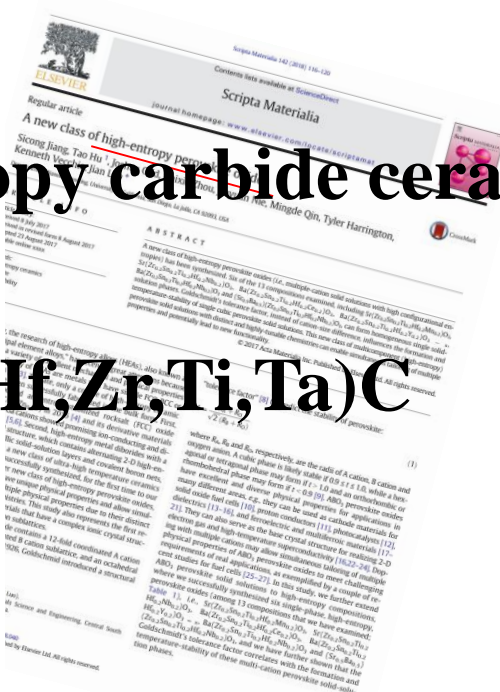
Recently, the fabrication and properties of metallic high-entropy alloys (HEAs) have attracted significant research interest<sup>1</sup>. In an HEA, the configurational entropy of a solid-solution phase is maximized to stabilize it against the formation of intermetallics. Typically, five or more elements can be mixed in a HEA in equimolar concentrations to produce a maximum molar configurational entropy of  $k_B \ln \Omega$ , where  $\Omega$  is the number of equimolar components and  $k_B$  is the gas constant<sup>2</sup>. HEAs have shown superior mechanical and physical properties<sup>3</sup>, especially, a series of recent studies fabricated a class of refractory metallic HEAs and demonstrated their excellent wear resistance and strength, including (especially) exceptional high-temperature properties<sup>4-6</sup>. Since the minimization of Gibbs free energy ( $G = H - TS$ , where  $H$  is enthalpy,  $S$  is entropy, and  $T$  is temperature) dictates the thermodynamic stability of a material at a constant pressure, a high-entropy material (with large  $S$ ) can be thermodynamically more stable (particularly) at high temperatures, motivating this study to explore the phase stability and fabrication feasibility of high-entropy metal diborides, as a new type of high-entropy materials as well as a new class of ultra-high temperature ceramics (UHTCs).

Most prior studies of crystalline high-entropy materials have been conducted for metallic HEAs of mostly simple face- and body-centered cubic (FCC) and BCC), as well as occasionally hexagonal close packing (HCP), crystal structures<sup>7</sup>. Much less studies have been done for making crystalline high-entropy ceramics (with the glass can be considered high-entropy materials in a broad definition), particularly those with more complex, non-cubic, crystal structures. Most recently, Koo *et al.* successfully fabricated an entropy-stabilized oxide,  $(Mo_{0.2}Ca_{0.2}Ni_{0.2}Cu_{0.2}Zr_{0.2})O_3$  that possessed a single-phase rock-salt (which is also a FCC) structure when it was

<sup>1</sup>Program of Materials Science and Engineering, University of California, San Diego, La Jolla, CA 92093-0448, USA; <sup>2</sup>Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093-0448, USA. Correspondence and requests for materials should be addressed to J.L. (email: jluo@alum.mit.edu)

Entropy-stabilized oxides  
Christina M. Ross<sup>1</sup>, Edward Saeed<sup>1</sup>, Trent Borman<sup>1</sup>, Ali Mollahajeri<sup>1</sup>, Elif Jacob L. Jones<sup>1</sup>, Stefano Curtarolo<sup>2</sup> & Jon-Paul Maria<sup>1</sup>

Configurational disorder can be compositionally engineered into metal oxides by populating a single sublattice with many distinct cations. The formulations promote novel and entropy-stabilized forms of crystalline matter where metal cations are incorporated in new ways. Here, through various experiments, a simple reasonable doubt that entropy predominates in the thermodynamic landscape of metal oxides is demonstrated. We prove, for the first time, that a multiaxial and homogeneous random and homogeneous configurational disorder can be achieved in metal oxides and discover new phases of crystalline matter.



## 2. Experimental

- Preparation of HfZrTiTa alloy



**Hf+Zr+Ta+Ti  
Powder (1:1:1:1)**



**Vacuum arc  
melting**



**HfZrTiTa HEA**

## 2. *Experimental*

- **Solid carburization**

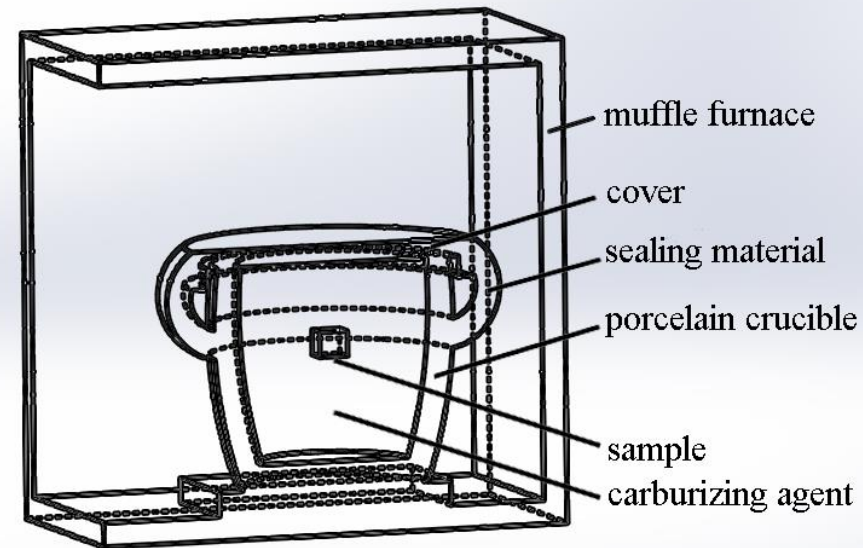
- Pack cementation (900°C, 10h)

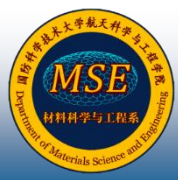
- Carburizing agent (powder):

- 90% C + 10%  $\text{Na}_2\text{CO}_3$
- 90% C + 10%  $\text{CaCO}_3$
- 100% C

- Loading amount

- Full
- Half full





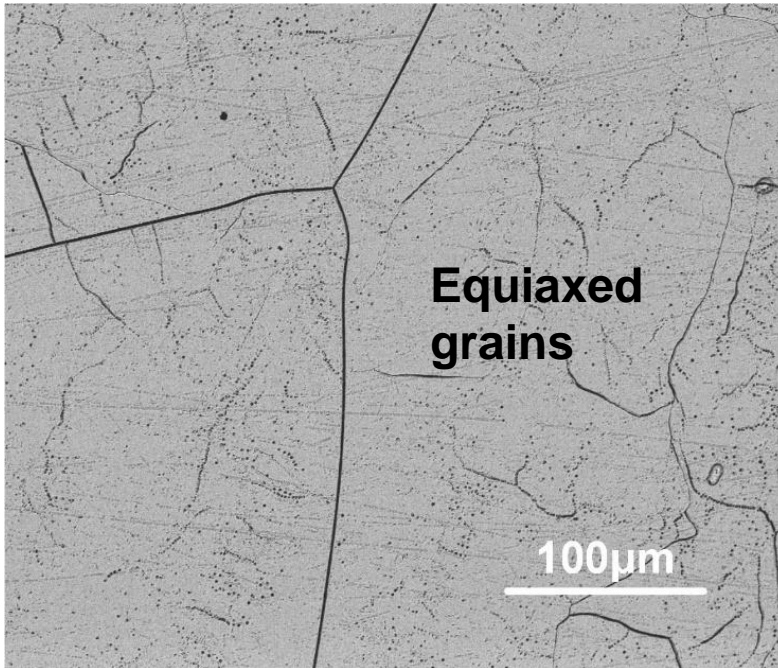
## 2. *Experimental*

- **Testing and characterization**
  - Micro-hardness
    - Load: 50 g; Holding time: 15 s
  - Cyclic oxidation
    - 1300°C 25min
  - XRD
  - SEM
  - EDS

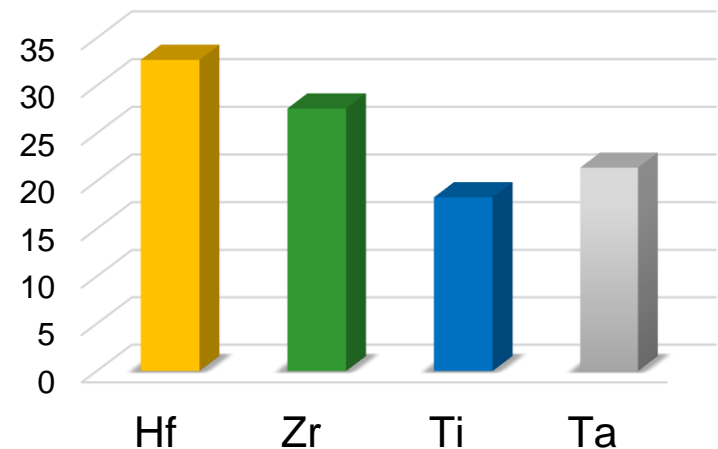
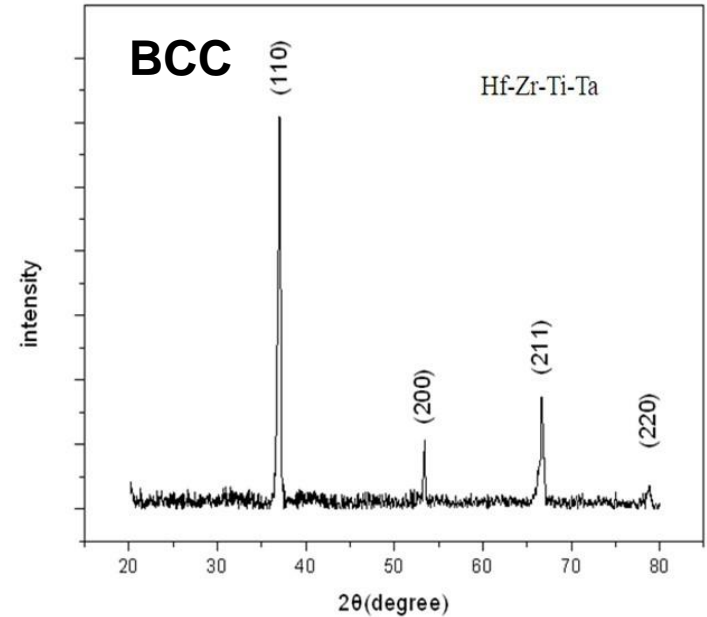


# 3. Results & Discussion

## ● HfZrTiTa alloy



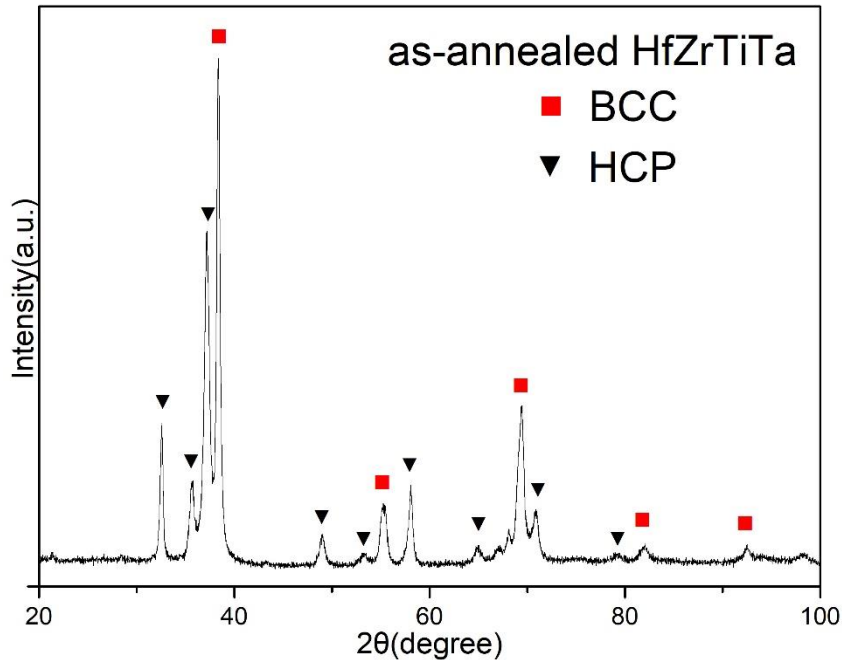
□ BCC single phase structure with near equal atomic percent



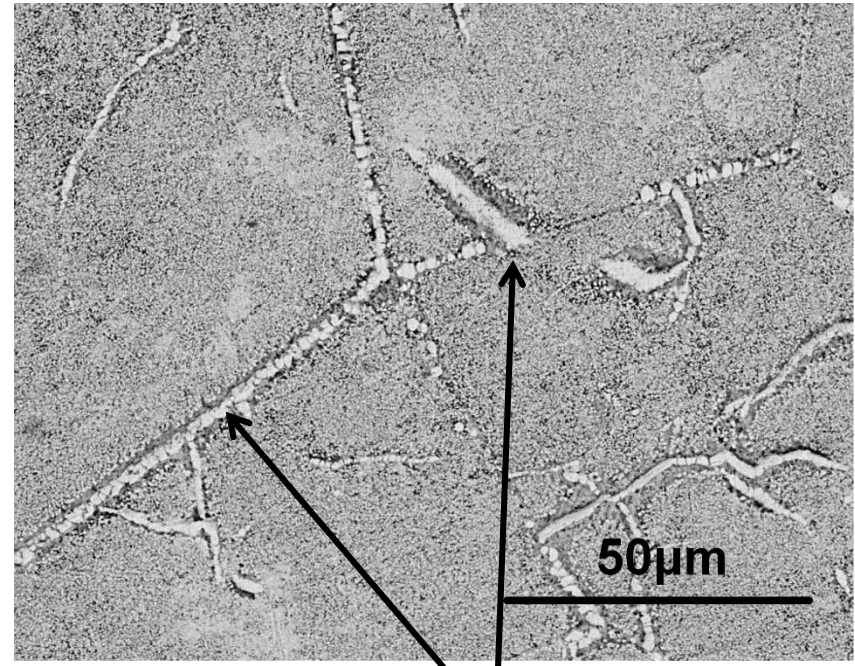
# 3. Results & Discussion

## HfZrTiTa alloy

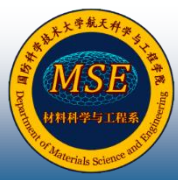
1000°C for 10h, then cooled to room temperature with 10°C/min



Single BCC → BCC+HCP



Grain boundary → precipitation  
enriched with Ta and depleted with Ti, Zr  
and Hf



# 3. Results & Discussion

- Pack cementation process

**Table 1 The results of pack cementation process**

| Loading amount | Carburizing agent                       | Carburized layer |
|----------------|---|------------------|
| Full           | 90%C+10%Na <sub>2</sub> CO <sub>3</sub> | ×                |
| Full           | 90%C+10%CaCO <sub>3</sub>               | ×                |
| Full           | 100%C                                   | ×                |
| Half full      | 90%C+10%Na <sub>2</sub> CO <sub>3</sub> | ×                |
| Half full      | 90%C+10%CaCO <sub>3</sub>               | ×                |
| Half full      | 100%C                                   | √                |



# 3. Results & Discussion

## ● Carburized HfZrTiTa

– Morphology



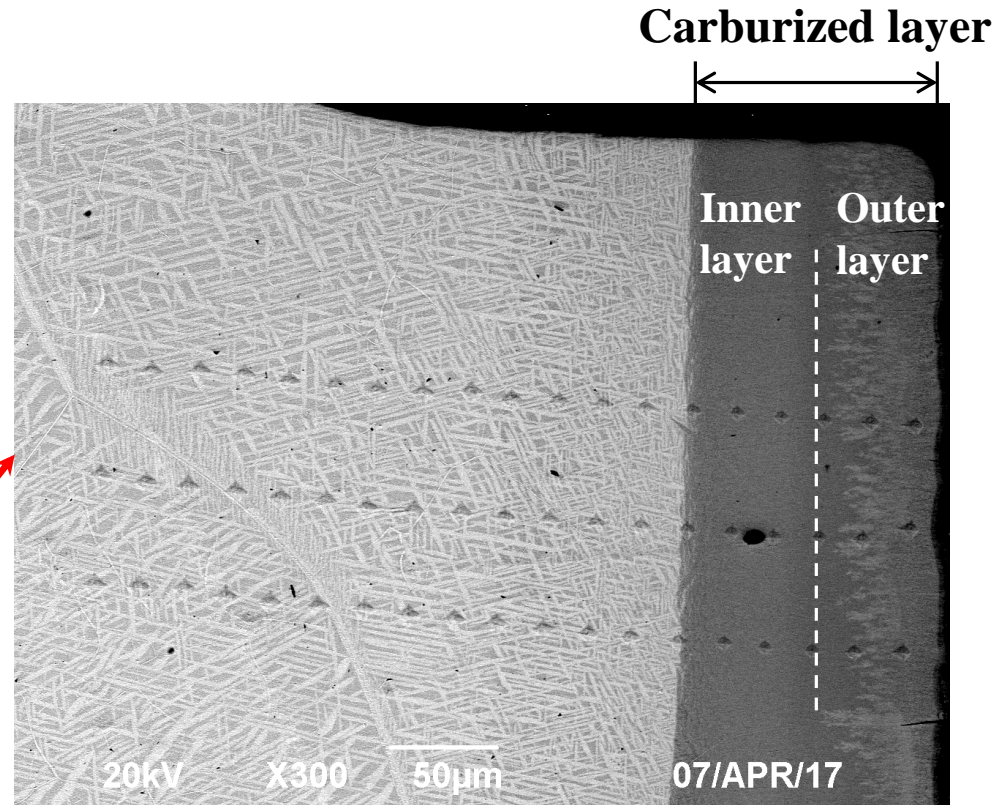
**HfZrTiTa**

100% C  
 ↓  
 900°C, 10h

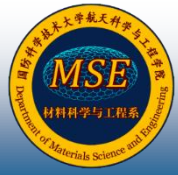
**Cutting**



**Carburized HfZrTiTa**



**Cross sectional morphology**

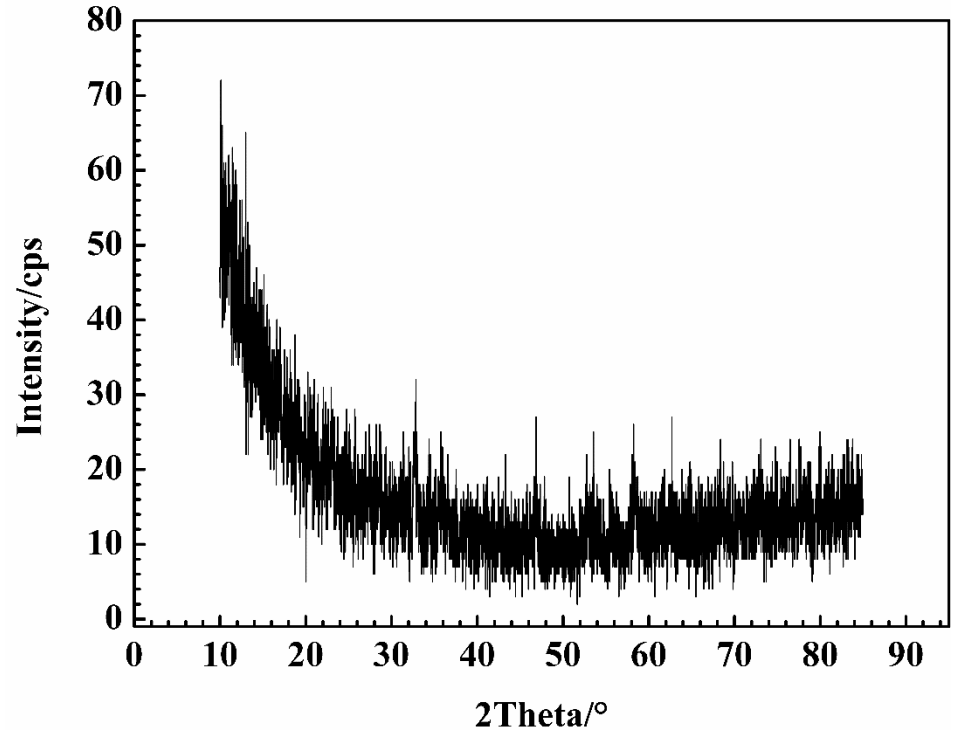


# 3. Results & Discussion

- **Carburized HfZrTiTa**

- XRD

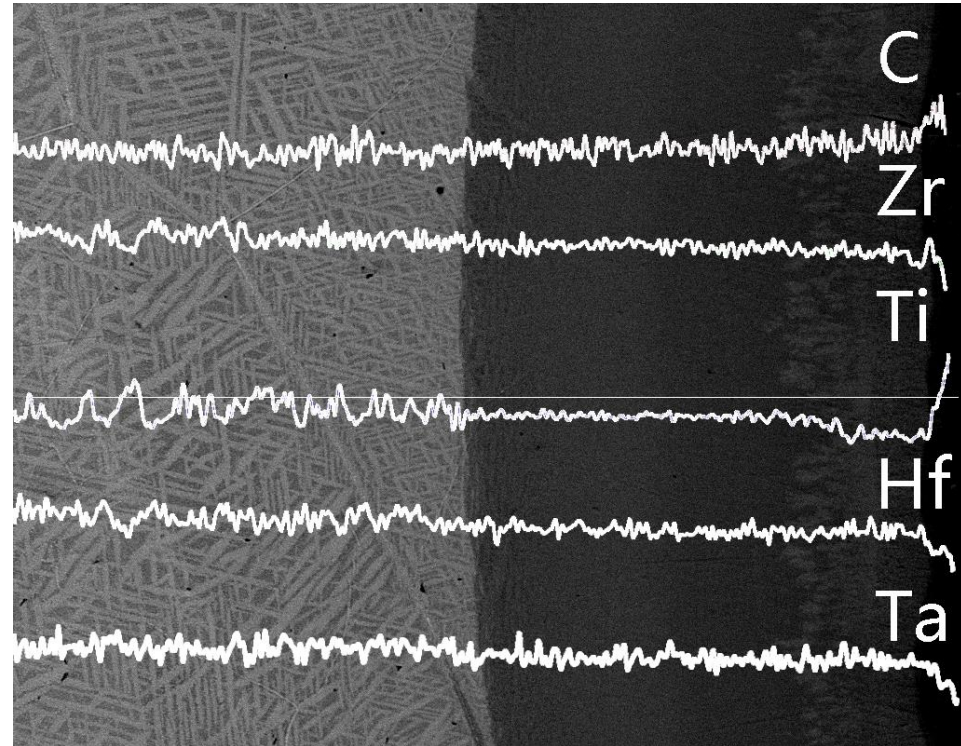
- **No obvious peaks**
    - **Amorphous structure**
    - **HEA based supersaturated solid solution containing C**



**XRD pattern of the carburized HfZrTiTa**

# 3. Results & Discussion

- **Carburized HfZrTiTa**
  - Elemental analysis
- **Uniform element distribution in inner carburized layer**
- **The surface is rich in Ti and C**
- **The substrate adjacent to the carburized layer exhibits an inhomogeneous composition**

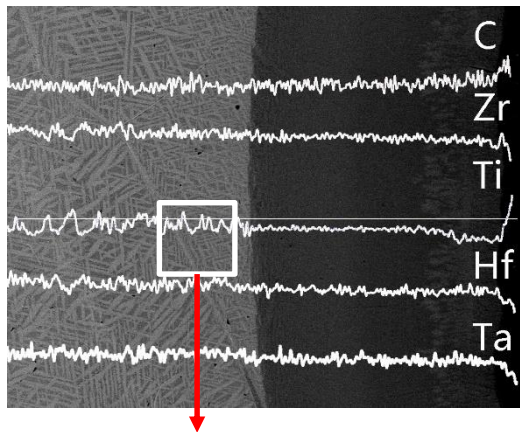


**EDS line-scanning of the sample**

# 3. Results & Discussion

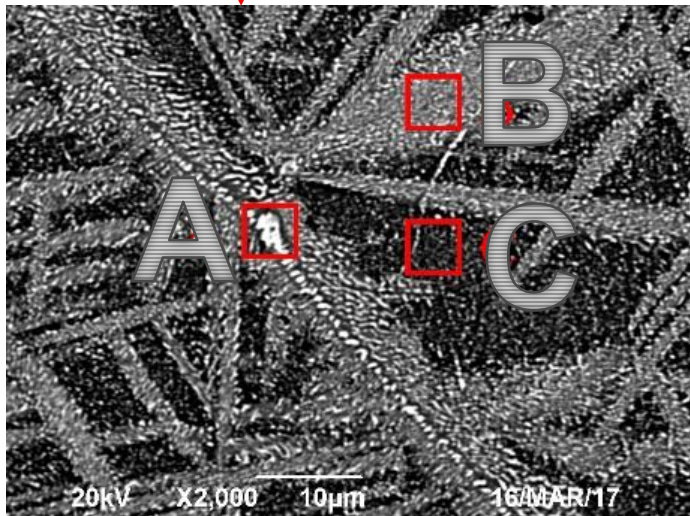
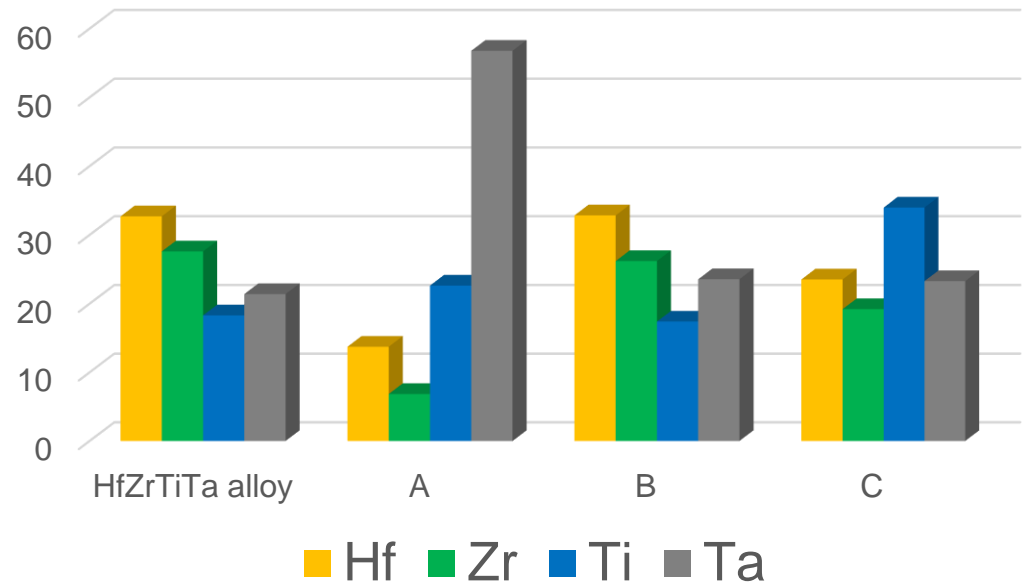
## ● Carburized HfZrTiTa

– Elemental analysis



- A: Ta-rich precipitates
- B: Similar element distribution as the initial alloy
- C: Ti-rich region

Element distribution in different regions

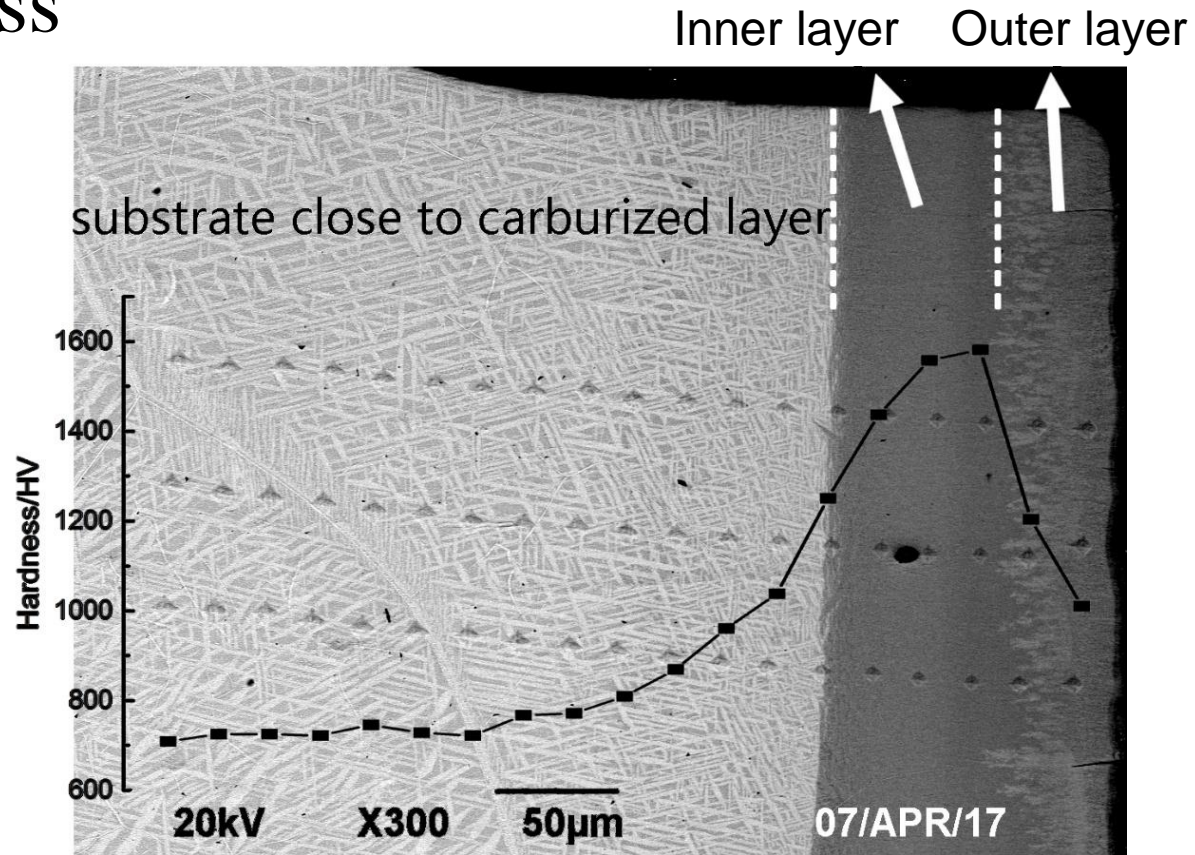


# 3. Results & Discussion

## ● Carburized HfZrTiTa

### – Micro-hardness

- ❑ The maximum hardness was ~1590 HV
- ❑ The average hardness was ~1341 HV
- ❑ The substrate adjacent to the carburized layer was harder than that of HfZrTiTa (~500HV)



The micro-hardness values and corresponding indentations

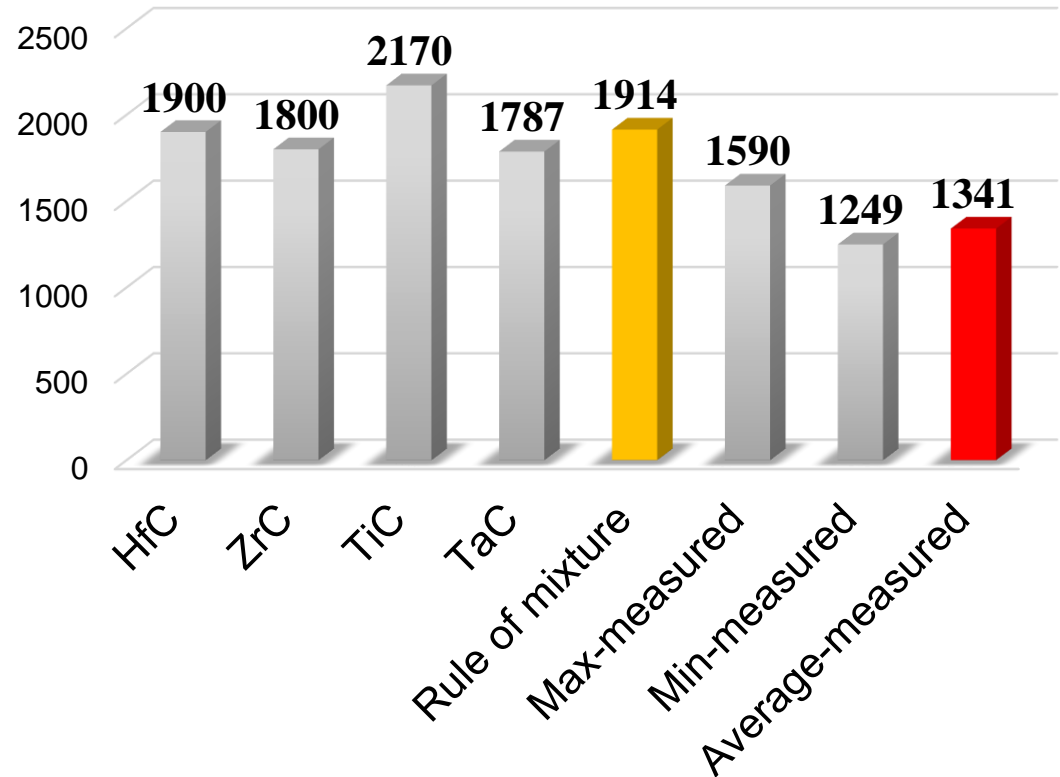


# 3. Results & Discussion

## ● Carburized HfZrTiTa

### – Micro-hardness

- ❑ The measured value is lower than the “rule-of-mixtures” average and that of each individual carbide
- ❑ The carburized coating could be a HEA based C containing supersaturated solid solution
- ❑ The hardness is mainly attributed to the solid solution strengthening

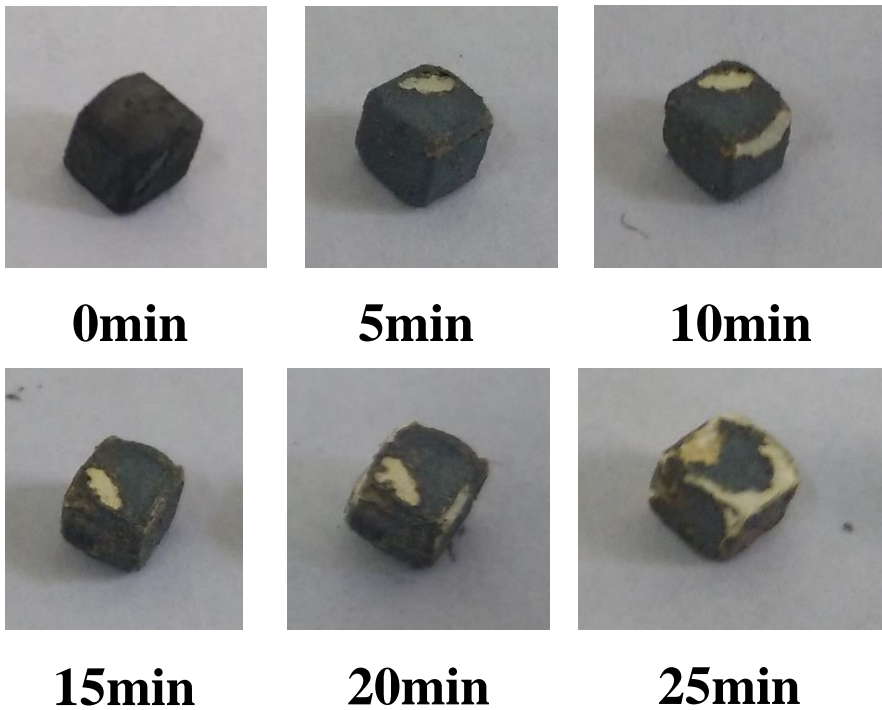


**Comparison of Vicker micro-hardness of carburized layer with the reported values**

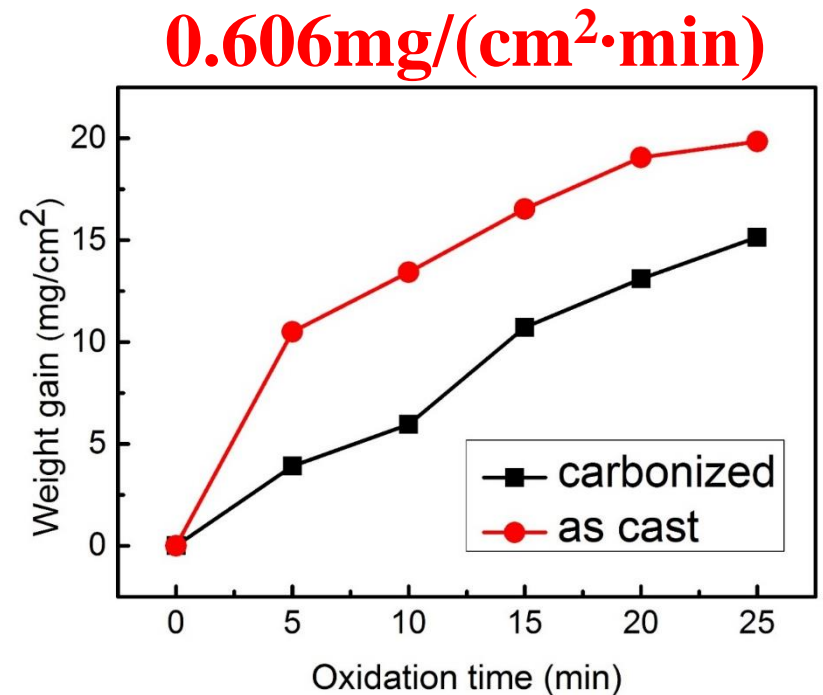
# 3. Results & Discussion

## ● Carburized HfZrTiTa

– Oxidation resistance



Morphology evolution during oxidation

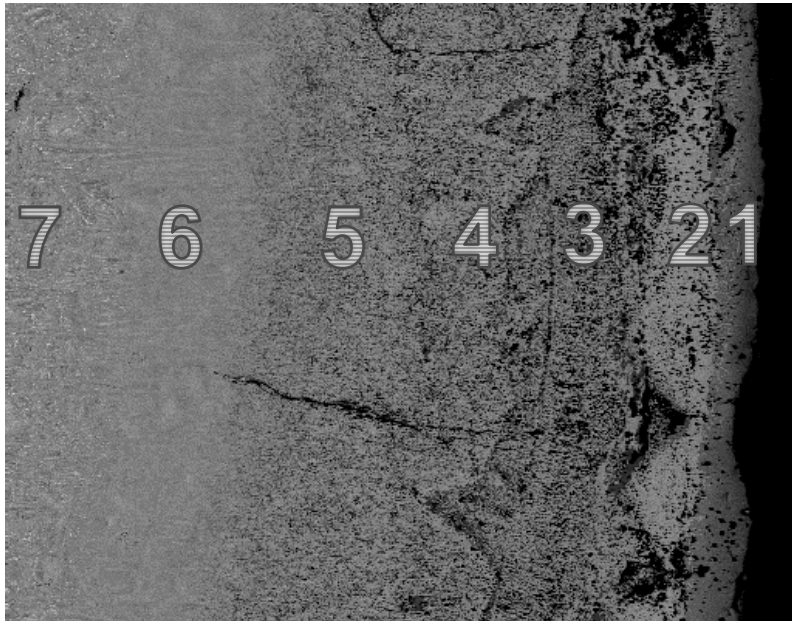


Weight gain VS oxidation time

# 3. Results & Discussion

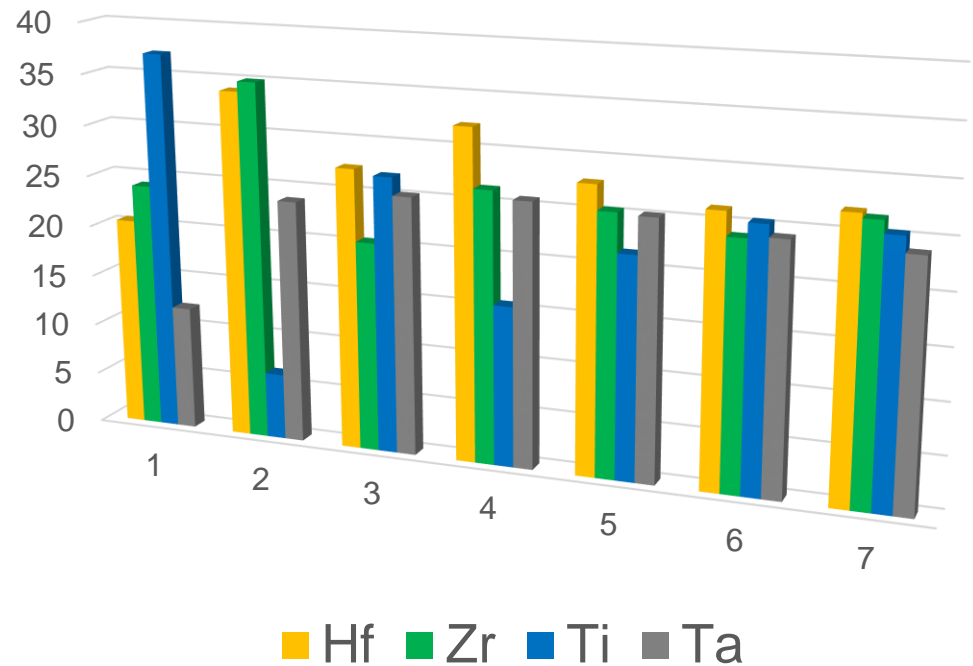
## ● Carburized HfZrTiTa

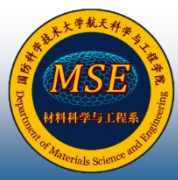
### – Oxidation resistance



The cross sectional morphology of oxidized sample

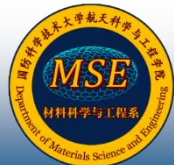
Element distribution in different regions after the oxidation test





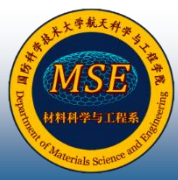
## 4. Conclusions

- A carburized coating with amorphous structure was produced by solid carburization of HfZrTiTa HEA using 100% graphite powder at 900°C for 10 hrs.
- The carburized coating could be a HEA based C containing supersaturated solid solution according to the micro-hardness, XRD and elemental analysis results.
- The poor oxidation resistance may be caused by the large internal stress generated during the oxidation and the quite low oxidation temperature adopted.



# *Acknowledgments*

- **National Natural Science Foundation of China (Grant No. 51501224 & 51371196)**
- **The colleagues and students in our group**
- **The organizers of the conference**



**Thanks for your attention!**