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Low temperature synthesis and sintering of mechanically activated ZrB2 powders

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Content

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- ZrB_2 Synthesis: Citrat gel process
- Mechanical activation of powders
- ZrB_2 materials containing second phase
- Ongoing researches
- Conclusion

The Aim of This Study

- **Synthesis nanocrystalline ZrB_2 powders using sol –gel method**

- **Densify ZrB_2 ceramics at low temperature via using mechanical activation process**

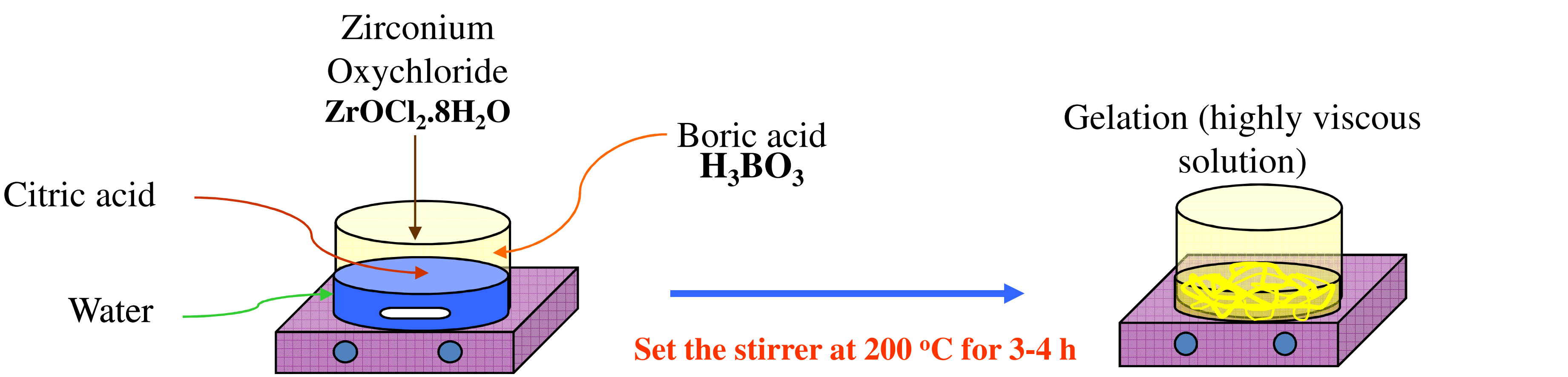
- **Produce ZrB_2 ceramics with addition of Fe, ZrO_2, B_4C and SiC**

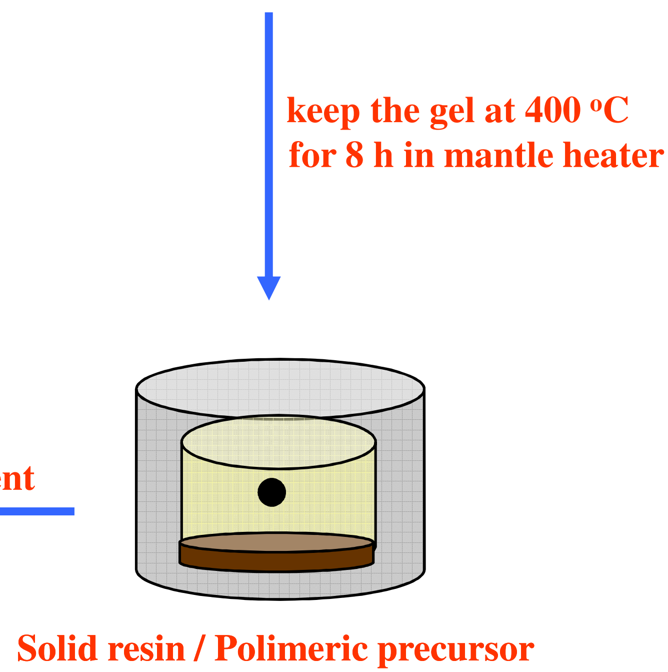
ZrB_2 Production

Different methods for producing zirconium diborides have been proposed ;

- Borothermal /carbothermal reduction
- Solution-based methods
- Self-propagating high temperature (SHS)

How to prepare powders: Citrat gel method



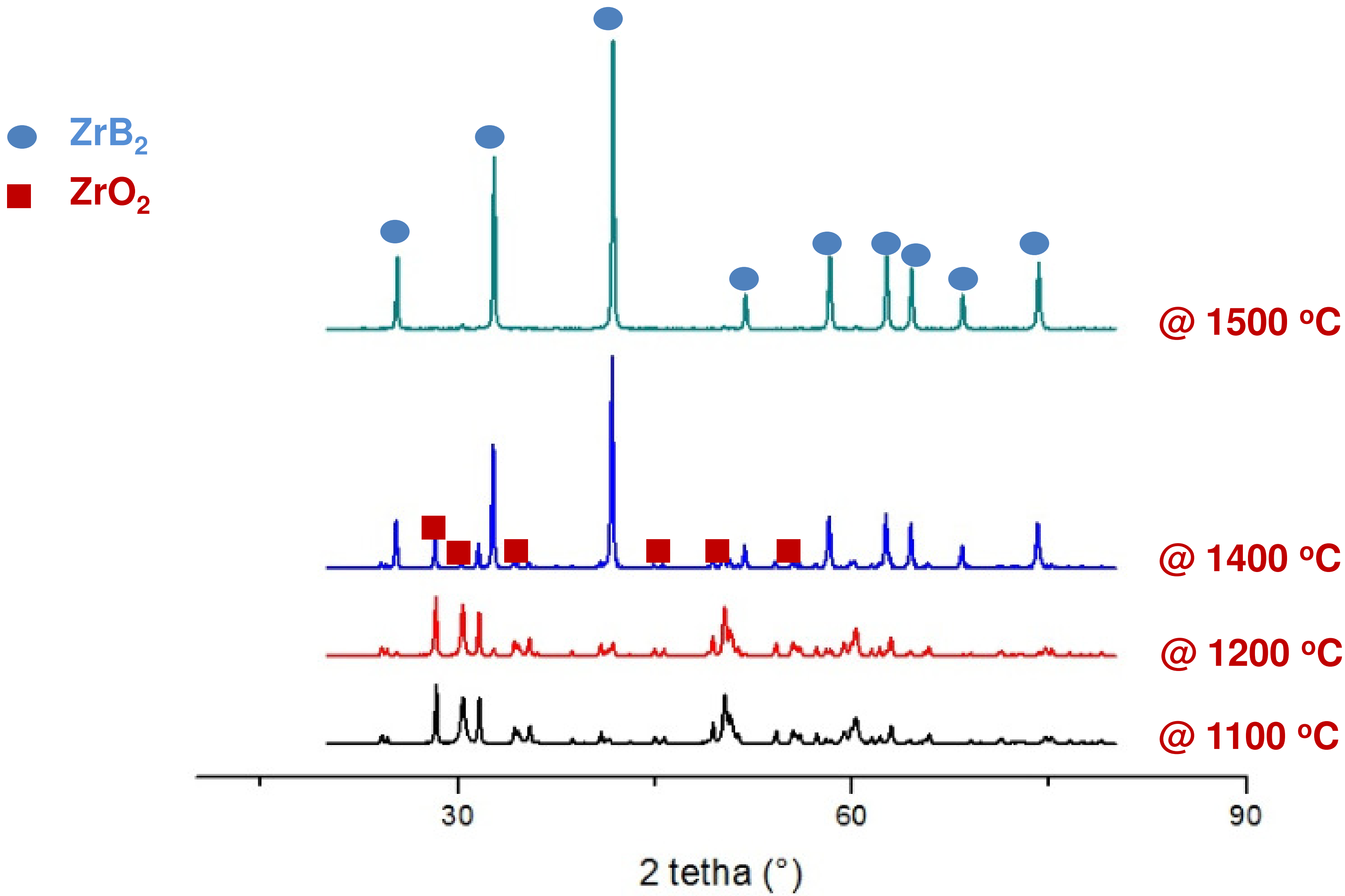


Advantages

- -Homogenous compositions
- -High purity
- -Size and morphology control
- -Simple to apply

Mole ratio: [Zr^{+4} + $B+^4$] / Citric acid= 4

XRD pattern of ZrB_2 at various temperatures



Powder characteristics for ZrB_2 @ 1500 ^oC for 2 h

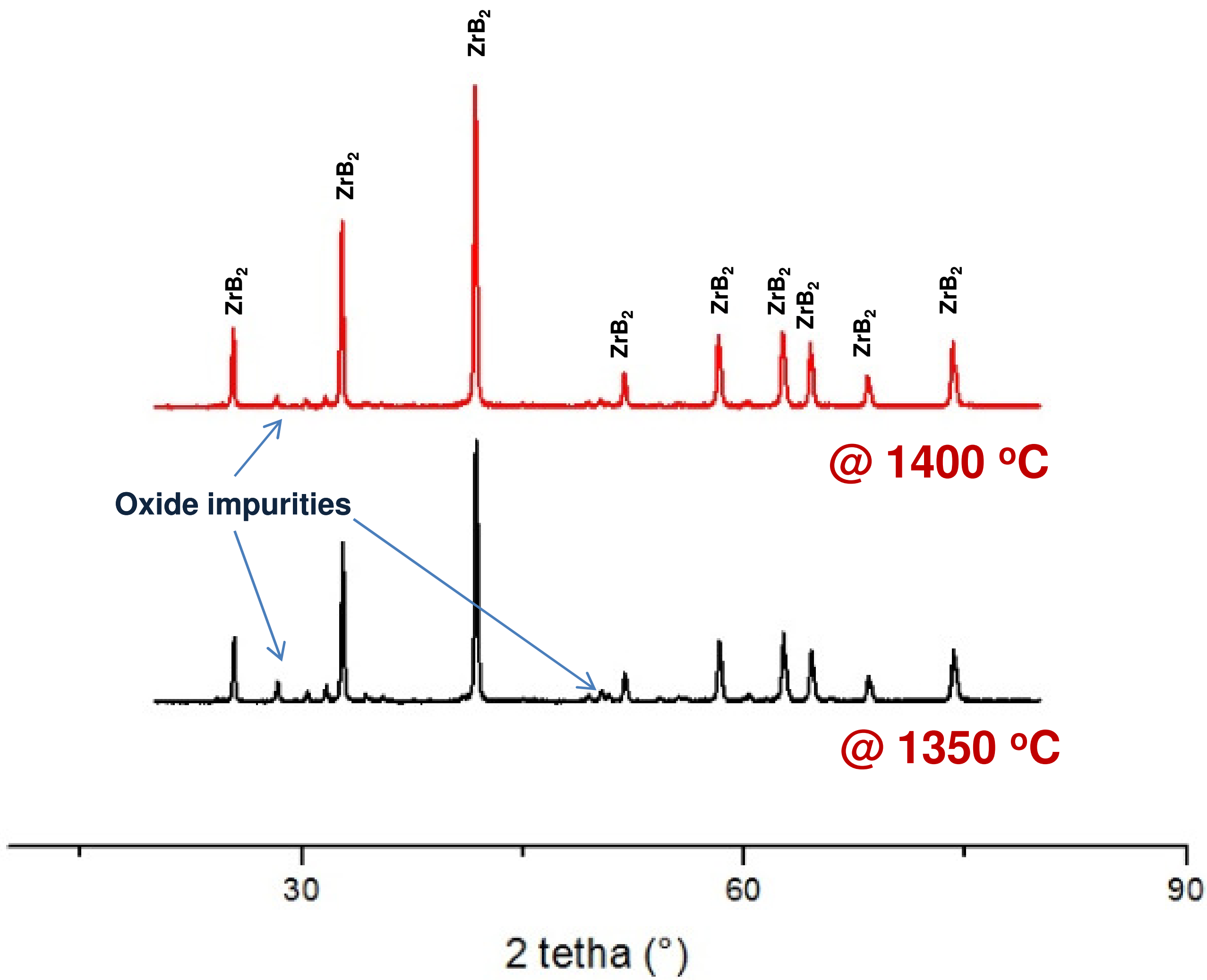
Density (g/cm^3)	Surface Area (m^2/g)	Crystalline size d_{XRD} (nm)	Particle size, d_{BET} (nm)	Carbon Content (wt %)
5.5	**1.6**	**60**	**682**	**3**

XRD pattern of activated-solid precursor gel

As-pyrolysized (400 ºC) solid precursor gel

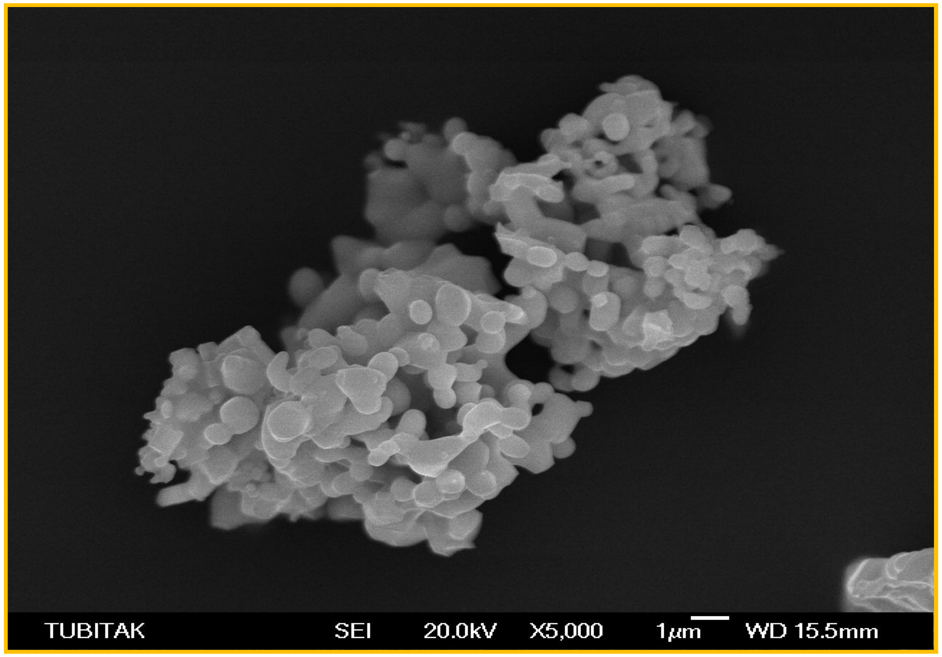
Dry activation for 1 h 1000 rpm, WC balls, WC vial

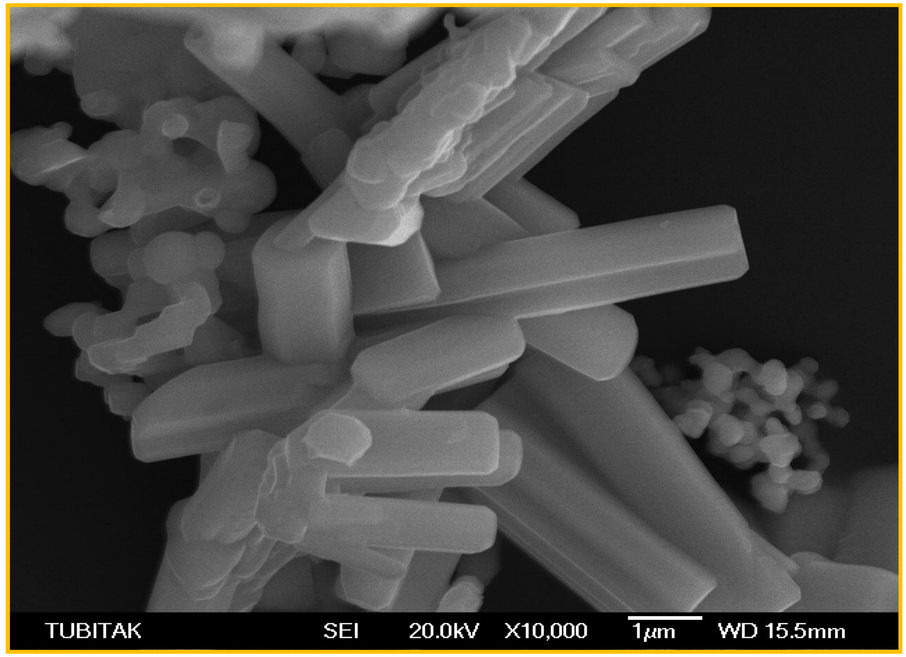
Thermal treatment at 1350 and 1400 ºC



Activation of solid precursor gel decreases the formation temperature of ZrB_2 phase

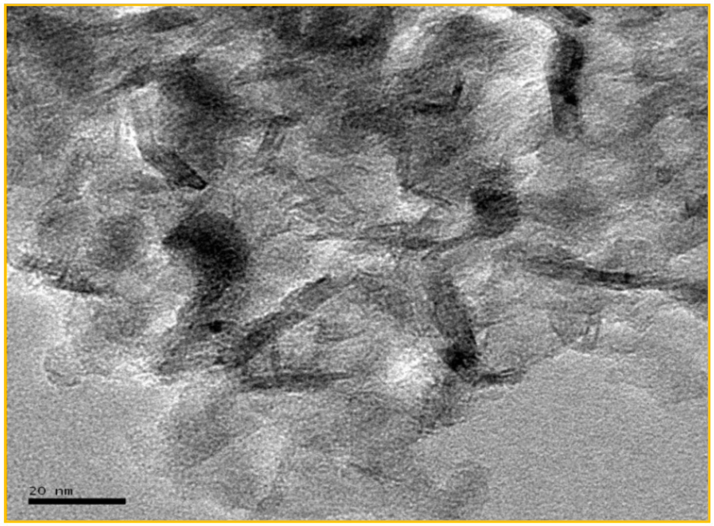
SEM images of ZrB_2 crystallized @ 1500

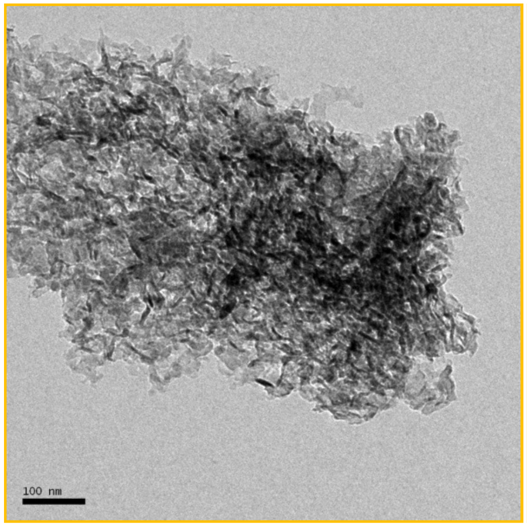


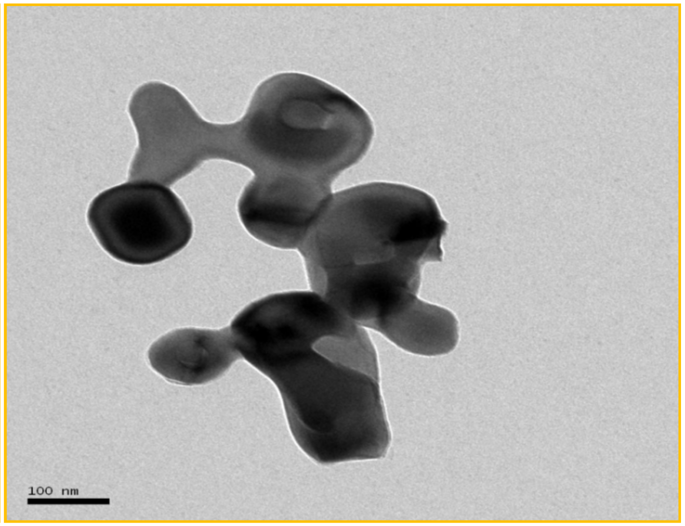


Faced morphology of ZrB_2 grain

TEM images of ZrB_2 crystallized @ 1500

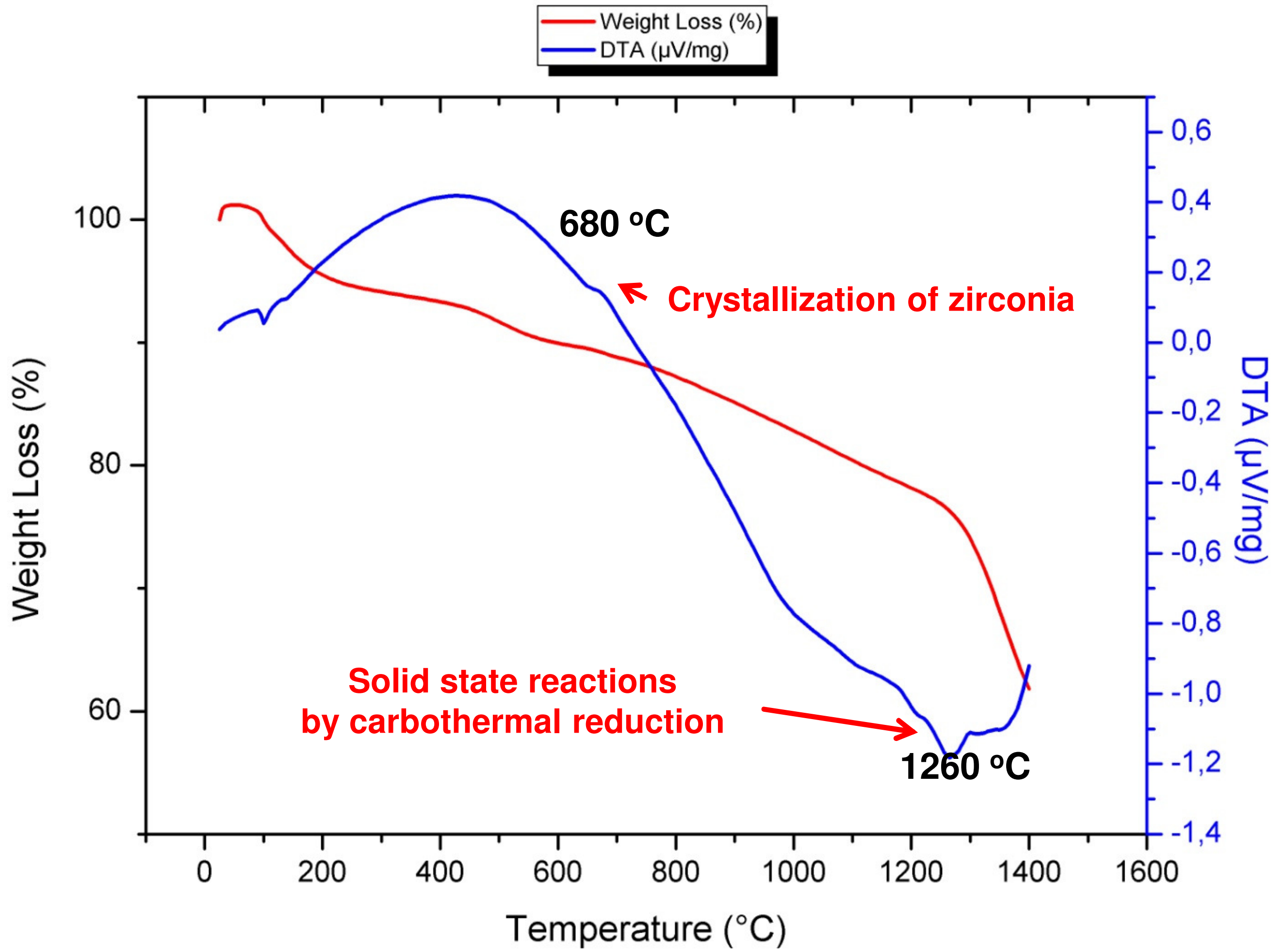






Crystalline size ~ 45 from TEM
~ 60 from XRD

DTA / TG curves for solid precursor gel post-pyrolysized @ 400 ºC



Total weight loss ~20% for gel @ 25 – 1400 °C

Estimated reaction pathway for formation of ZrB_2

Boric acid dissociation[1]

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

Citric acid dissociation[1]

$$C_6H_8O_7.H_2O \rightarrow 3C + 5H_2O + 3CO$$

ZrB_2 formation[2]

$$ZrO_{2\ (s)} + B_2O_{3(l,g)} + 5C_{\ (s)} \rightarrow ZrB_{2\ (s)} + 5CO_{\ (g)}$$

[1] Khanra, Bull. Mater. Sci., 2007
[2] Huang, Am.,Cer.,Sc., 2006

Densification of ZrB_2 Ceramics

It is difficult to densify ZrB_2 ceramics due to covalent binding characteristic and high melting point.

Different methods are used to densify ZrB_2 ceramics

- ❑ to use sintering agents
- ❑ advanced sintering techniques (e.g. SPS, HP)
- ❑ to synthesis the fine powders with high surface area

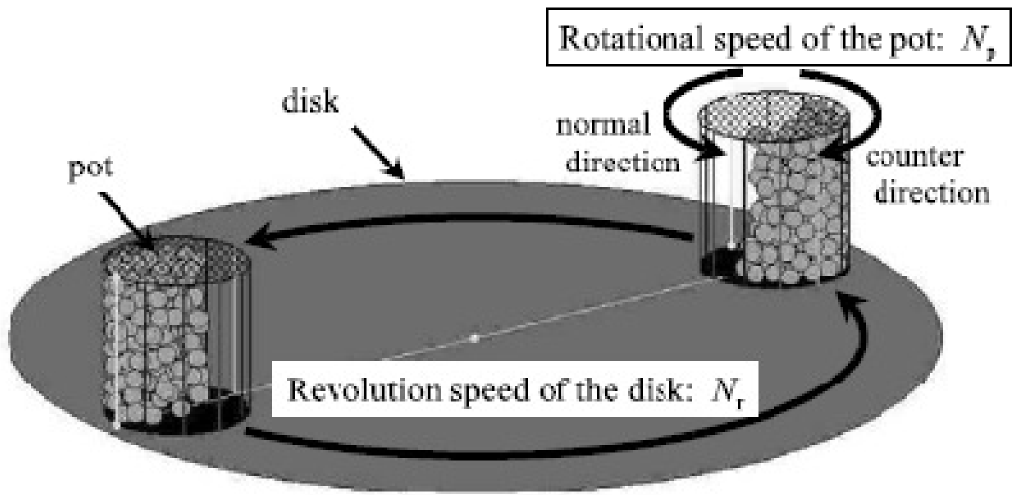
In this study, mechanical activation process was used to lower formation and sintering temperature of ZrB_2 BECAUSE

Mechanical activation enhance:

- reactivity,
- structural defect
- sinterability at low temperature

So it will be possible to densify boride ceramics at lowered temperatures without external pressure

Mechanical activation by planetary mill



Mechanical energy supply deformed crystal structure under the milling action

Preparation of Powders for Sintering

- Step 1: **SYNTHESIZED (1500 °C) ZrB_2 POWDERS**

- Step 2: **ACTIVATION**

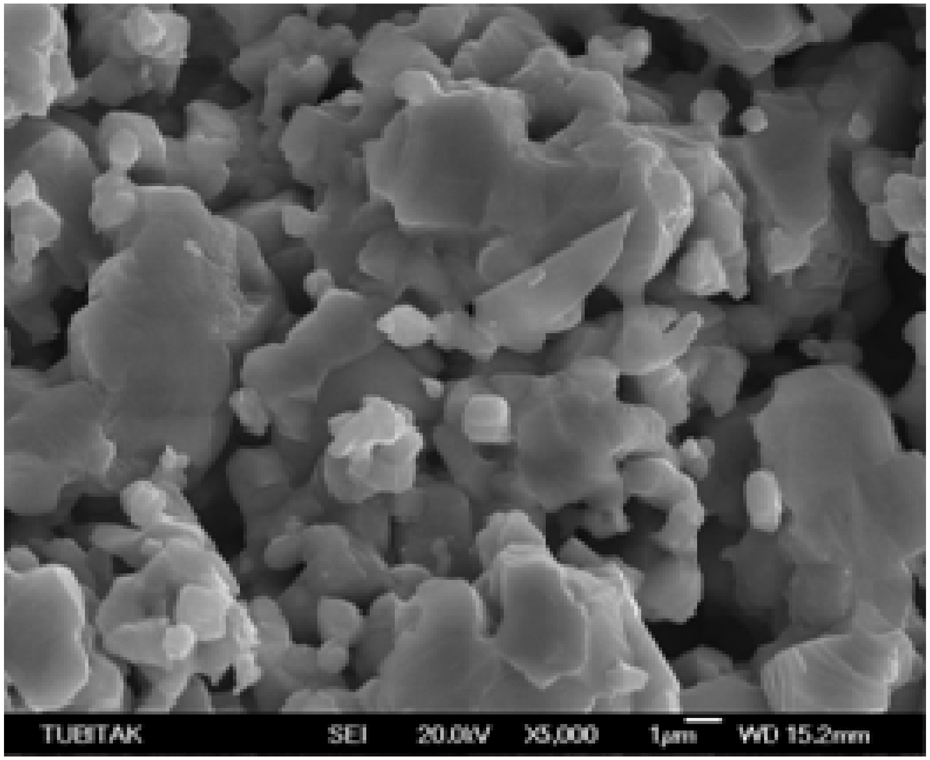
- 850 rpm rotation speed
- Zirconia Balls (10 mm in diameter)
- Zirconia Jar (80 ml capacity)
- Milling time of 1 h

- Step 3: **COMPACTION AND PRESSURELESS SINTERING**

- Dry pressing (40 MPa) and CIP (150 MPa)
- @1775 °C for 5 hours in inert gas atmosphere

Sintering of ZrB_2

Produced from activated powders



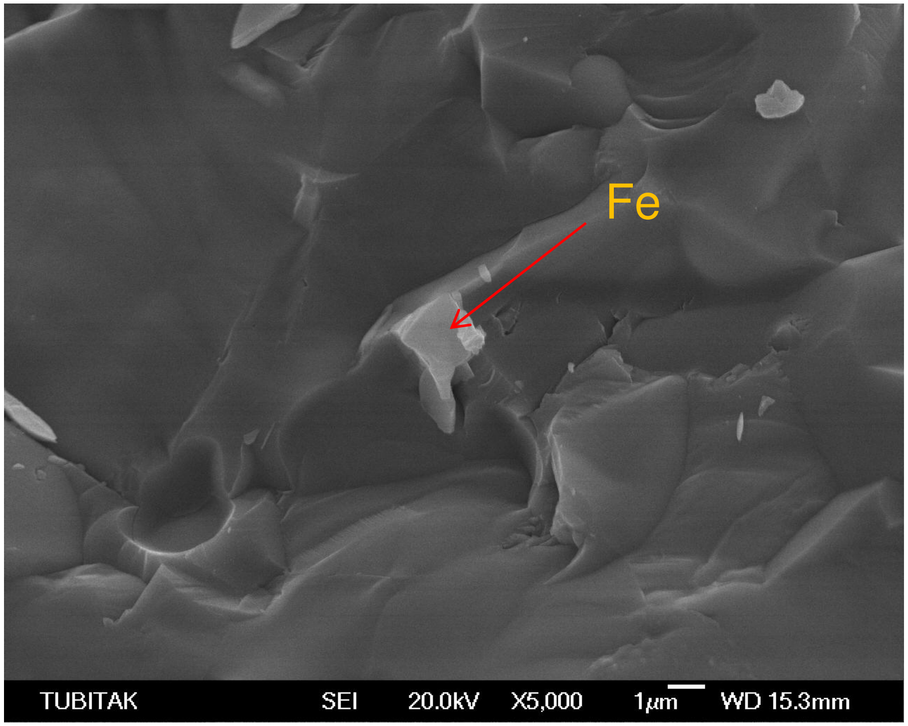
ρ = 86 %

Hv = 3.9 GPa under the 9.8 N

SEM images of sintered material compacted from mechanical activated ZrB_2-Fe (2.5 vol %) powders

ρ = 99.9 %

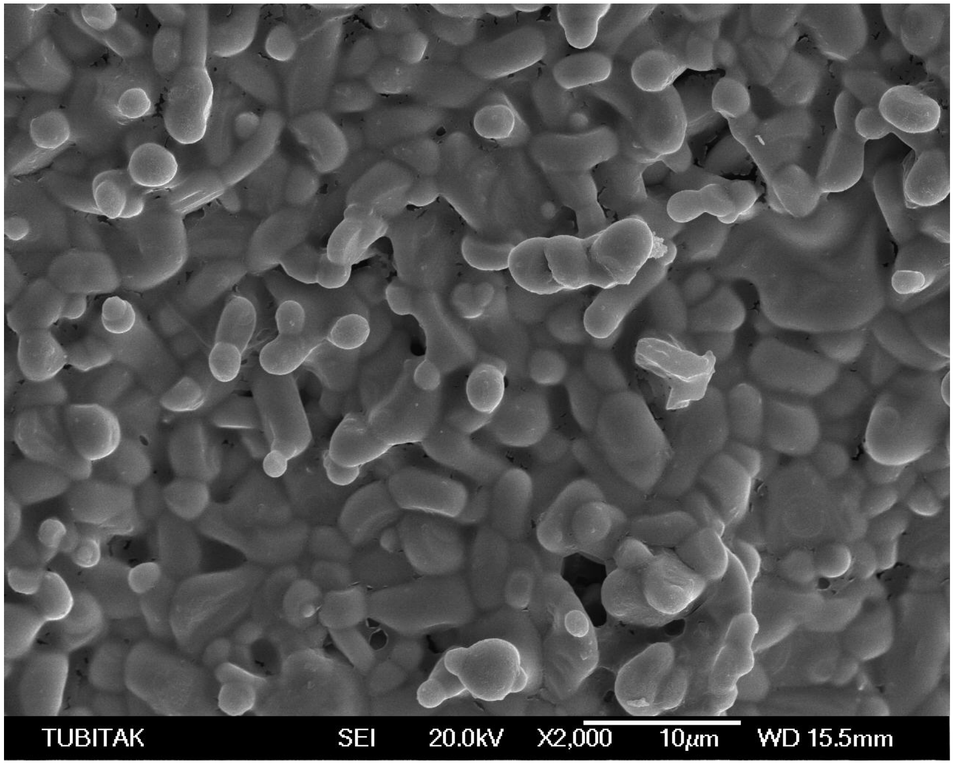
Hv = 14.9 GPa under the 9.8 N



Pressureless Sintering @ 1775 for 5 hours

SEM images of composite material compacted from mechanical activated ZrB_2-SiC (14 vol %) powders

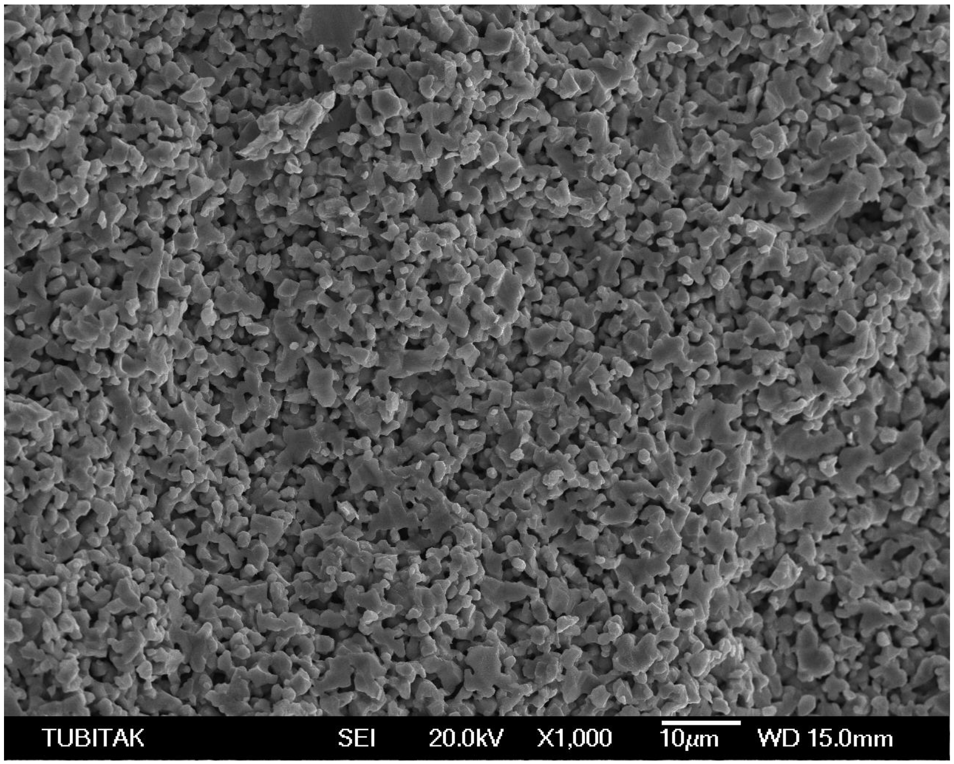
ρ = 80 %
Hv = 1.65 under the 9.8 N



Pressureless Sintering @ 1775 for 5 hours

SEM images of composite material compacted from mechanical activated ZrB_2-ZrO_2 (7 vol %) powders

ρ = 92 %
Hv = 3.1 GPa under the 9.8 N

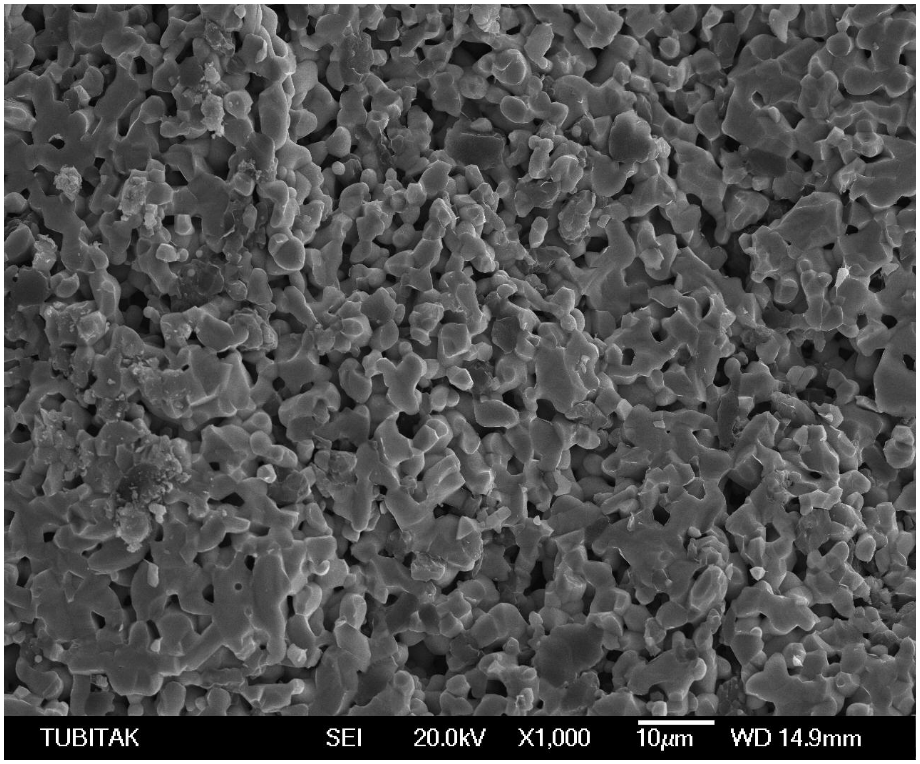


Pressureless Sintering @ 1775 for 5 hours

SEM images of composite material compacted from mechanical activated ZrB_2-B_4C (3 vol %) powders

ρ = 92 %

Hv = 12.7 GPa under the 9.8 N



Pressureless Sintering @ 1775 for 5 hours

The driving forces induce densification at low temperature;

1- Wet Chemical Synthesis

Nanocrystalline ZrB_2 powders via citrat gel metod

2- Mechanical Activation

Activation process give broken surface (unbinding atoms), leading to high surface energy.

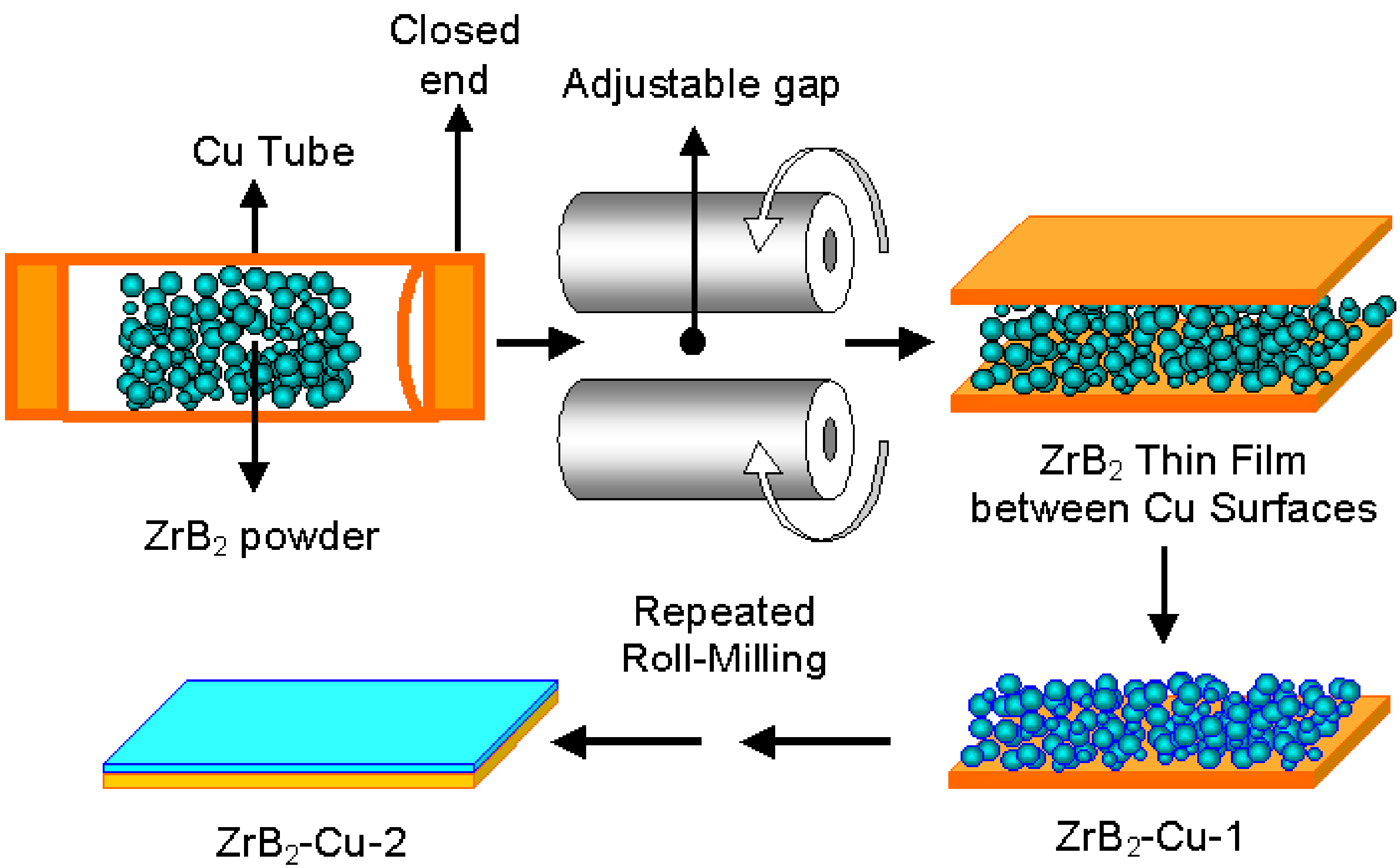
CONCLUSIONS

- ZrB_2 powders were synthesized using citrat-gel method.
- Sintered ZrB_2 ceramics from activated powders (ZrB_2-Fe, ZrB_2 -ZrO_2, ZrB_2-BC) were obtained at lower temperature (1775 ^oC) without external pressure

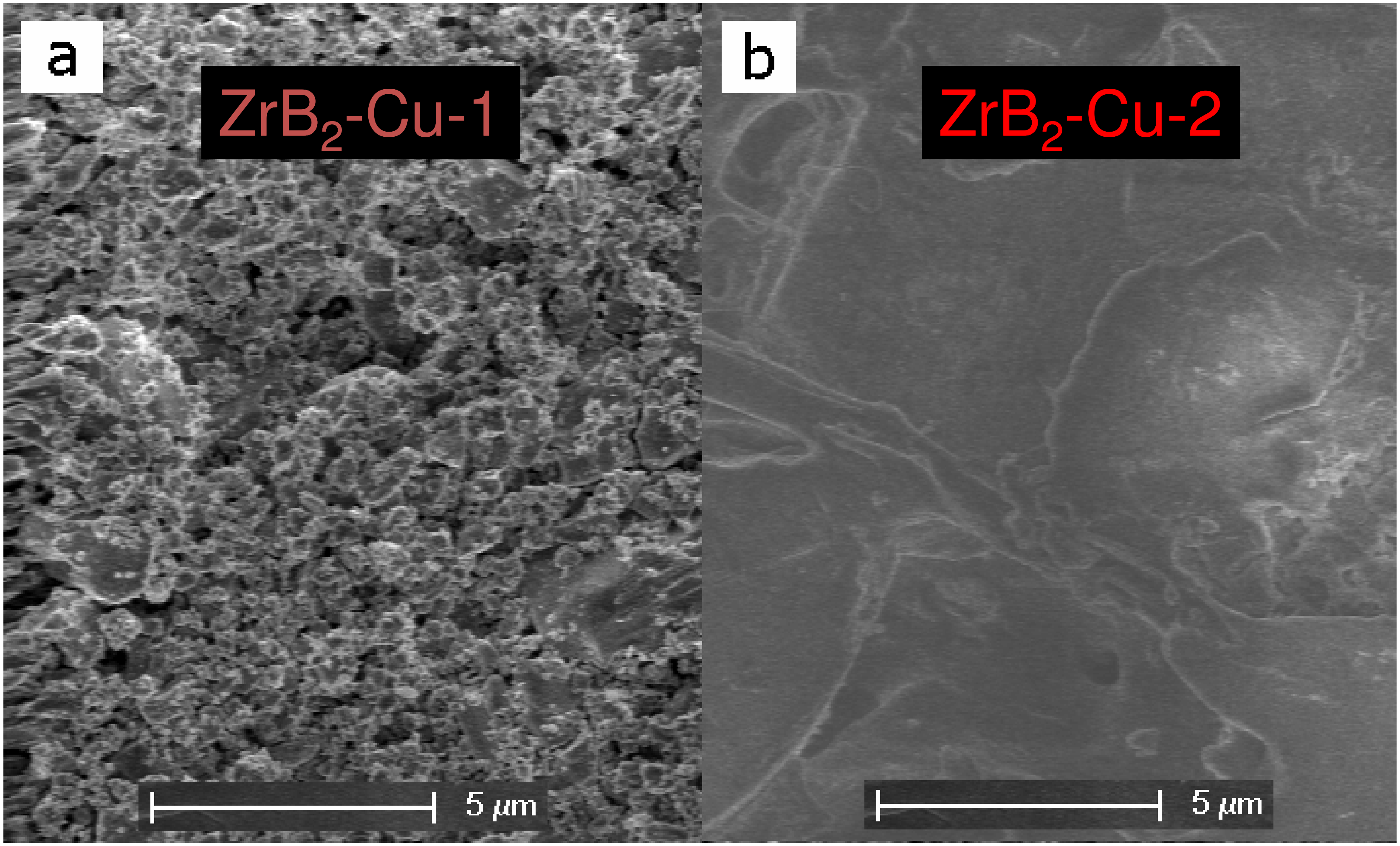
Future Efforts on ZrB_2

- ZrB_2 films by electroforetic deposition
- Microwave-sintering of ZrB_2 materials
- Pressure slip-casting
- Characterization of the electrical and mechanical properties of zirconium diboride films

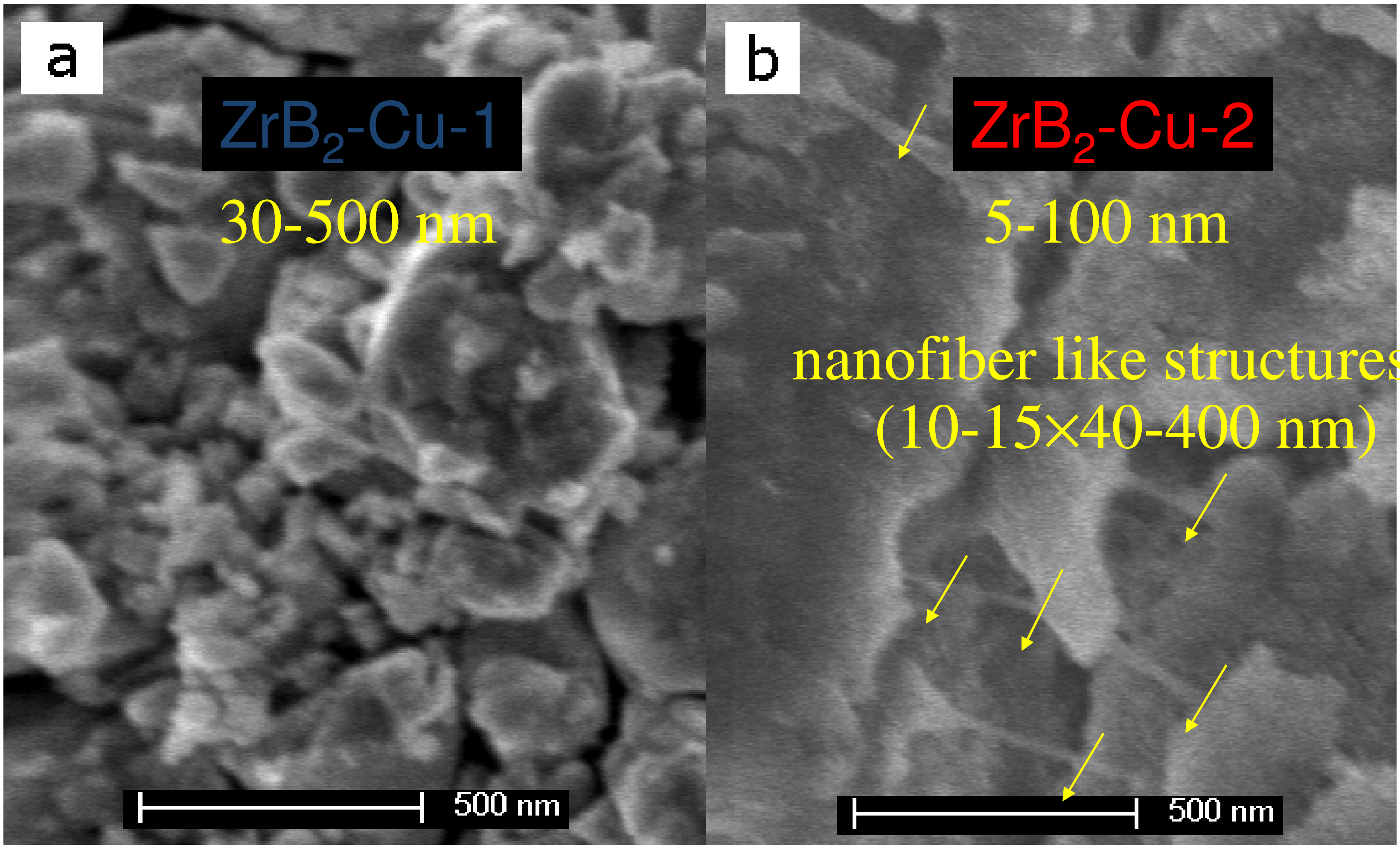
Shear Roll-Milling Process for Coating of Nano ZrB_2 on Cu



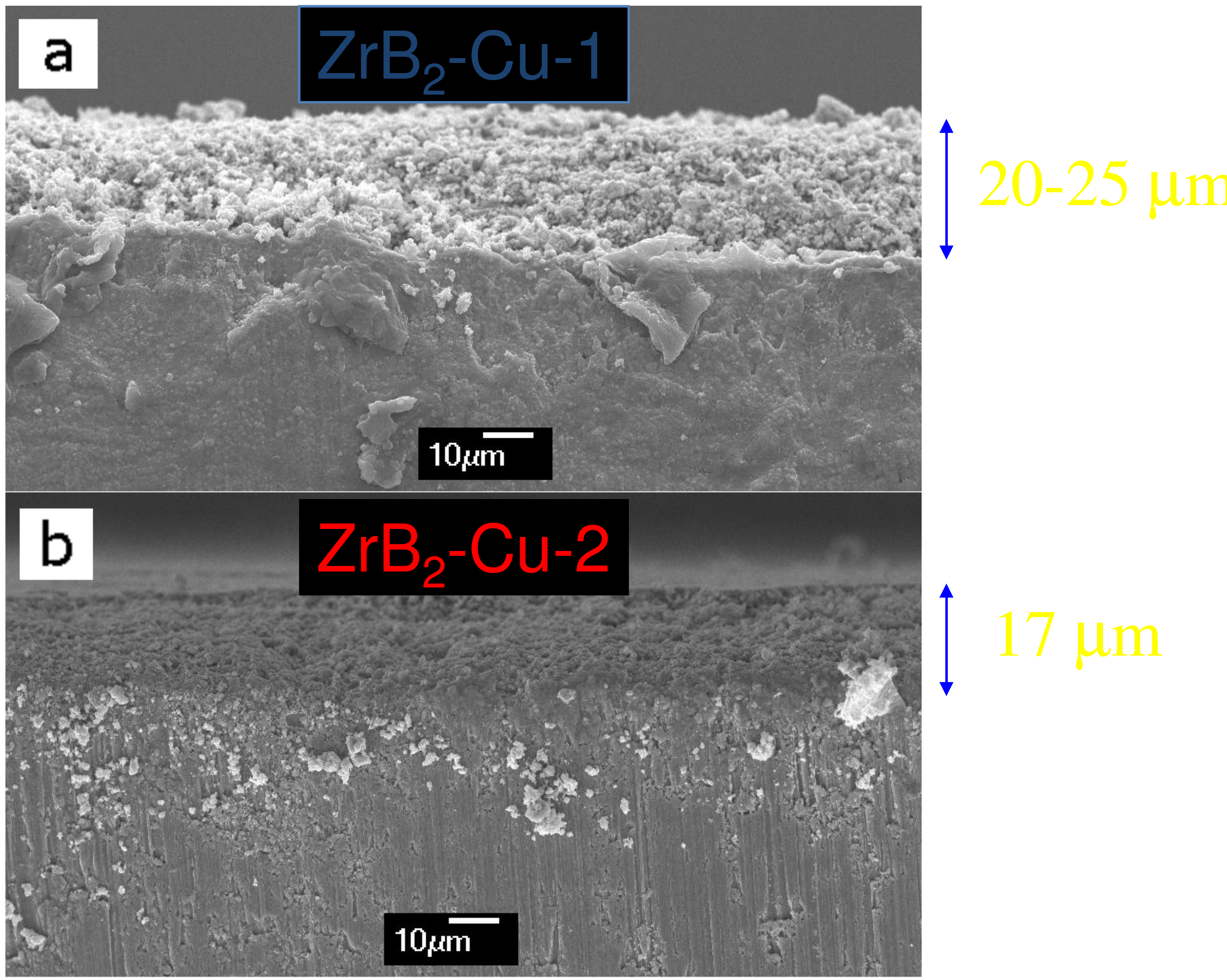
Surface Microstructure of ZrB_2 Coating for ZrB_2-Cu-1 and ZrB_2-Cu-2



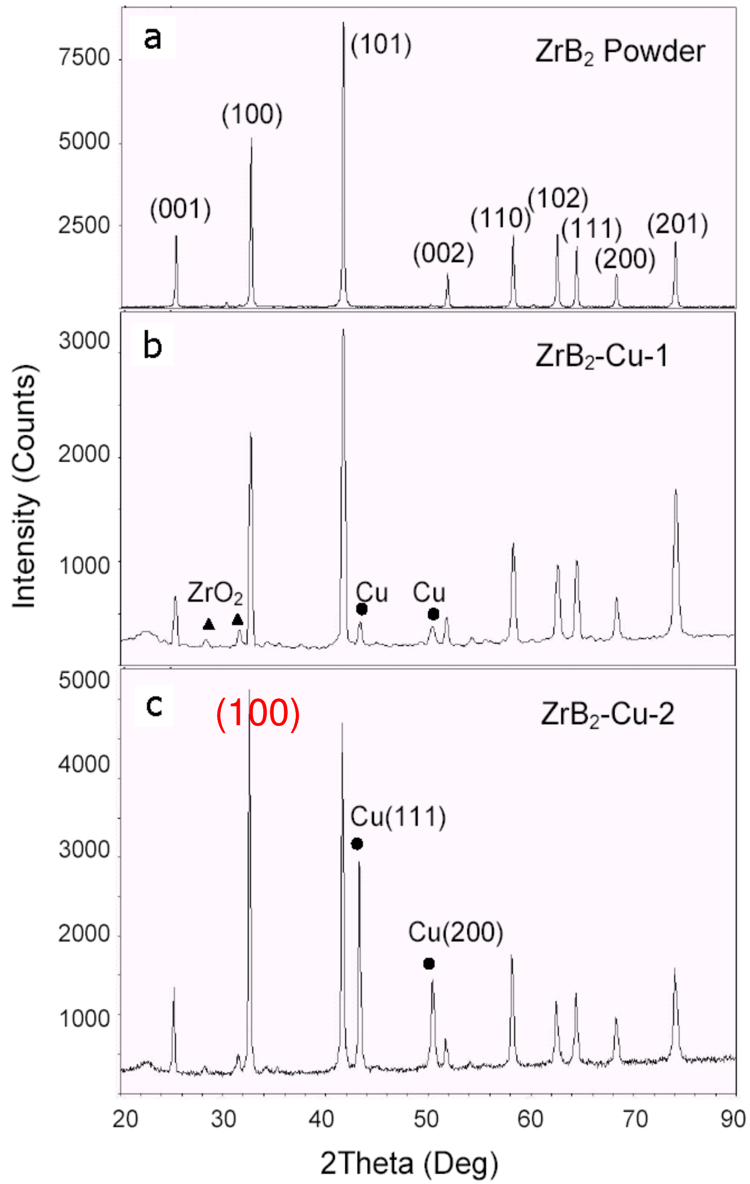
FE-SEM Images of ZrB_2 Coating for ZrB_2-Cu-1 and ZrB_2-Cu-2



ZrB_2 Coating Layers for ZrB_2-Cu-1 and ZrB_2-Cu-2



XRD Pattern

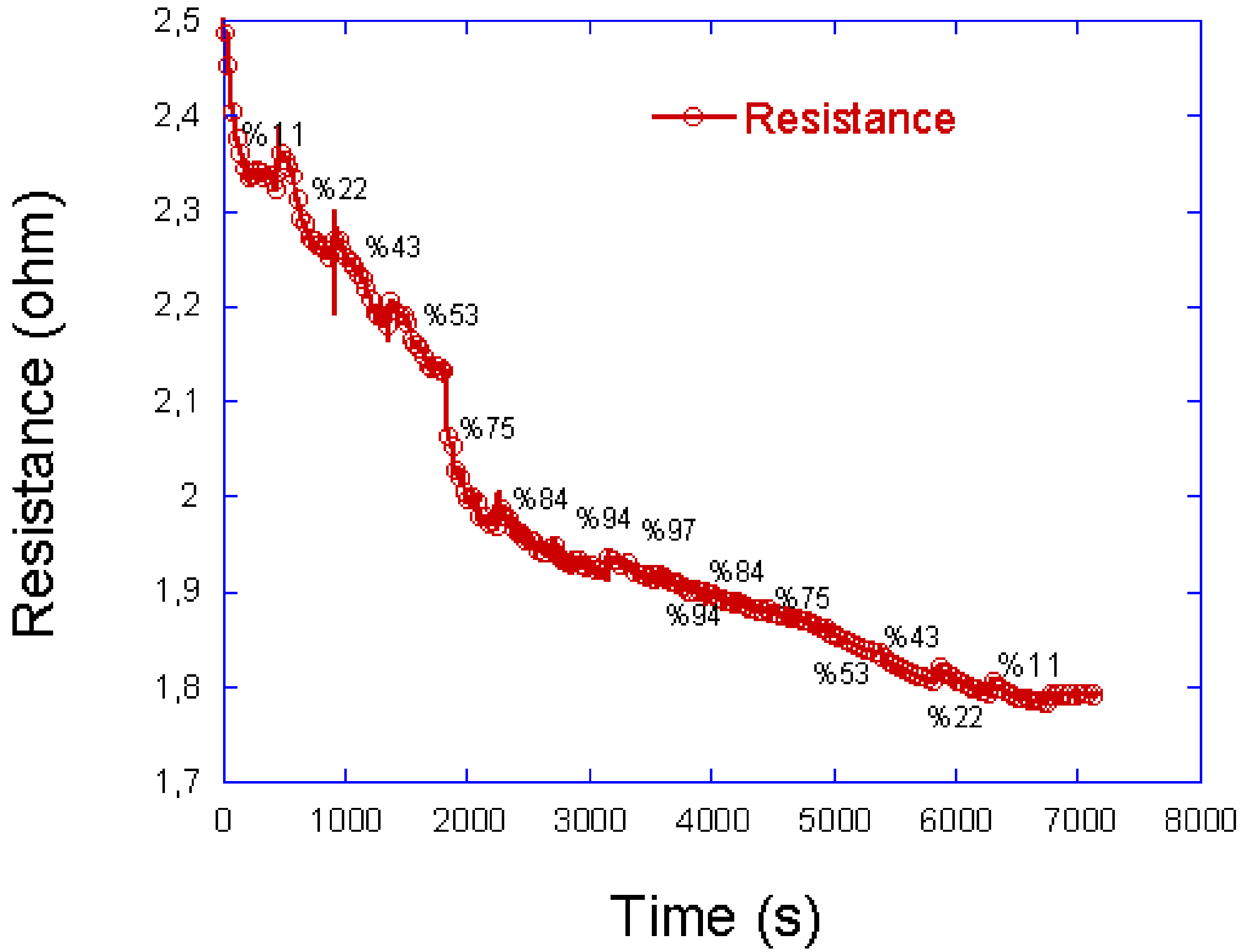


ZrB_2

ZrB_2-Cu-1

ZrB_2-Cu-2

Resistance-Time Graph at Different Relative Humidity Levels for ZrB_2-Cu-1



Acknowledgements

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Thank you for your attention