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DEGRADATION OF TUNGSTEN CARBIDE IN LIQUID ZIRCONIUM IN A PROCESS LEADING TO MANUFACTURING OF COMPOSITE ROCKET ENGINES

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Literature

1. M. B. Dickerson, Z. Grzesik, K. Sandhage, "Nowa generacja materiałów kompozytowych wytwarzanych metodą PRIMA-DCP", in Proc. 7th Polish Corrosion Conference, p. 560-564, 17-21.06.2002, Kraków, Poland.

2. Z. Grzesik, M. B. Dickerson, K. Sandhage, "Heterogeniczna reakcja węglika wolframu z cyrkonem w środowisku ciekłego Zr_2Cu", in Proc. 7th Polish Corrosion Conference, p. 575-578, 17-21.06.2002, Kraków, Poland.

3. Z. Grzesik, M. B. Dickerson, K. Sandhage, "Incongruent reduction of tungsten carbide by a zirconium-copper melt", Journal of Materials Research, **18**, 2135-2140 (2003).

Classification of chemical rocket engines

- rocket engines powered by solid fuel
- rocket engines powered by liquid fuel
- hybrid rocket engines

Columbia space shuttle

Exocet anti-ship missile

BGM-71 TOW guided anti-tank missile

FIM-92 Stinger ground-air missile

Advantages of rocket engines powered by solid fuel

- simple build
- no moving parts
- reliability
- a lot of power
- relatively low costs

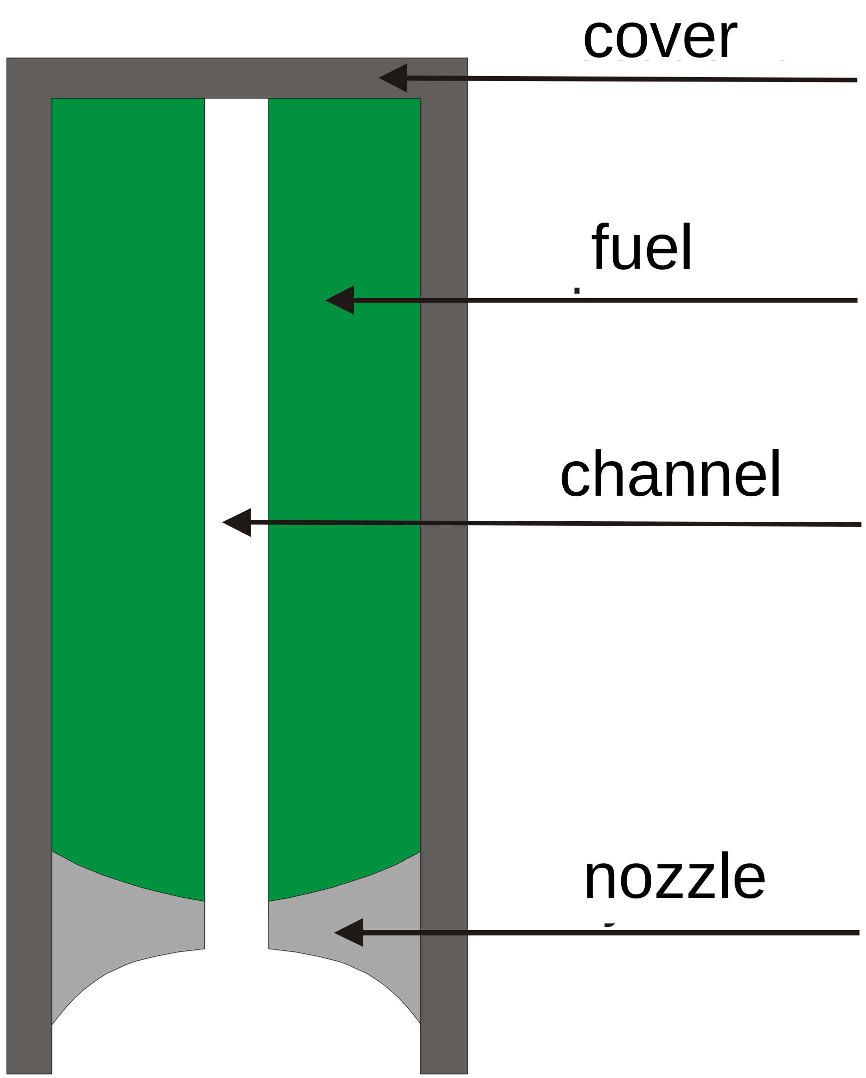
Components of solid fuels

- nitrocellulose
- nitroglycerin
- polybutadiene
- ammonium perchlorate
- polyvinyl chloride
- polyurethane
- aluminum, beryllium

Typical exploatation conditions for rocket missile nozzles

- temperature: ~2500 ^{o}C
- outlet gas velocity: ~2500 m/s
- sequence duration: 10 s

Schematic illustration of a rocket engine powered by a solid propelling material



Composites built of high-melting metals and their carbides

- high hardness
- high abrasion, creep and cracking resistance
- resistance against thermal shocks
- relative low specific weight

W/ZrC composites

- melting temperature: ~3000 ^oC

  T_W=3410 ^oC, T_{ZrC}=3540 ^oC
- low vapor volatility
- similar thermal expansion coefficients

  in the temperature range 25 – 3000 ^oC:

  $\alpha_W = 4{,}5\cdot10^{-6} – 9{,}2\cdot10^{-6}$ deg^{-1}

  $\alpha_{ZrC} = 4{,}0\cdot10^{-6} – 10{,}2\cdot10^{-6}$ deg^{-1}
- density: ρ(W/ZrC) = 12.9 g/cm^3

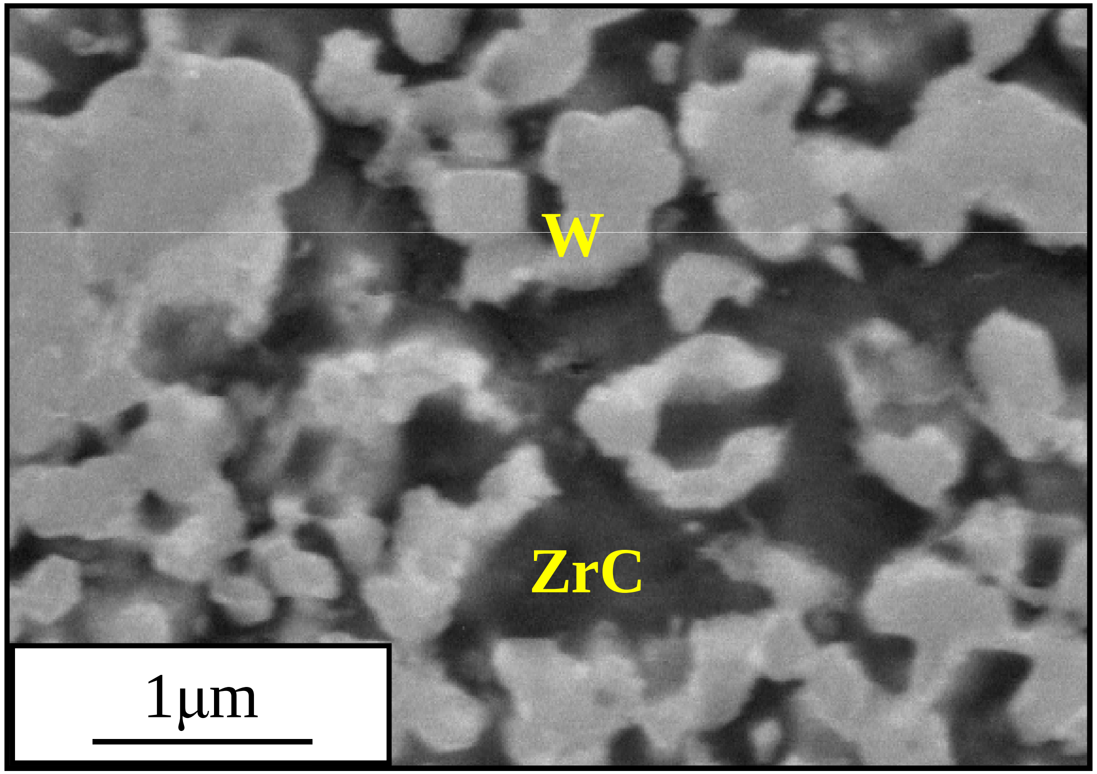
  ρ(ZrC) = 6.6 g/cm^3; ρ(W) = 19.3 g/cm^3
- great endurance against cracking

Disadvantages of the methods used up to now

- significant degree of process complication
- deformed shapes of the products
- application of high temperatures (~ 2000 ^{o}C)
- high costs

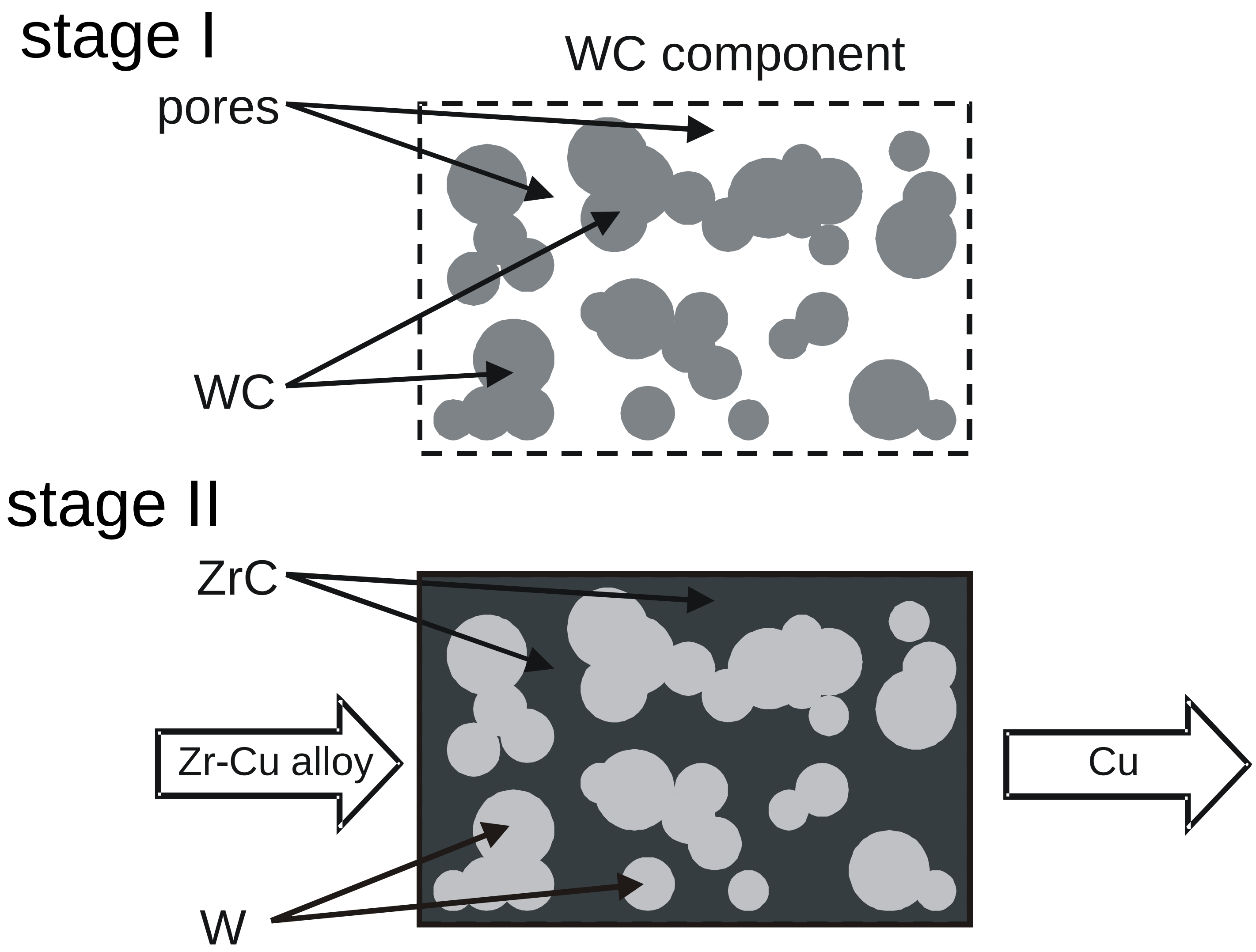
Incongruent reduction method

$$WC_{(s)} + Zr_{(l)} \longrightarrow W_{(s)} + ZrC_{(s)}$$



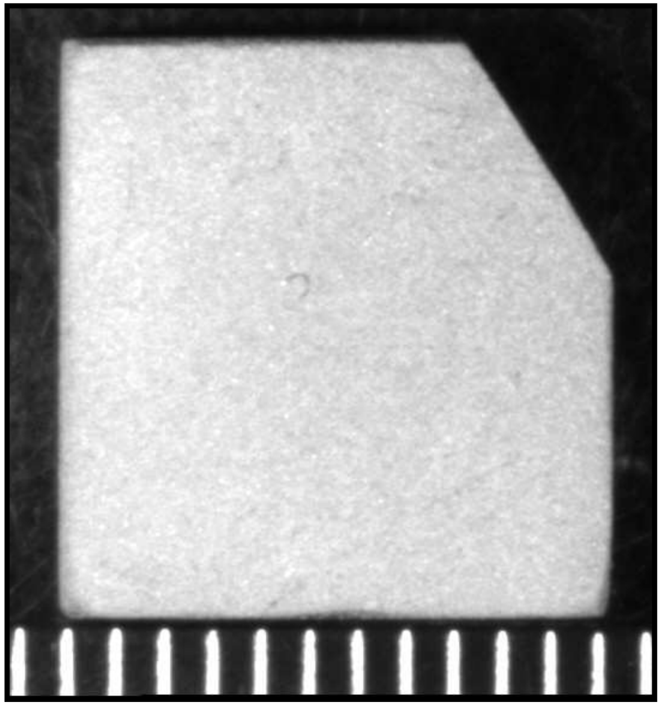
temperature: 1150 – 1400 ^{o}C; time: 1 – 4 h

Incongruent reduction method

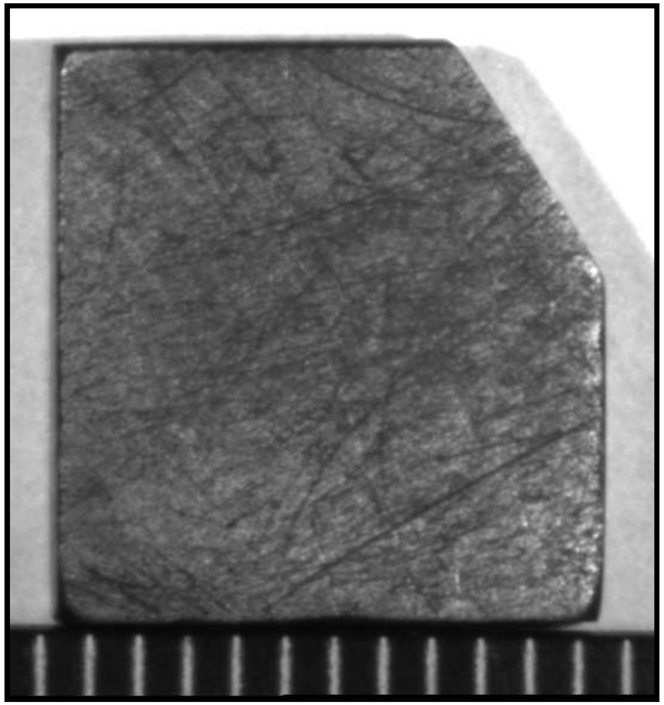


Incongruent reduction method

Before the reaction



After the reaction

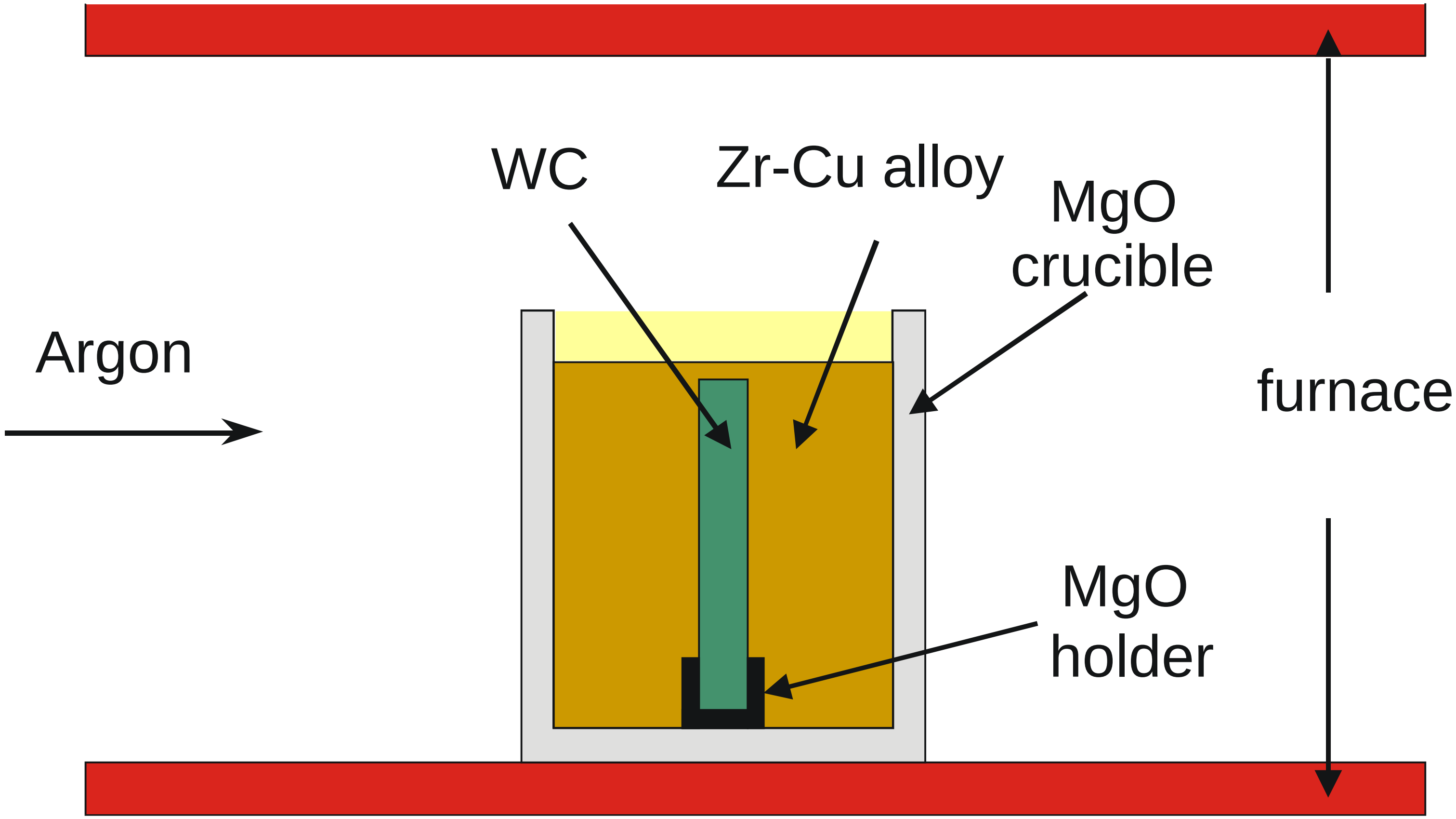


5 mm

change in linear dimensions: 0,8 %
change in volume: 1,6 %

Composite rocket nozzle

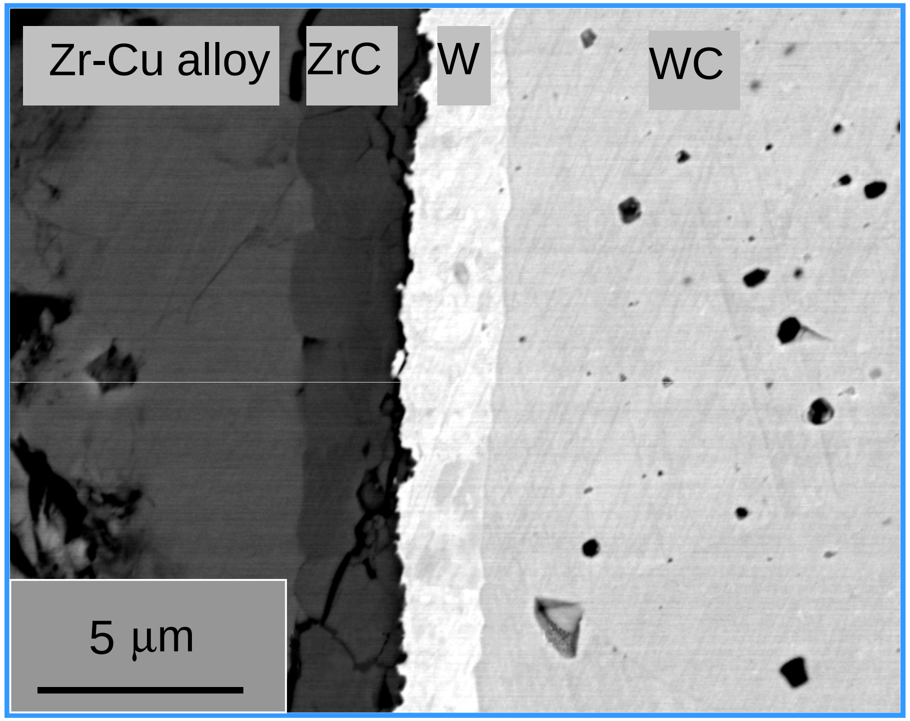
Scheme of a test stand for studying the kinetics and mechanism of the reaction between WC and Zr

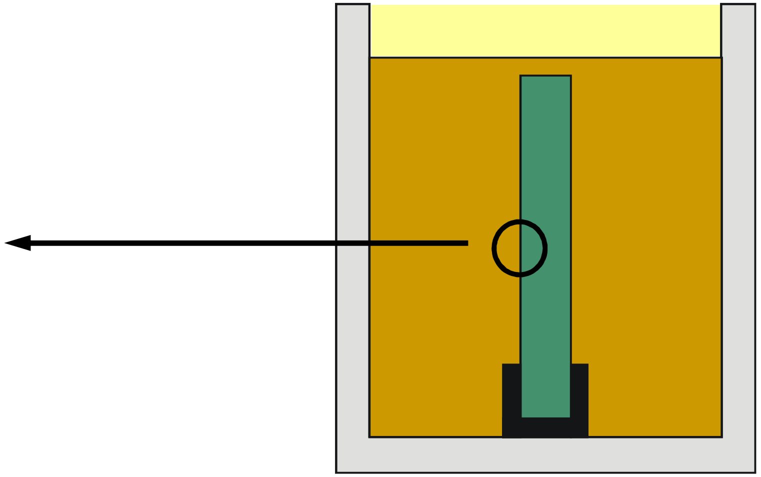


temperature: 1150 ^oC – 1400 ^oC

time: 1.5 – 24 h

Cross-section of a WC sample that reacted with Zr



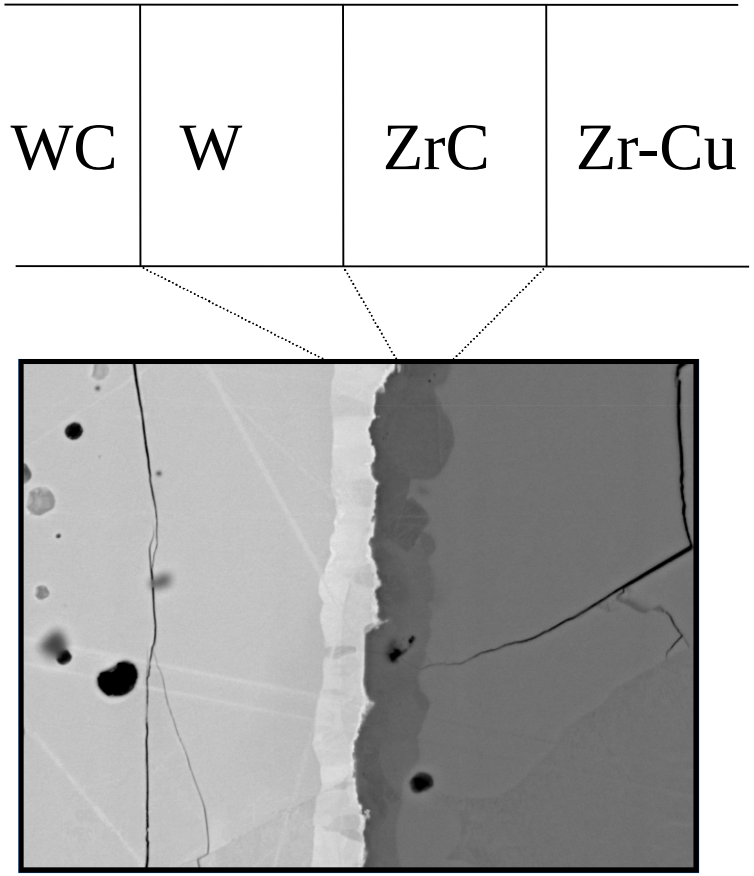


temperature: 1400 °C

time: 1,5 h

Cross-section of a WC sample that reacted with Zr

$$WC_{(s)} + (Zr_{(l)}) \rightarrow W_{(s)} + ZrC_{(s)}$$



temperature: 1300 ^{o}C

time: 6 h

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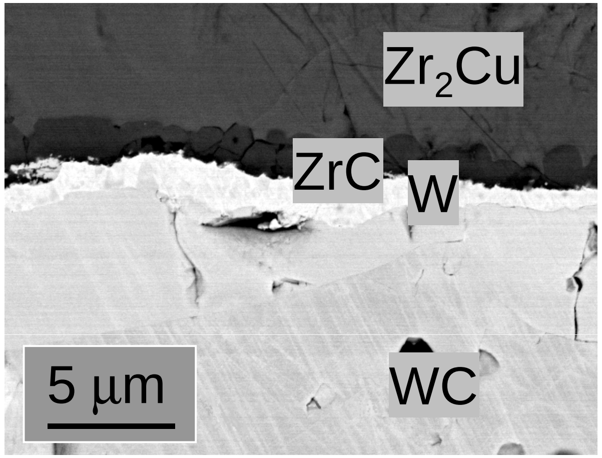
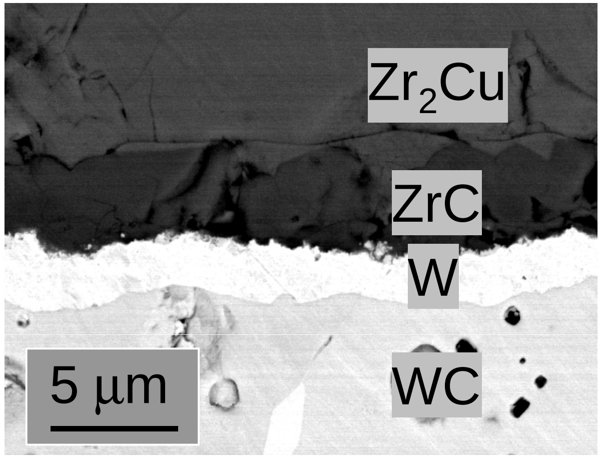
Cross-section of a WC samples that reacted with Zr

1300 °C

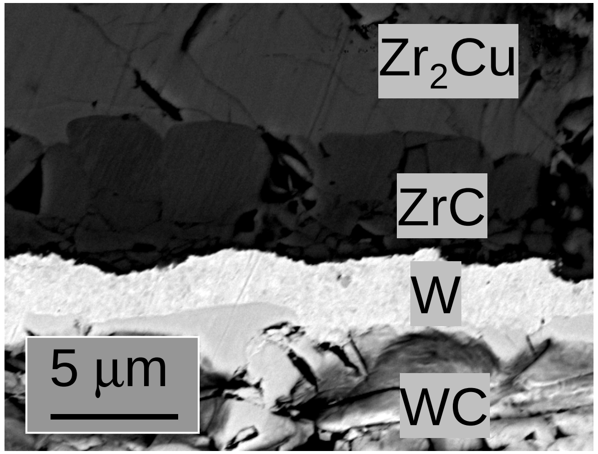
1.5 h



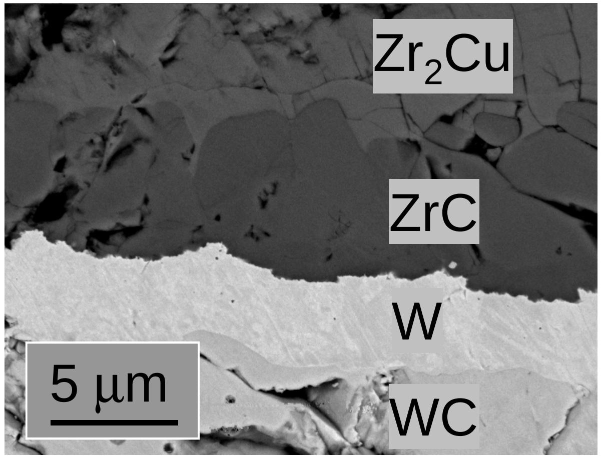
6 h



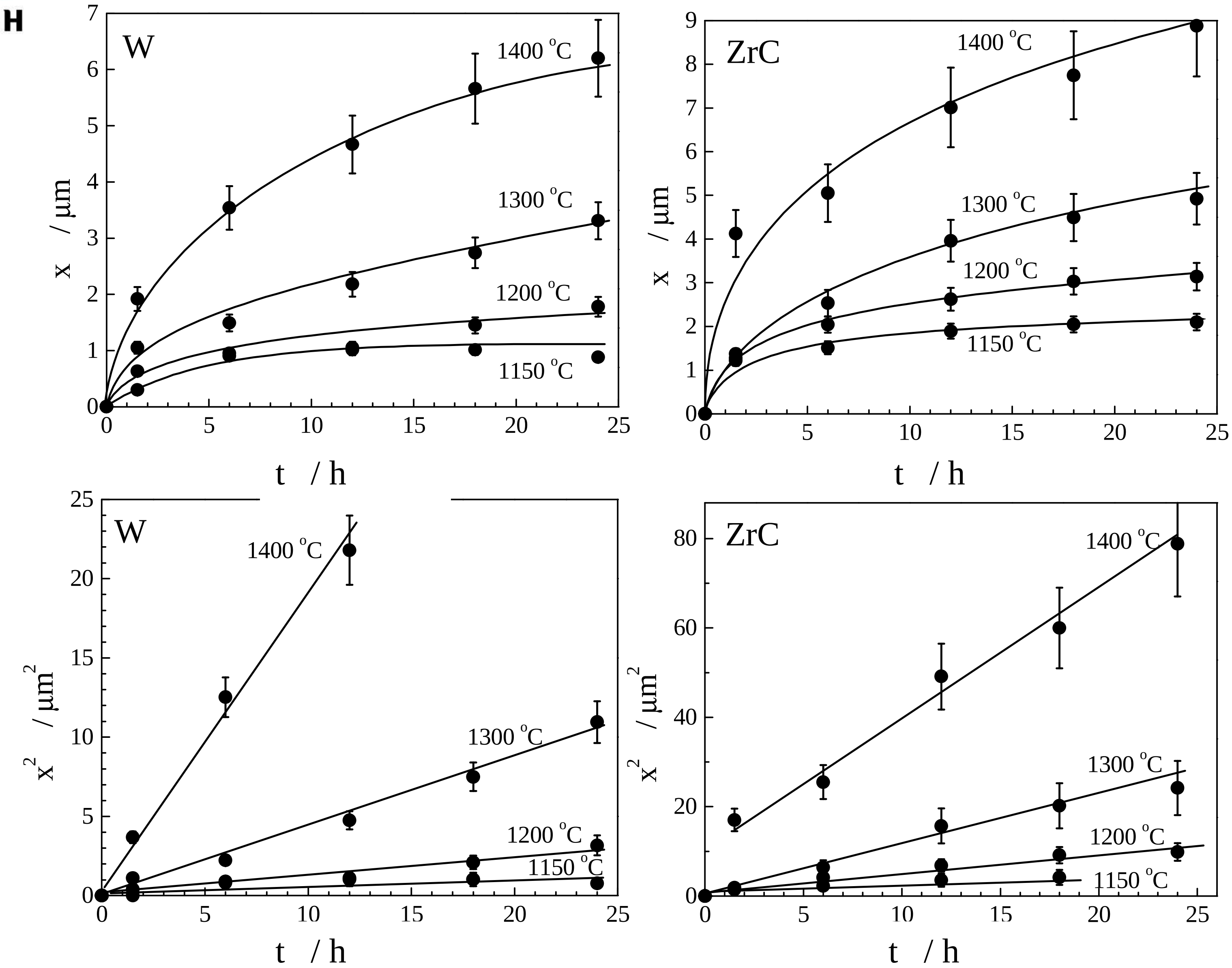
12 h



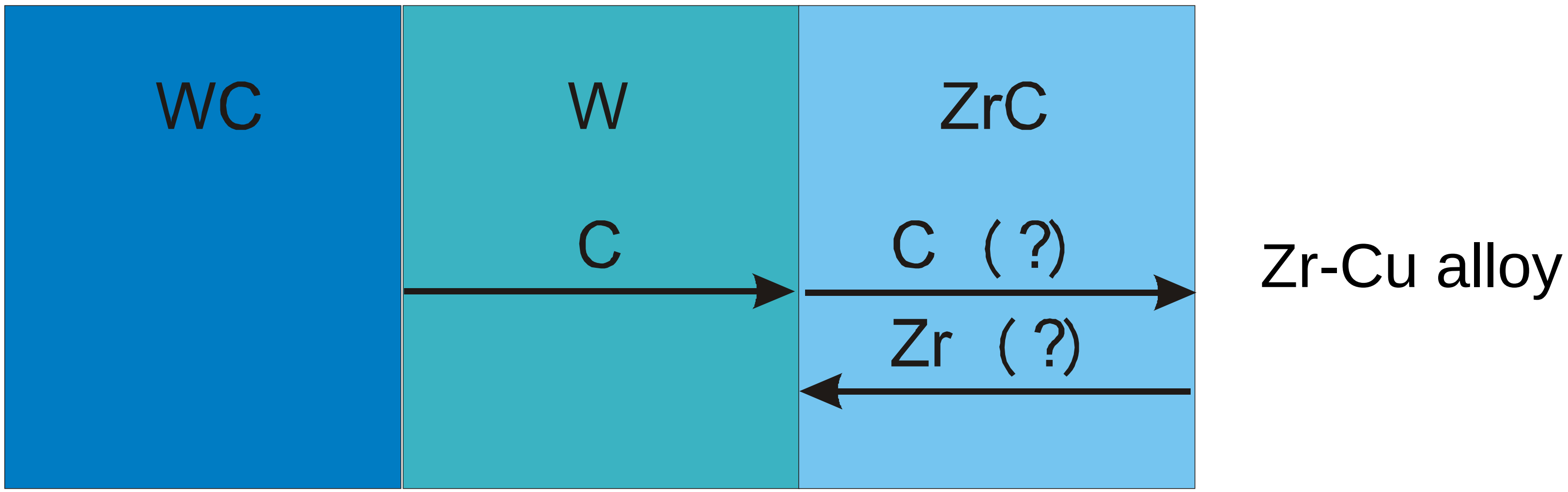
24 h



Kinetics of the reaction between WC and Zr



Mechanism of the reaction between WC and Zr



Comparison between the activation energy of different processes analyzed by determining the mechanism of the reaction between WC and Zr

Activation energy kJ/mol			
Reaction: $WC_{(s)} + Zr_{(l)} \rightarrow W_{(s)} + ZrC_{(s)}$	Self-diffusion		
	Carbon C^{14} in W	Carbon C^{14} in ZrC	Zirconium Zr^{95} in ZrC
255	169	**288**	540
	34%	**13%**	112%

Temperature range of reaction kinetics studies: 1150 - 1400 °C

Temperature range of C^{14} and Zr^{95} self-diffusion studies: 1000-1500 °C

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Summary

Compostion rocket nozzles currently manufactured using the incongruent reduction method have proven to be unusually durable at operating temperatures around 2500 ^{o}C, ensuring a continuous sequence of rocket missiles for the required duration of 10 seconds.

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THE END