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

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

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National University of Defense Technology, China

Outline

1 Introduction

2 Experimental

3 Results and discussion

4 Conclusions

1. Introduction

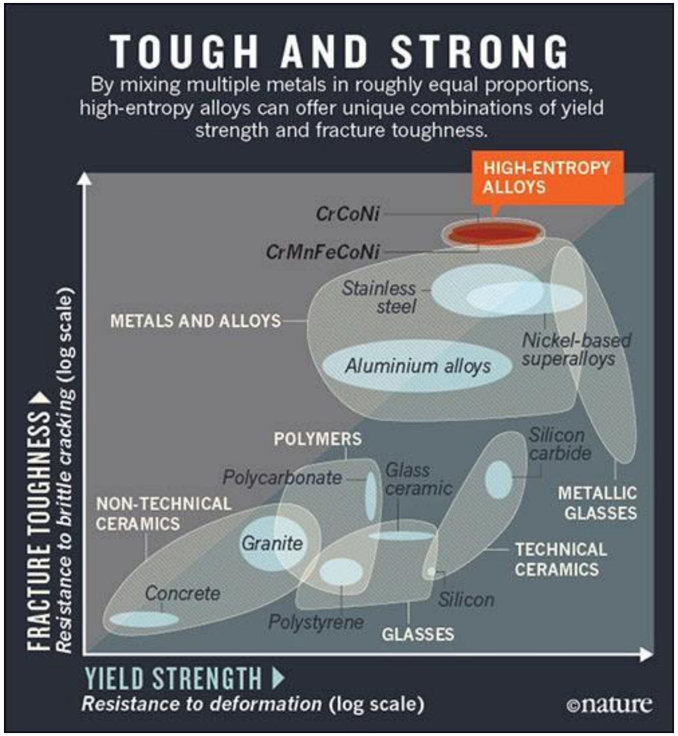
- **High-entropy alloys (HEAs)**
  - First proposed by Yeh in 2004
  - Excellent comprehensive properties
  - 4 core effects

Sluggish diffusion

High-entropy

Severe lattice-distortion

Cocktail



TOUGH AND STRONG

By mixing multiple metals in roughly equal proportions, high-entropy alloys can offer unique combinations of yield strength and fracture toughness.

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 $\xrightarrow{\textbf{Carburization}}$ (Hf,Zr,Ti,Ta)C

nature COMMUNICATIONS

OPEN

Entropy-stabilized oxides

Christina M. Rost, Edward Sachet, Trent Borman, Ali Moballegh, Elizabeth C. Dickey, Dong Hou, Jacob L. Jones, Stefano Curtarolo & Jon-Paul Maria

SCIENTIFIC REPORTS

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High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics

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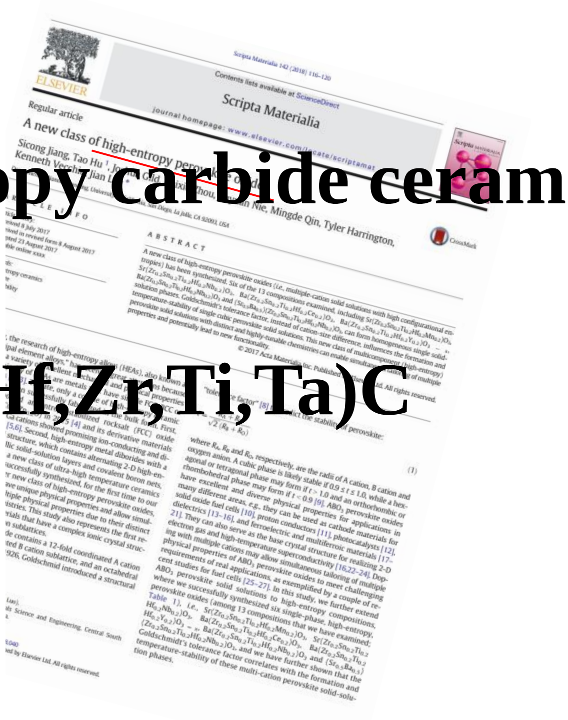
Published: 29 November 2016

Joshua Gild[1], Yuanyao Zhang[1], Tyler Harrington[1], Sicong Jiang[1], Tao Hu[2], Matthew C. Quinn[2], William M. Mellor[2], Naixie Zhou[1], Kenneth Vecchio[1,2] & Jian Luo[1,2]

Seven equimolar, five-component, metal diborides were fabricated via high-energy ball milling and spark plasma sintering. Six of them, including $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$, $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Mo_{0.2}Ti_{0.2})B_2$, $(Hf_{0.2}Zr_{0.2}Mo_{0.2}Nb_{0.2}Ti_{0.2})B_2$, $(Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$, $(Mo_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$, and $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Cr_{0.2}Ti_{0.2})B_2$, possess virtually one solid-solution boride phase of the hexagonal AlB_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 largely uniform compositions from nanoscale to microscale. Aberration-corrected scanning transmission electron microscopy (AC STEM), with high-angle annular dark-field … type of ultra-high temperature ceramics (UHTCs) as well as a new class of high-entropy materials, which not only exemplify the first high-entropy non-oxide ceramics (borides) fabricated but also possess a unique non-cubic (hexagonal) and layered (quasi-2D) high-entropy crystal structure that markedly differs from all those reported in prior studies. … and the oxidation resistance of these high-entropy metal diborides are generally higher/better than the average performances of five individual metal diborides made by identical fabrication processing.



ELSEVIER

Scripta Materialia

Regular article

A new class of high-entropy perovskite oxides

Sicong Jiang, Tao Hu, Joshua Gild, Naixie Zhou, Jiuyuan Nie, Mingde Qin, Tyler Harrington, Kenneth Vecchio, Jian Luo

2. Experimental

- **Preparation of HfZrTiTa alloy**

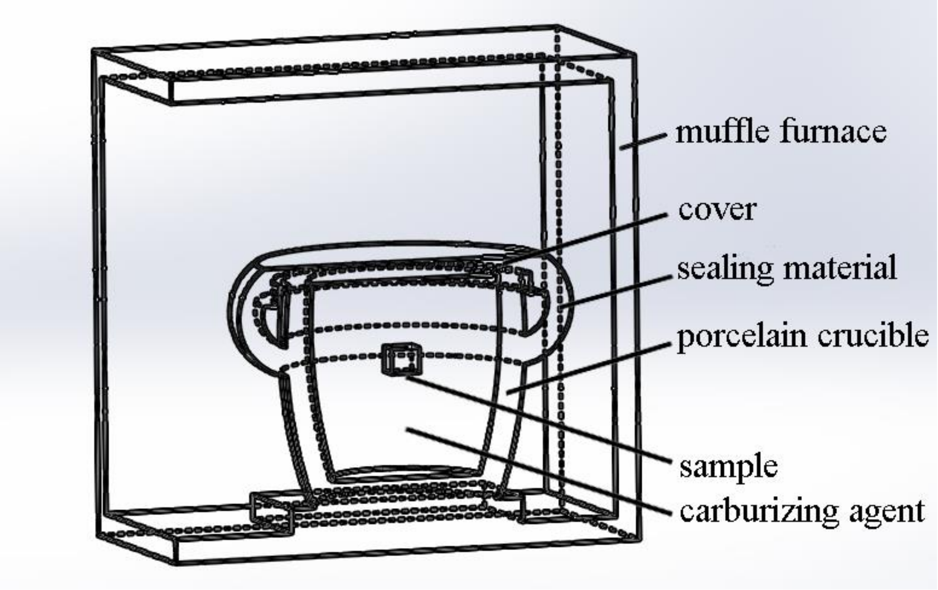
Hf+Zr+Ta+Ti Powder (1:1:1:1)

Vacuum arc melting

HfZrTiTa HEA

2. Experimental

- **Solid carburization**
  - Pack cementation (900℃, 10h)
  - Carburizing agent (powder)：
    - 90%C+10%Na_2CO_3
    - 90%C+10%$CaCO_3$
    - 100%C
  - Loading amount
    - Full
    - Half full

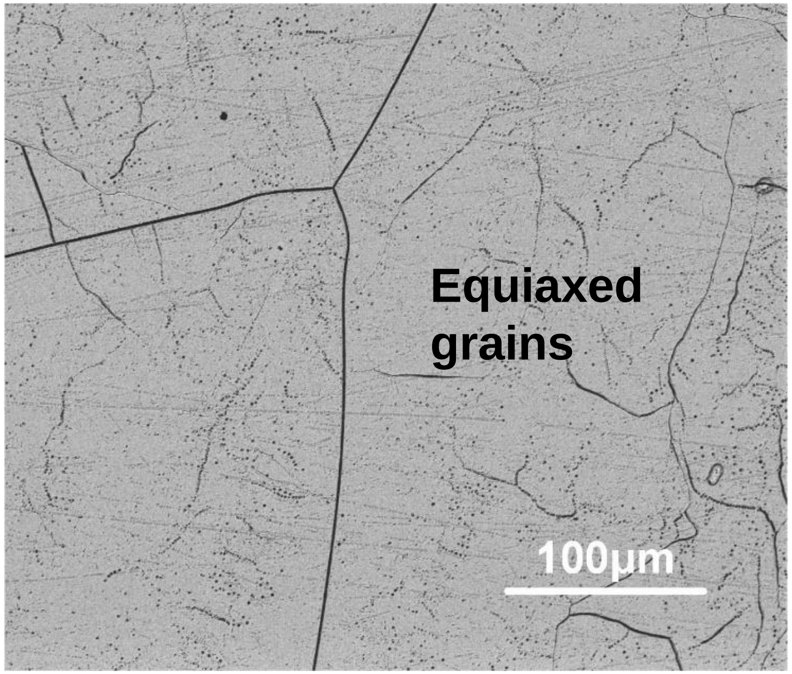


2. Experimental

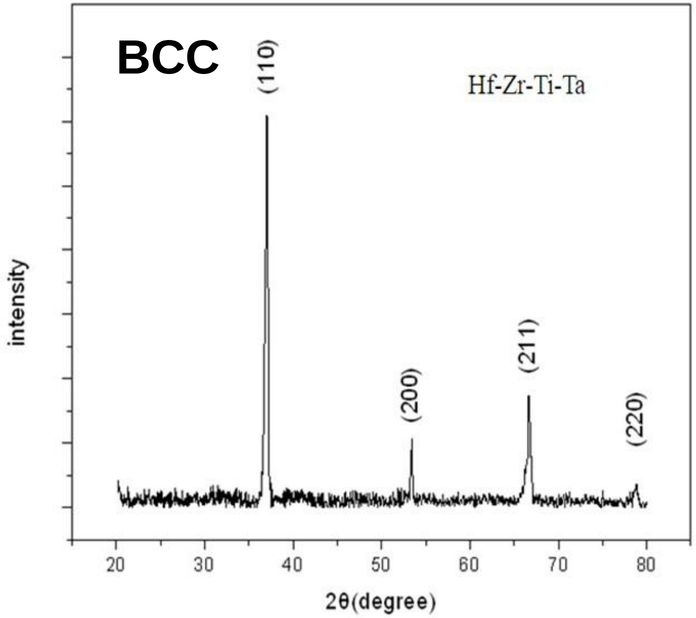
- **Testing and characterization**
  - Micro-hardness
    - Load: 50 g; Holding time: 15 s
  - Cyclic oxidation
    - 1300℃ 25min
  - XRD
  - SEM
  - EDS

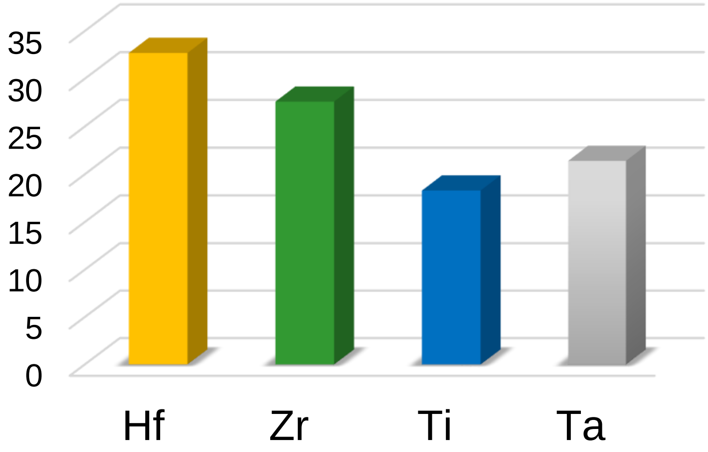
3. Results & Discussion

- **HfZrTiTa alloy**



☐ **BCC single phase structure with near equal atomic percent**

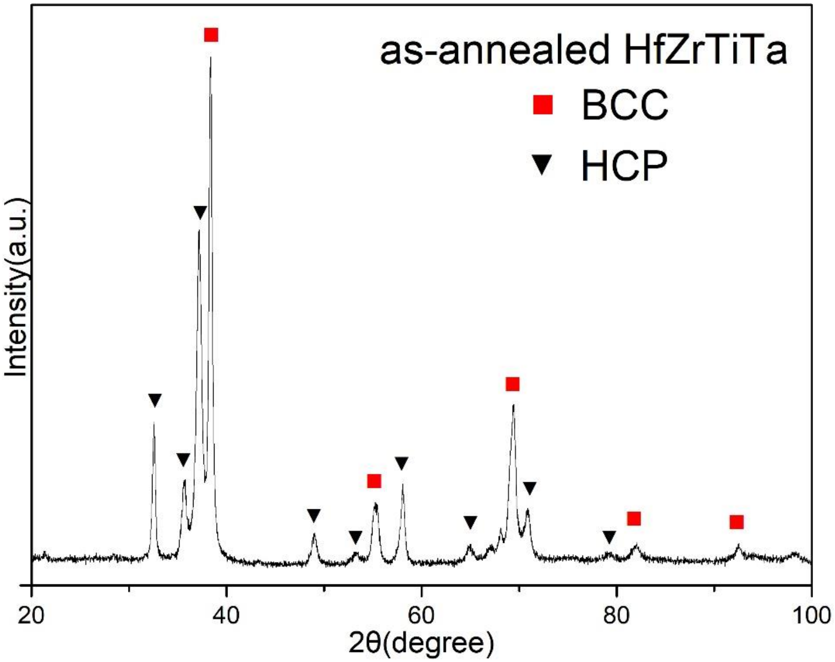




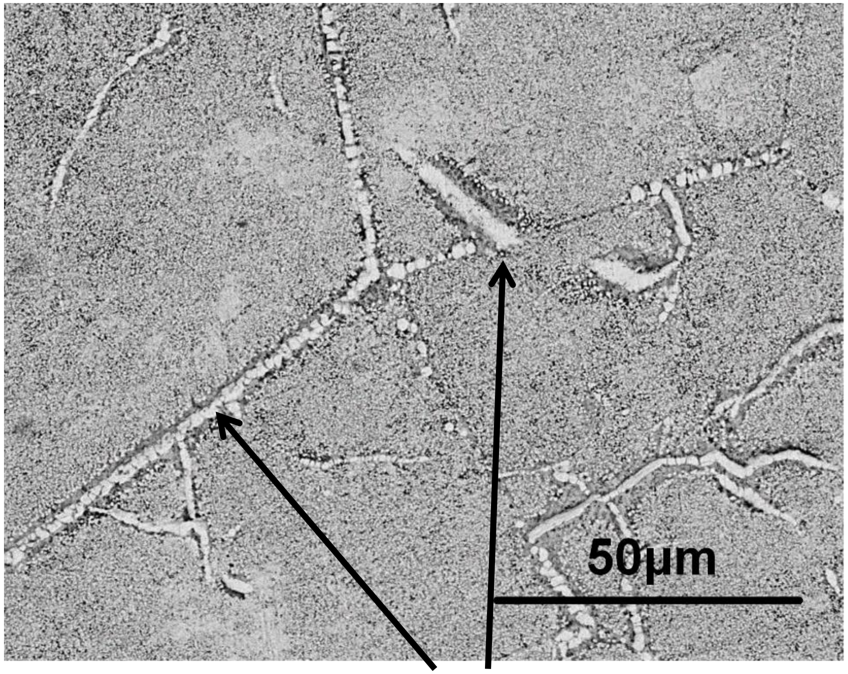
3. Results & Discussion

- **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_2CO_3**	×
Full	**90%C+10%$CaCO_3$**	×
Full	**100%C**	×
Half full	**90%C+10%Na_2CO_3**	×
Half full	**90%C+10%$CaCO_3$**	×
Half full	**100%C**	√

$$C+O_2=CO_2 \quad CO_2+C=2CO$$

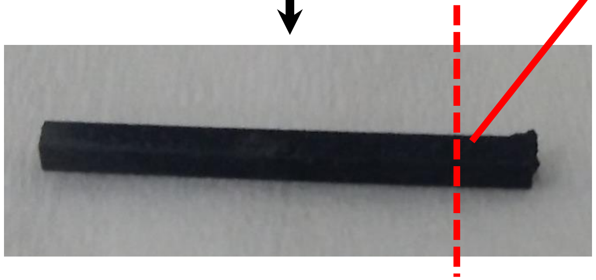
3. Results & Discussion

- **Carburized HfZrTiTa**
  - Morphology

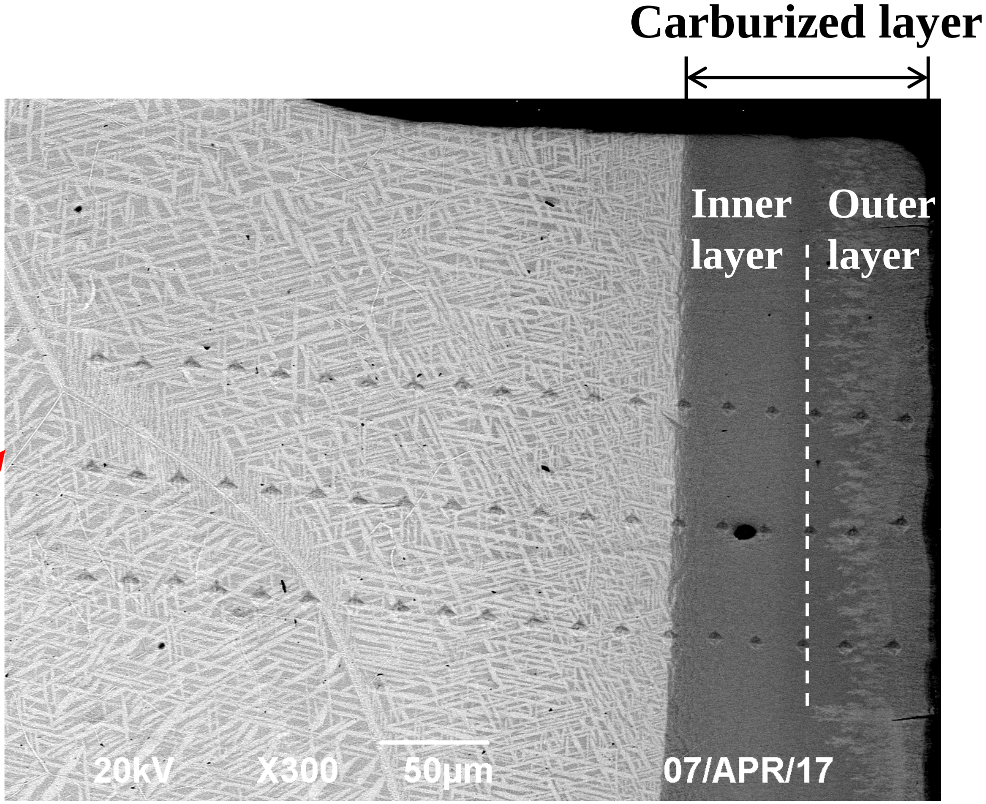
HfZrTiTa

100%C **900℃, 10h**

Cutting



Carburized HfZrTiTa



Cross sectional morphology

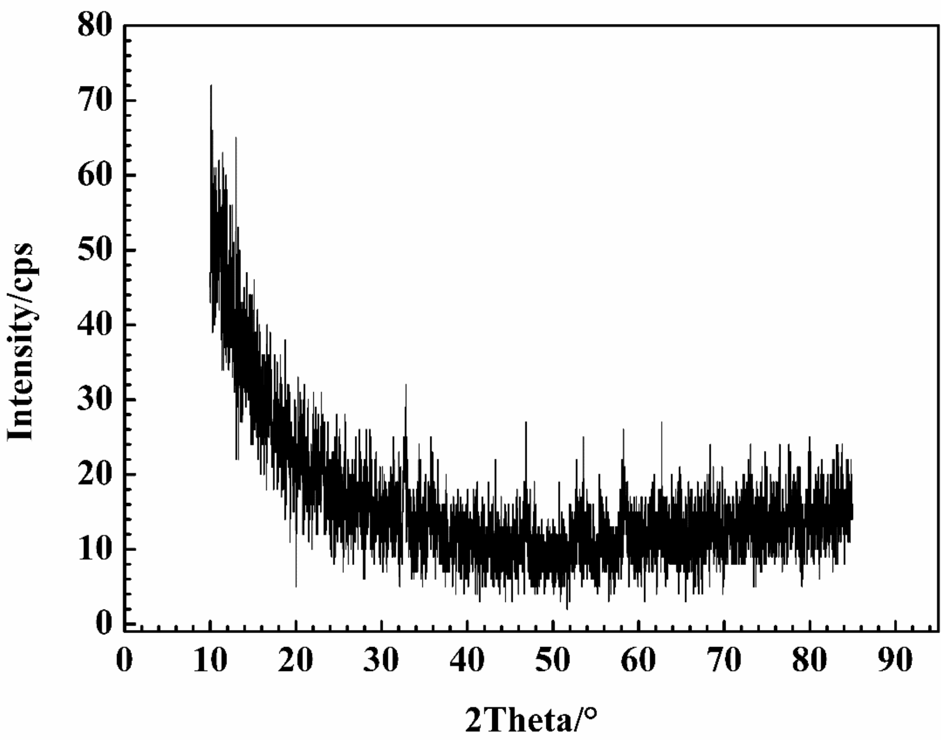
3. Results & Discussion

- **Carburized HfZrTiTa**
  - XRD

☐ **No obvious peaks**

☐ **Amorphous structure**

☐ **HEA based supersaturated solid solution containing C**



XRD pattern of the carburized HfZrTiTa

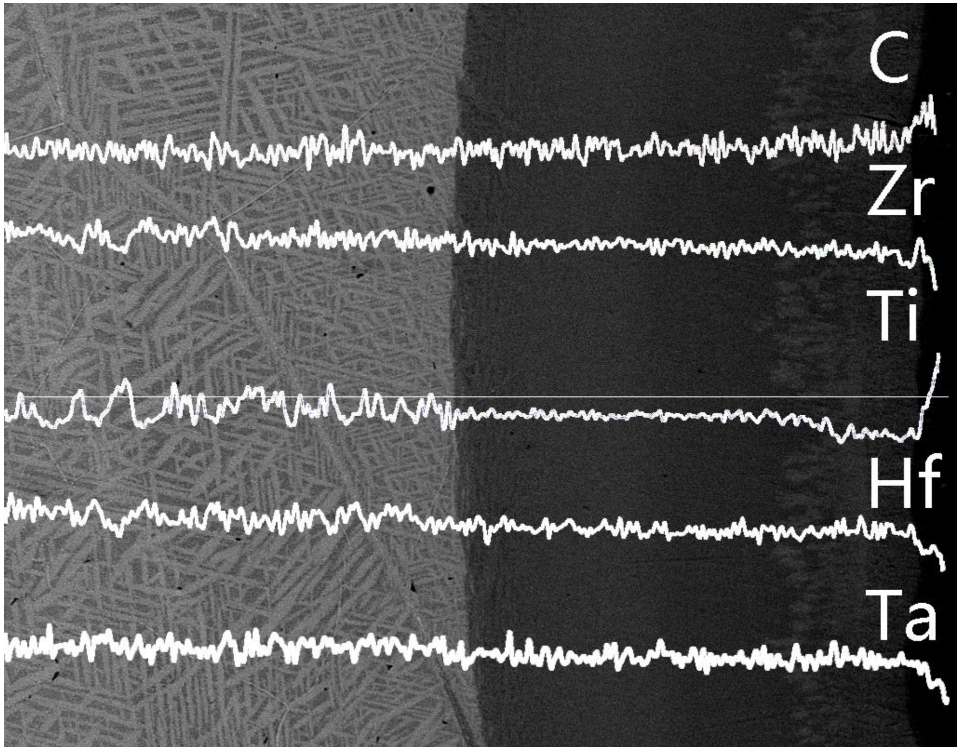
3. Results & Discussion

- **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**

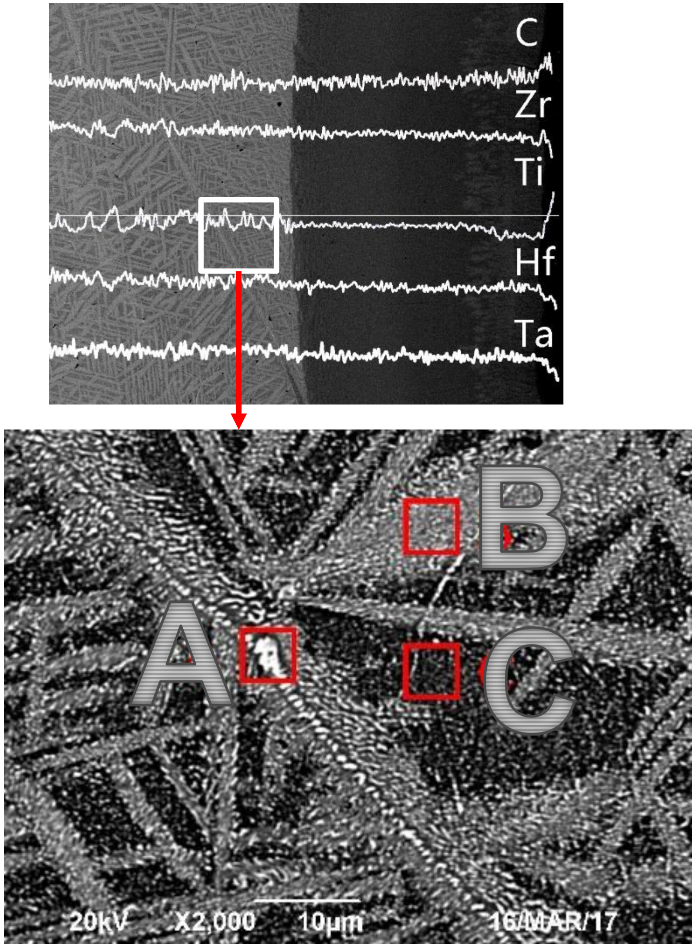


EDS line-scanning of the sample

3. Results & Discussion

Carburized HfZrTiTa

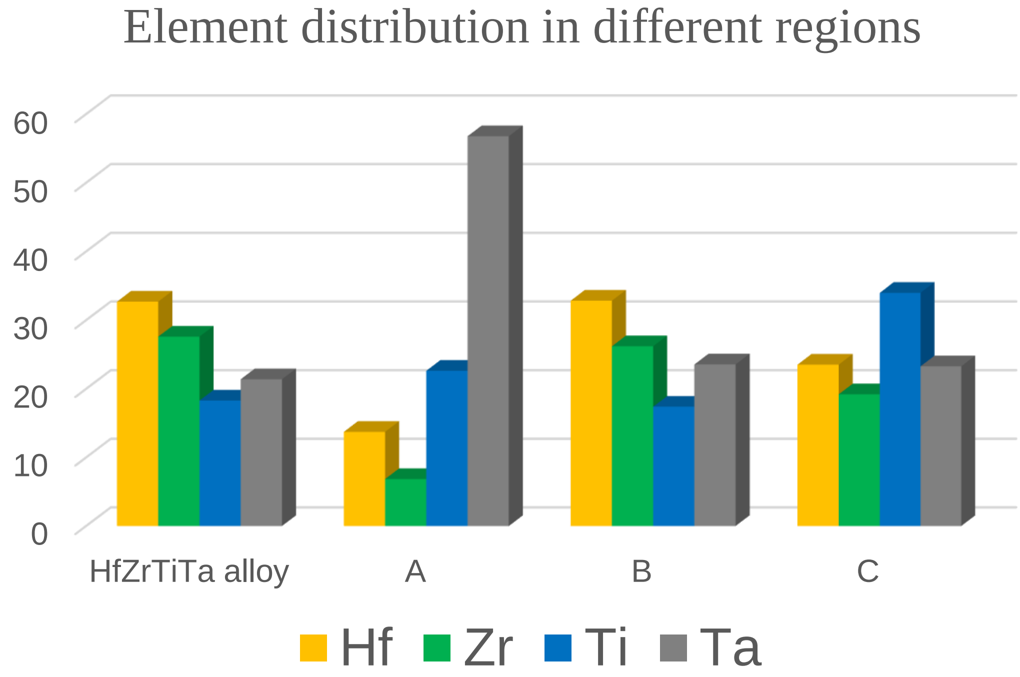
– Elemental analysis



☐ **A: Ta-rich precipitates**

☐ **B: Similar element distribution as the initial alloy**

☐ **C: Ti-rich region**

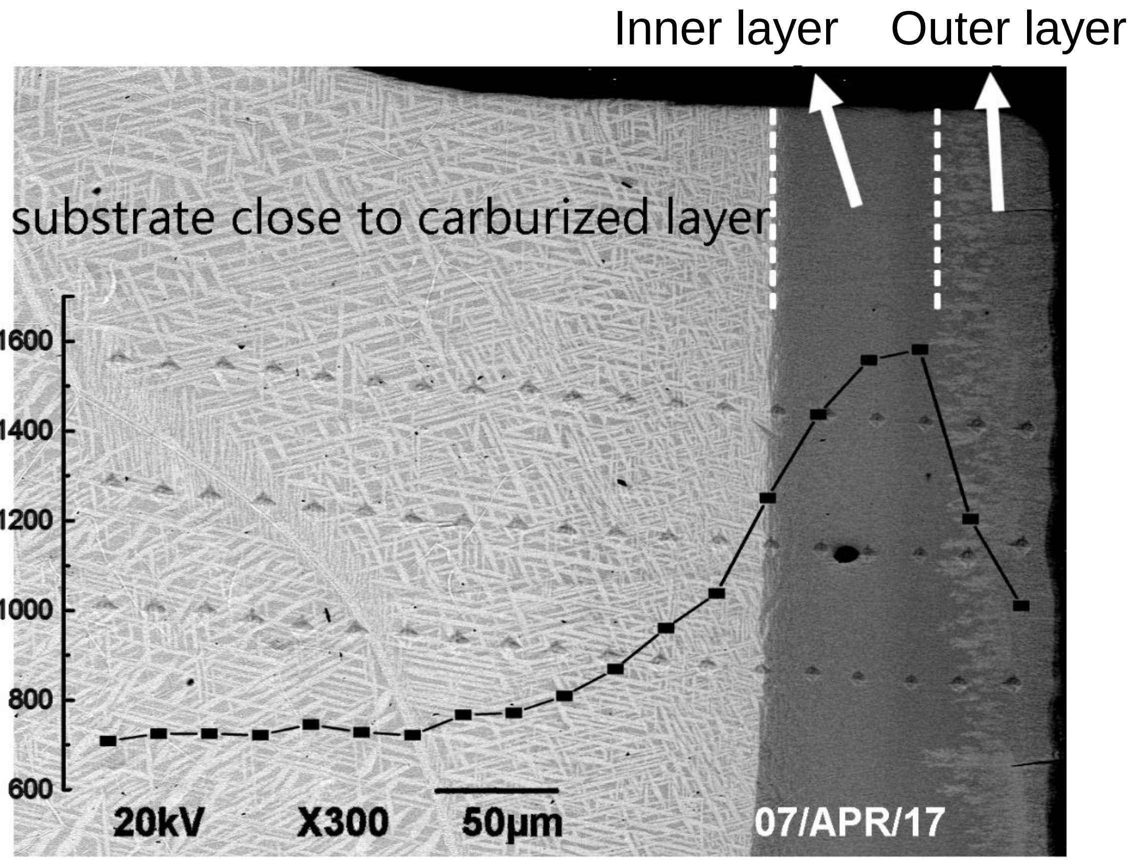


3. Results & Discussion

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)



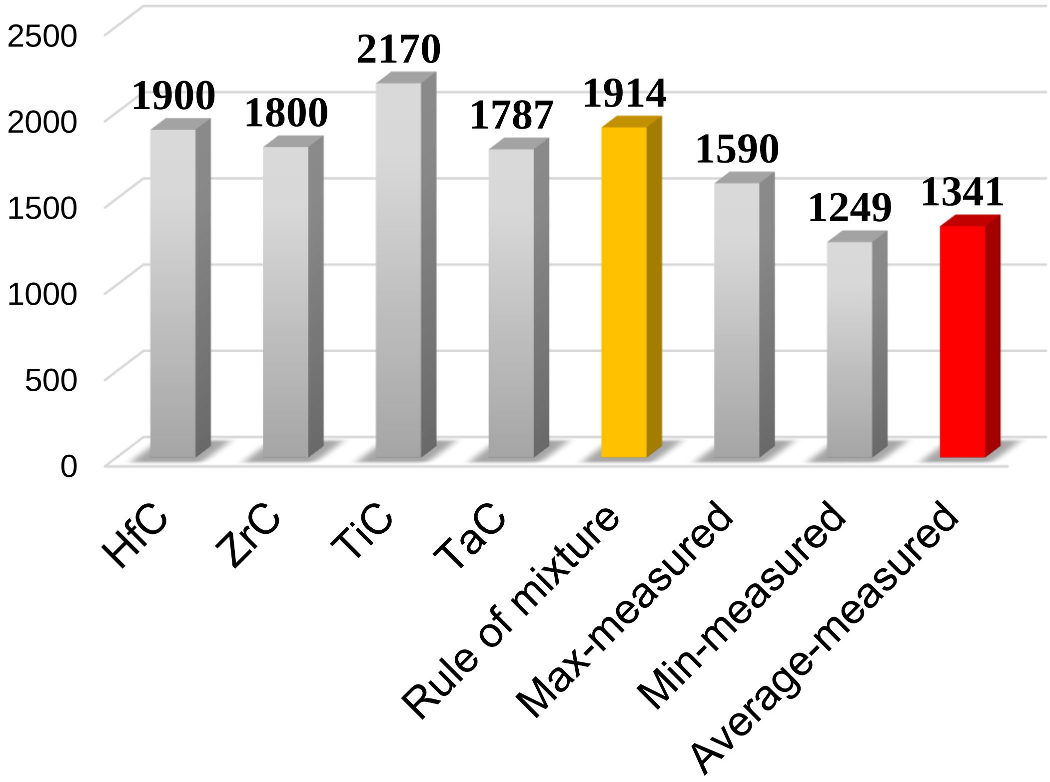
The micro-hardness values and corresponding indentations

3. Results & Discussion

Carburized HfZrTiTa

– Micro-hardness

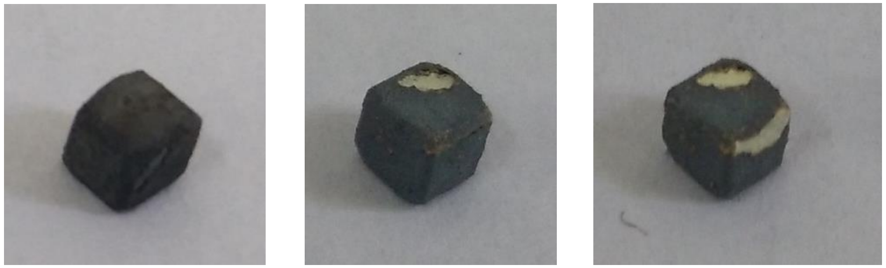
- ☐ The measured value is lower than the "rule-of-mixtures" average and that of each individual carbide
- ☐ The carburized coating could be a HEA based C containing supersaturated solid solution
- ☐ The hardness is mainly attributed to the solid solution strengthening



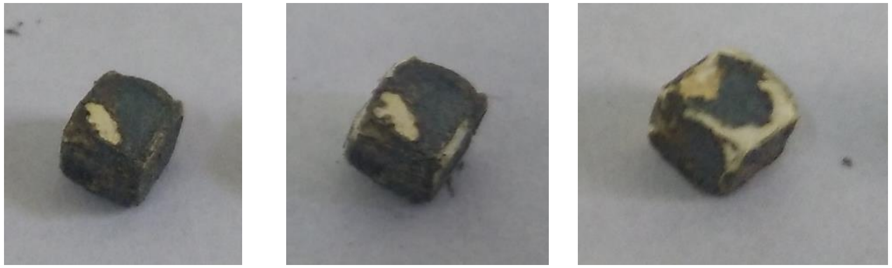
Comparation of Vicker micro-hardness of carburized layer with the reported values

3. Results & Discussion

- **Carburized HfZrTiTa**
  - Oxidation resistance

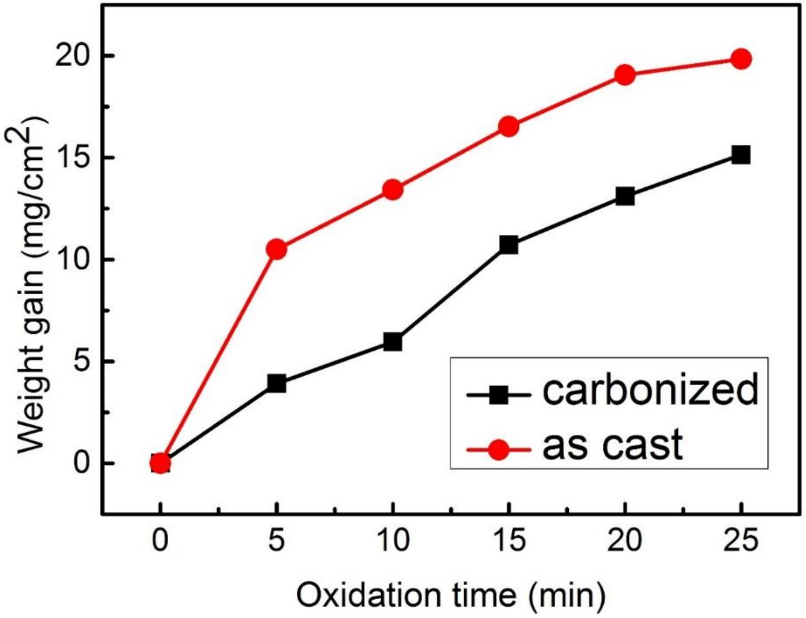


0min **5min** **10min**



15min **20min** **25min**

Morphology evolution during oxidation



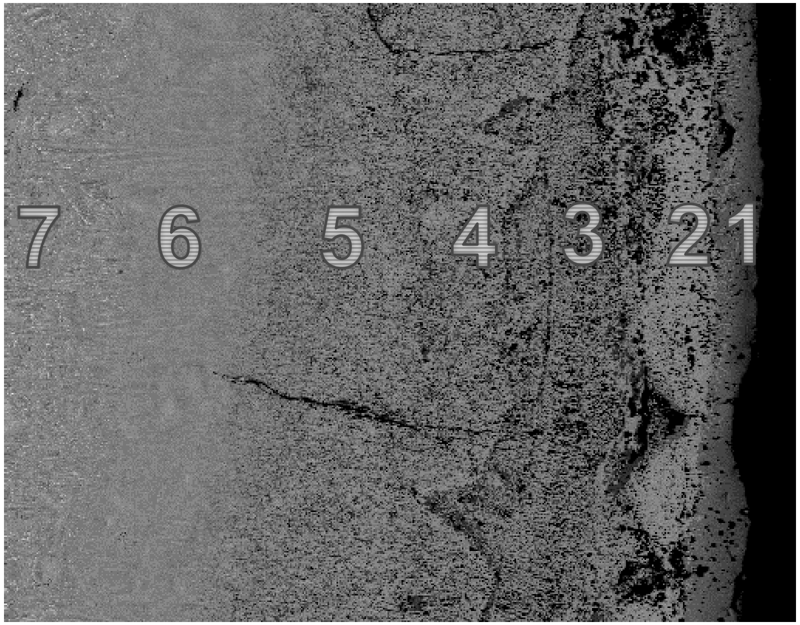
0.606mg/(cm^2·min)

Weight gain VS oxidation time

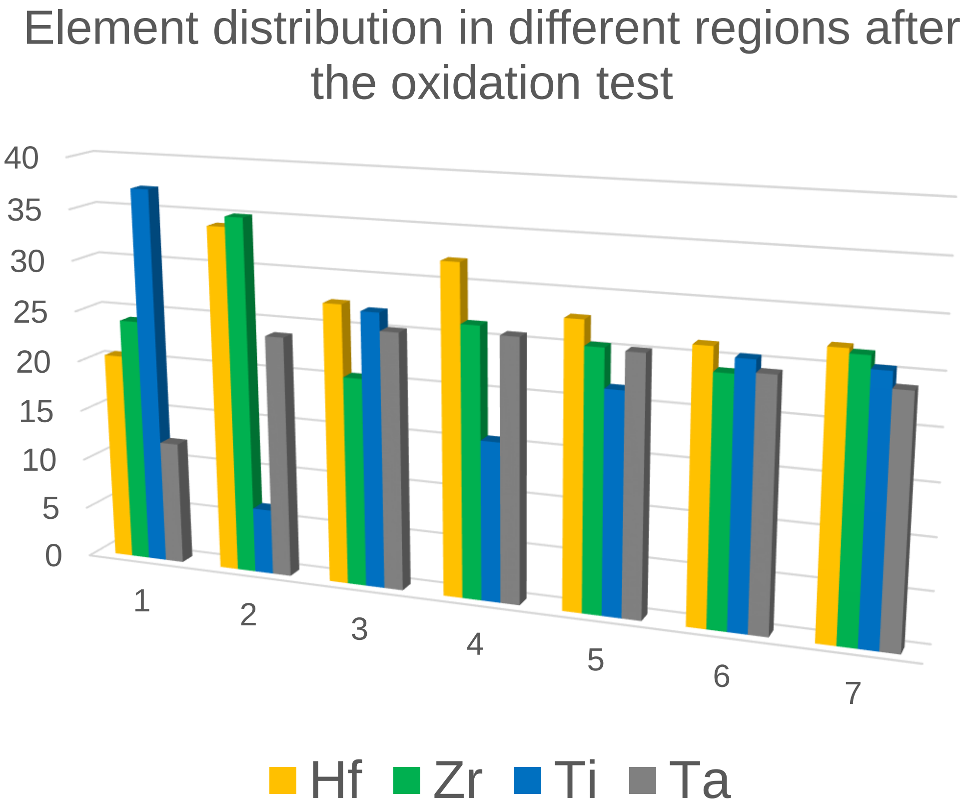
3. Results & Discussion

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℃ 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

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- **The colleagues and students in our group**
- **The organizers of the conference**

Thanks for your attention!