



Destabilization of magnesium hydride by embedding in TiH₂ matrix

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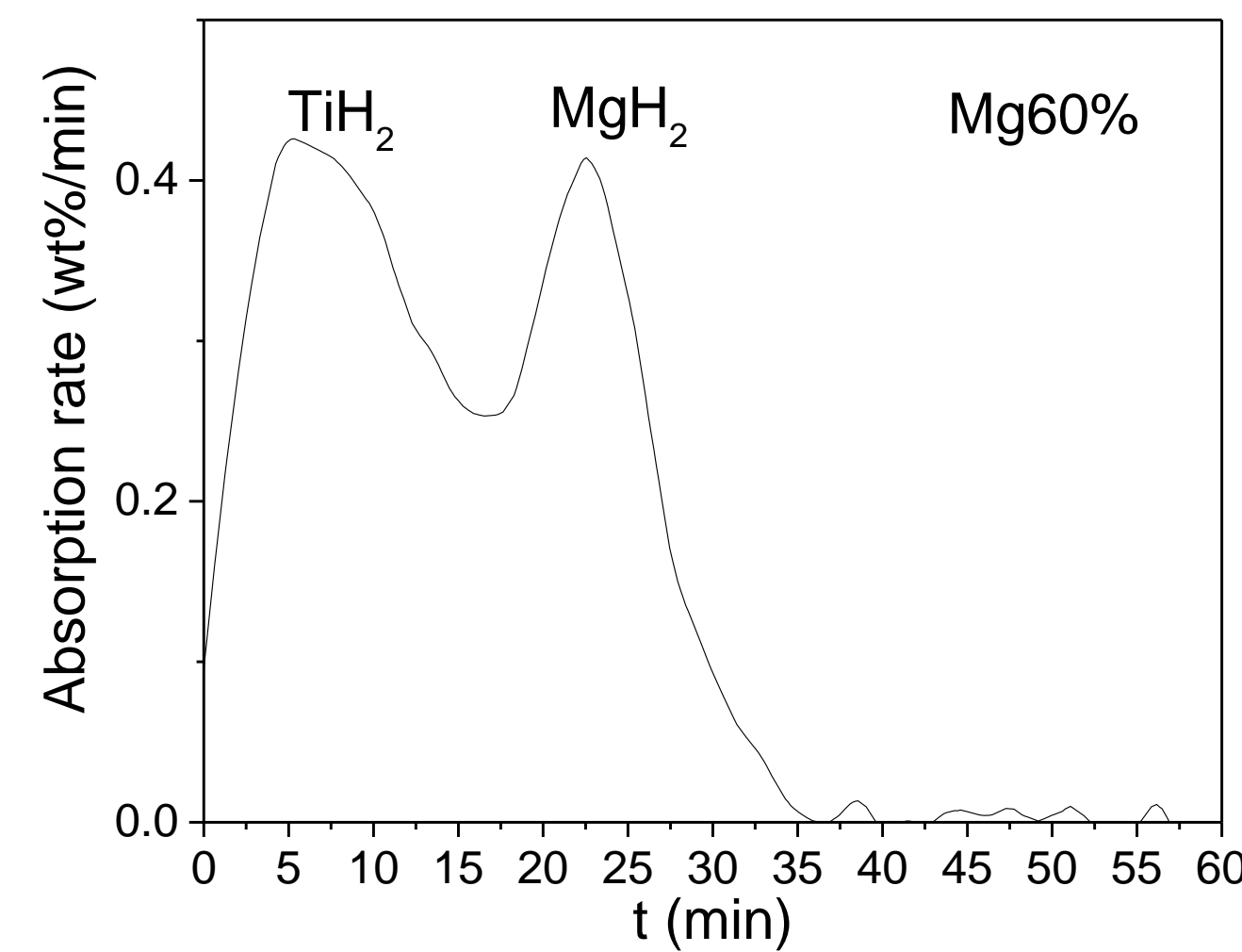


Introduction

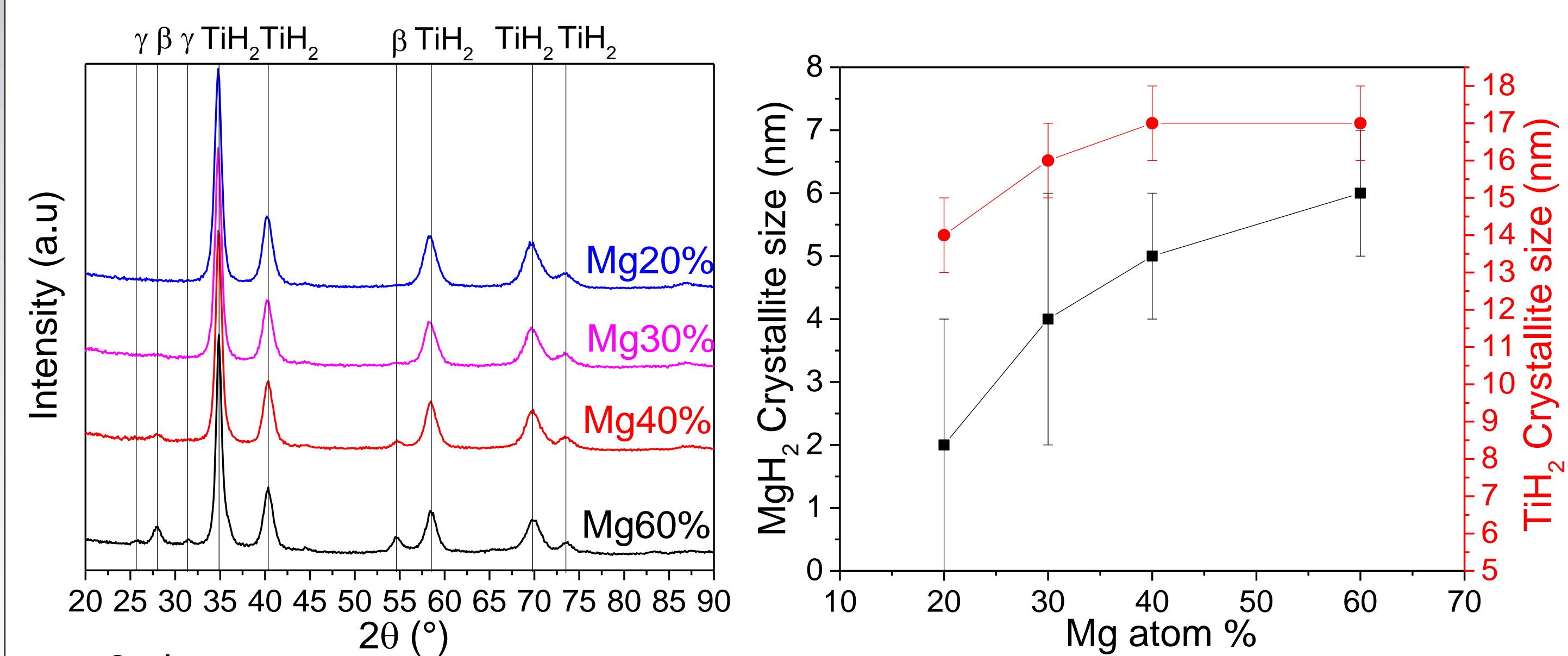
Embedding MgH₂ clusters in an immiscible transition metal lattice can promote destabilization of MgH₂ by size and interface effects [1], as well as an improvement in hydrogen sorption kinetics[2]. The aim of this work is to ascertain whether thermodynamic and kinetic modifications of the Mg/H₂ reaction can operate by embedding MgH₂ clusters in a hydride matrix. For this, Ti-rich nanocomposites are elaborated by mechanochemistry of Mg and Ti under hydrogen gas [3]. Their structural properties were determined by X-Ray Diffraction (XRD). Pressure Composition Isotherms (PCI) and isothermal reaction kinetics were measured in Sieverts' rigs. Further thermal analysis was performed by Thermal Desorption Spectroscopy (TDS) and Temperature Programmed Desorption (TPD).

Synthesis

- Reactive ball milling, P4 Planetary mill
 - milling time: $t_m = 1h$
 - Ball to powder mass ratio: 70:1
 - milling speed: 400 (disk), - 800 rpm (bowl)
 - Hydrogen pressure : $P_{H_2} = 8 MPa$
 - Stainless steel balls and vials
 - P and T monitoring during the reaction (H_2 absorption with time)
- Targeted compositions $(Mg_xTi_{1-x})H_2$:
 - $x = 0,2$ (Mg20%)
 - $x = 0,3$ (Mg30%)
 - $x = 0,4$ (Mg40%)
 - $x = 0,6$ (Mg60%)
- 2-steps reaction:
 - TiH₂ formation ($0 < t_m < 15 min$)
 - MgH₂ formation ($15 < t_m < 35 min$)

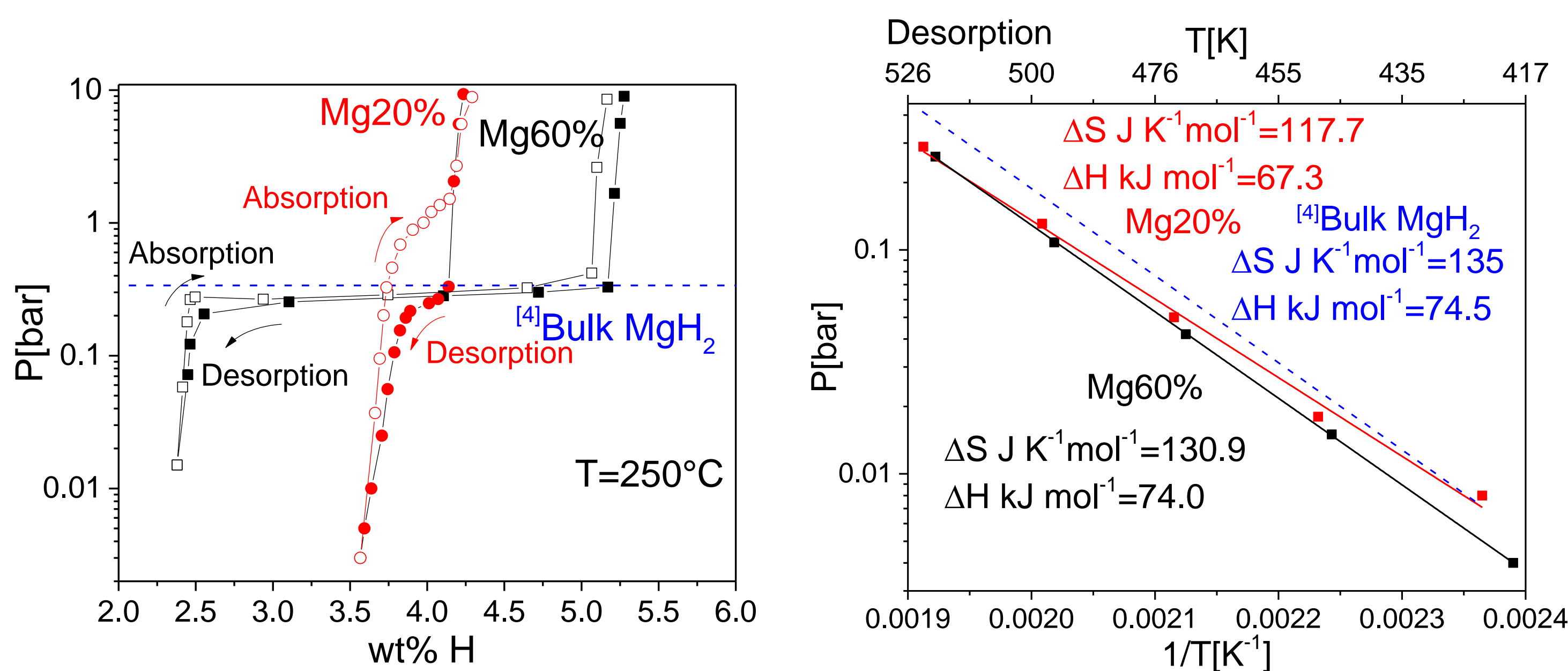


Characterization XRD



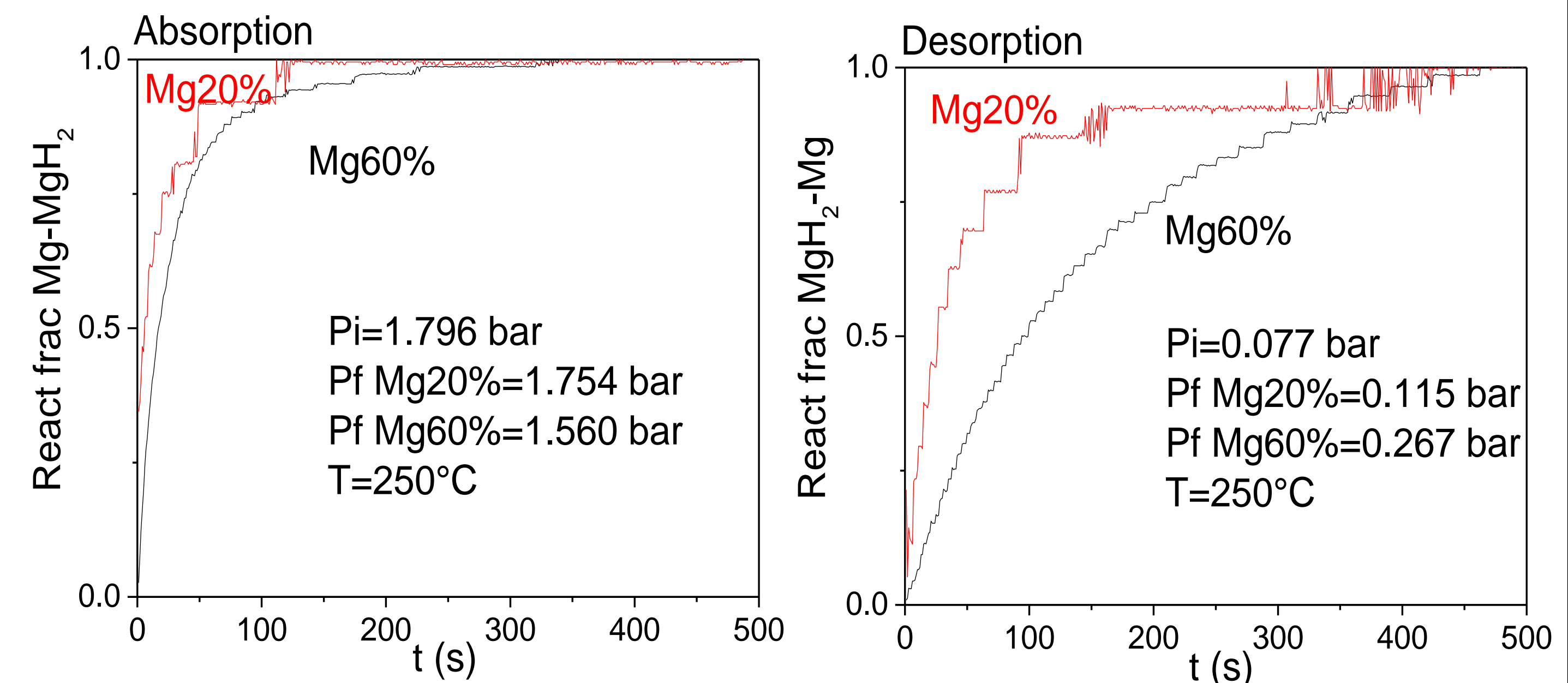
- 3 phases:
 - β -MgH₂ (P4₂/mnm, tetragonal, rutile type)
 - γ -MgH₂ (Pbcn, orthorhombic)
 - ϵ -TiH₂ (I4/mmm, tetragonal)
- Crystallite size reduction of MgH₂ phase with the increase of Ti content
- Crystallite size of TiH₂ phase reduces also with the increase Ti content

Thermodynamics



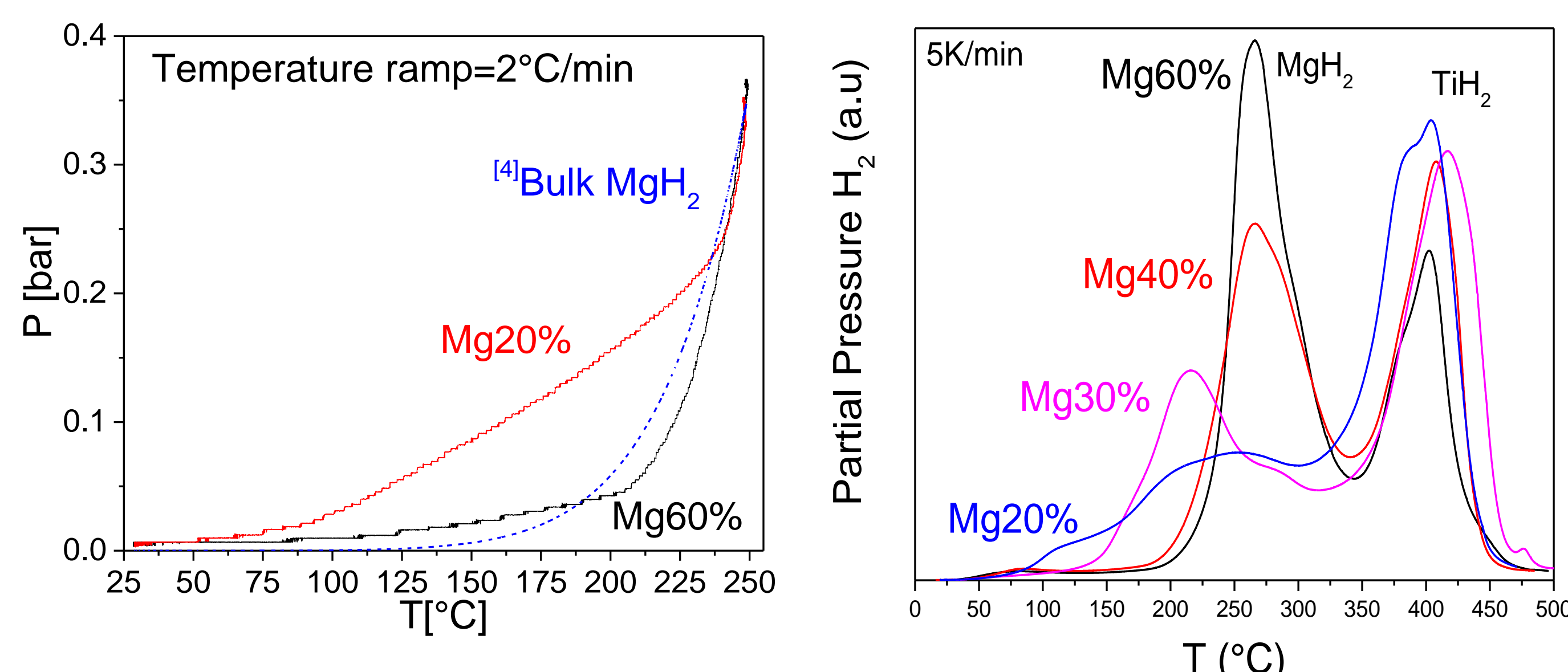
- Mg-H thermodynamics deviate from the bulk ones for low Mg content (20%)
 - Higher absorption pressure
 - Larger hysteresis
- Enthalpy and entropy reduction for low Mg content (20%) as compared to bulk Mg (compensation effect)

Kinetics



- Faster kinetics both on absorption and desorption by decreasing Mg content
- Kinetic enhancement is attributed to size effects

Thermal analysis



- TPD: For low Mg content, desorbed hydrogen pressure exceeds Mg/MgH₂ thermodynamics, evidencing destabilization effects
- TDS: On decreasing Mg content, the onset and peak temperature of the first peak, assigned to MgH₂ desorption, decreases

Conclusions

- MgH₂ clusters with crystallite size as low as 2 nm for Mg_{0.2}Ti_{0.8}H₂ are formed by mechanochemistry of Mg and Ti under hydrogen gas
- This reduced size modifies the thermodynamics of Mg-H.
- Both enthalpy and entropy decrease leading to compensation effects.
- Kinetics are enhanced on decreasing Mg content due to size effects.
- Outlook: further characterization of the nanostructure by NMR and TEM

References

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