Metal Based Phase Change Materials And Their Metallic Encapsulation For High Power Thermal Energy Storage

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Background

Integration of renewable energy sources in existing electric grid imparts huge pressure on conventional power plants for flexible operation. Large scale thermal energy storage units could be a tool for balancing fluctuations in demand and during excess energy periods. High storage capacity and fast loading and unloading cycles are a must.

Metal based Phase Change Materials (PCM) with metallic encapsulation provide these properties. Consequently, the present work develops storage concepts and investigates metallic PCM in steel based encapsulations for different applications in energy generation. The PCM storage systems in view shall be suitable for being operated at specific temperatures within the range from 250 °C up to 580 °C. A main topic of this work is the resistance of the encapsulation metals against attack by the molten PCM alloys.

Materials selection

- Suitable PCM metallic materials are alloy compositions with eutectic melting temperatures. Table- 1 lists the chosen alloy compositions for the present investigations.
- For encapsulation three different steel qualities have been selected.

Preparation and testing of PCM and encapsulation materials pairs

Alloys and encapsulations

- Alloying of PCM: Induction melting of the elemental metals (purity levels >99.9) under N_2
- Manufacturing of steel based encapsulation materials: In tubular form by filling with the PCM and by closing the ends through welding.

Heating cycle tests

- Long-term continious heating above melt temperature as well as to cyclic heating and cooling in order to simulate real working conditions.
- Specifically ZnAl6 alloys have been tested in-depth due to its relevance for a specific application in view: heating cycles in a temperature range from 450 °C down to 290 °C (or room temperature).

Characterization methods

- Differential thermal analysis DTA/TG (NETZSCH STA 409 PC Luxx)
- Phase change enthalpy and specific heat capacity (NETZSCH DSC 204 F1 Phoenix)
- Light, stereo and electron microscopy (SEM) with energy dispersive X-ray analysis (EDX)
- Thermal conductivity (NETZSCH LFA 467 HyperFlash)
- Dilatometry (Linseis L75)

Results

- Aluminium has been identified to be the most aggressive alloying element.
- The three steel variants show considerable differences in their resistance against the Al containing PCM alloys:
  - **Steel variant 1:** Strong reaction by forming FeAl phases at the PCM – steel interface with continuous dissolution of the steel (Fig. 5a)
  - **Steel variant 2:** Reduced reaction with dissolution of Fe in the PCM and the formation of Cr rich layers at the interaction zone which delaminate during cooling in order to create new blank steel – PCM contact sufraces (Fig. 5b)
  - **Steel variant 3:** Formation of a stable reaction layer with no further degradation within the relevant temperature range (Fig. 5c)
- Table- 2 summarizes the stability results of the three steel variants and the four investigated PCM qualitatively.

Pilot test rig

- Based on the results, a pilot test rig is under construction at our facility in Sulzbach-Rosenberg for steam generation under application oriented conditions.
- Test rig characteristics:
  - PCM capacity 1000 kg ZnAl6 alloy
  - Cyclic heating up to 500 °C
  - Storage capacity 53 kWh under operating conditions in a temperature range from 296 °C to 410 °C.

Conclusions

- Metallic PCM and capsule materials exhibit superior heat transfer and volume related storage capacities, if compared to organic or salt based PCM.
- A stable steel has been identified for the application with ZnAl6
- Work will go on with optimizing steel variants for higher Al containing alloys

Application Case

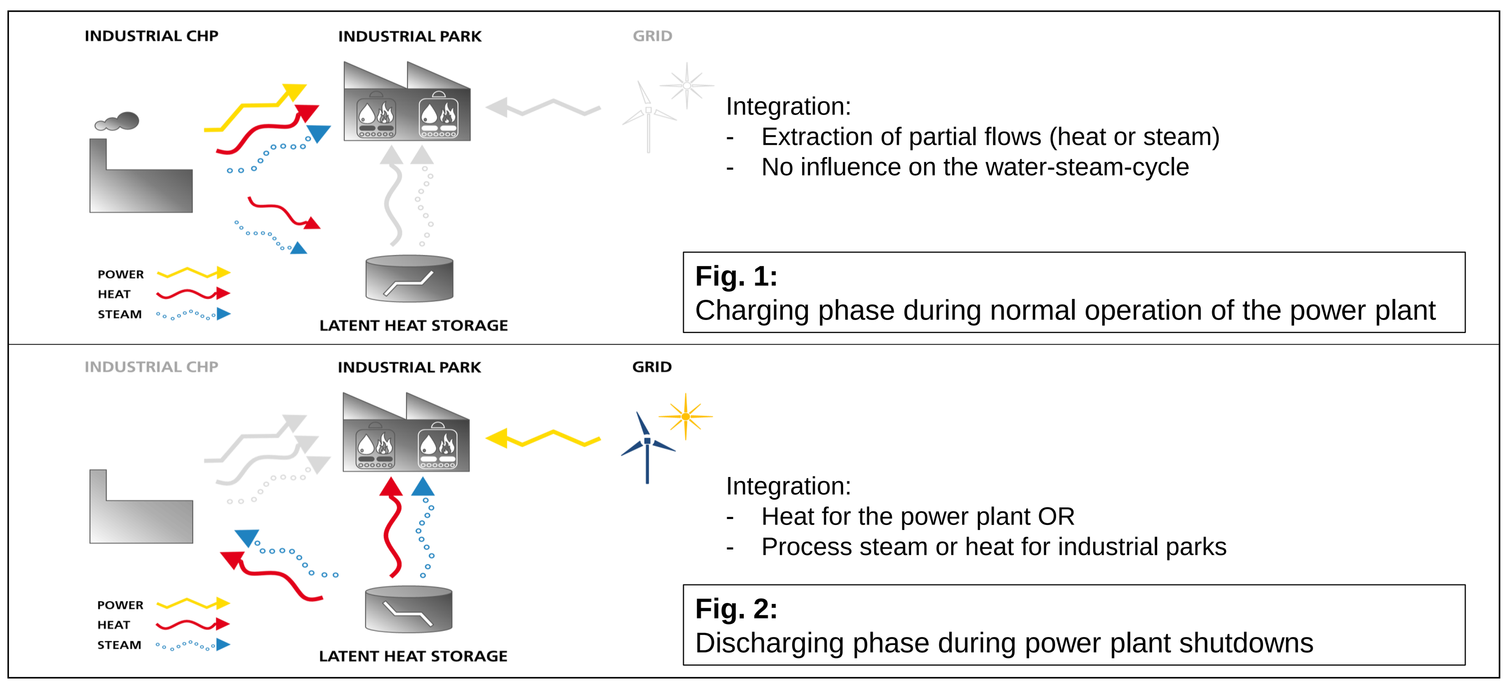

Fig. 1: Charging phase during normal operation of the power plant

Fig. 2: Discharging phase during power plant shutdowns

Selected materials properties

Table 1: Investigated alloy compositions along with their nominal and measured eutectic melting temperatures, mass specific latent heat, thermal expansion coefficients and heat conductivity.

Sr. No.	PCM alloy composition	Nominal /measured eutectic melting temperature in °C	Heat of fusion in J/g	CTE in 10^{-6}/°C	Heat conductivity in W/mK
1	ZnMg46.3	340 / 341	101	25	n.e.
2	ZnAl6	382 / 382	120	26	Solid: 130 Liquid: 70
3	AlMg35.8	450 / 452	225	n.e.	n.e.
4	Al68.5Cu26.5Si5	548 / 548	411	18	n.e.

Thermo-physical properties of the manufactured PCM

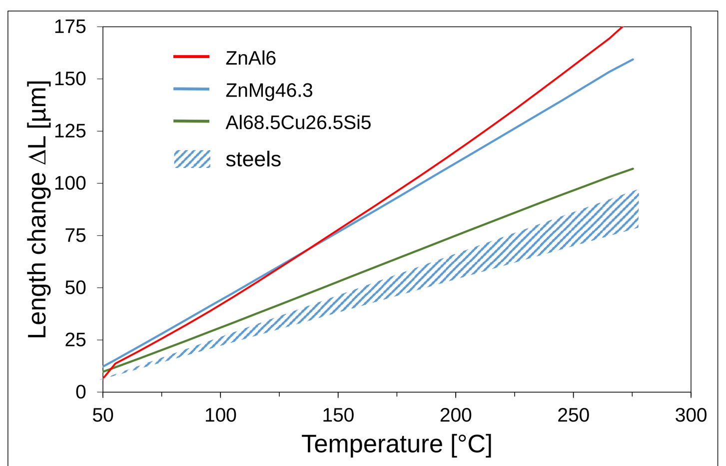

Fig. 3. Measured linear thermal expansion ΔL for PCM alloys and range from selected steels.

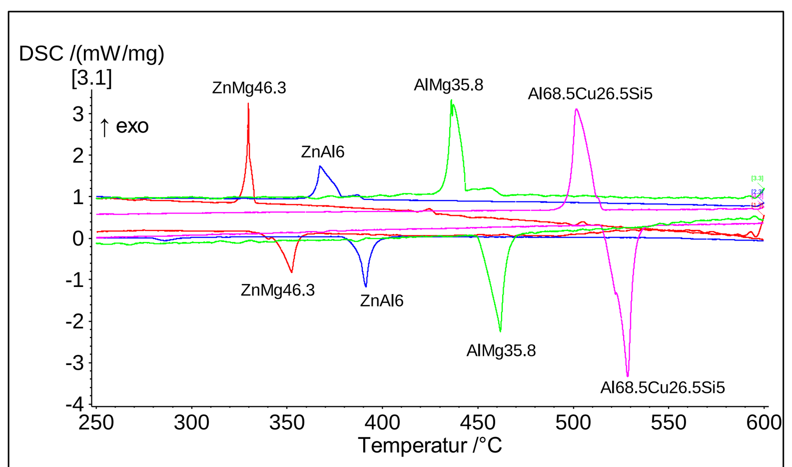

Fig. 4. DTA measured melting and solidifcation behaviour of the manufactured PCM eutectic alloys

Interface microstructures after heating cycles

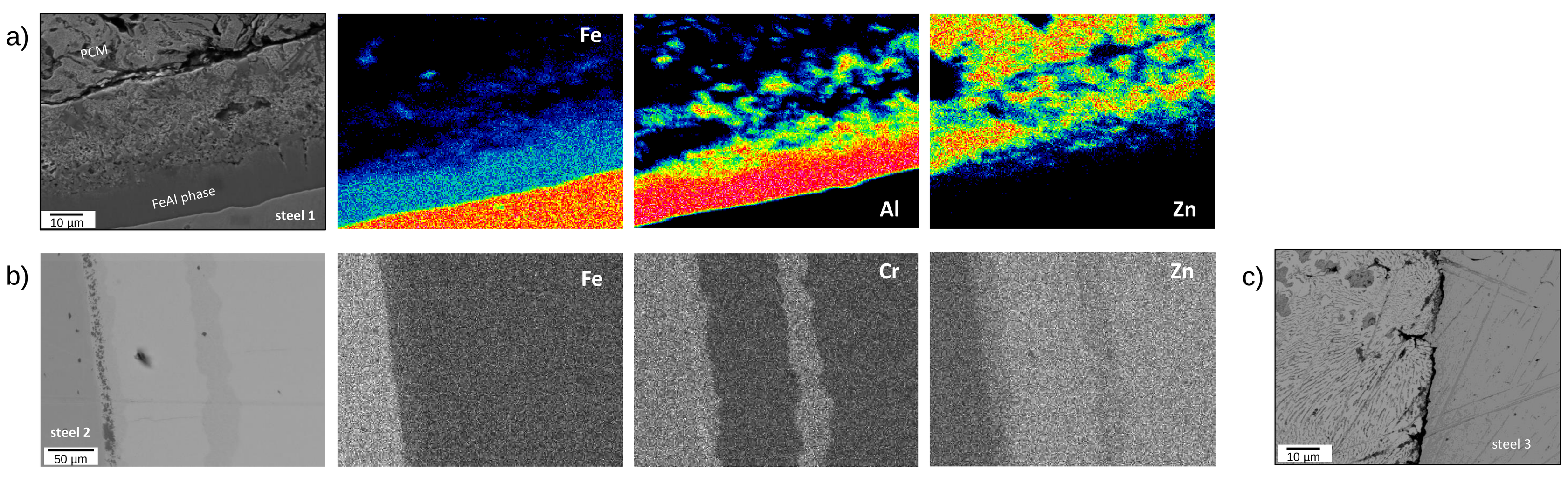

Fig. 5: SEM and EDX mappings of ZnAl6 PCM at steel front after thermal cycling in encapsulations from a) steel 1 (FeAl inter-metallics formation), b) steel (Cr-rich layer formation) and c) the resistant steel 3 quality.

Qualitative scheme for steel resistance against the PCM

PCM alloy	Steel Variant		
	Steel 1	Steel 2	Steel 3
ZnAl6	High reactivity	Low reactivity	Very low reactivity
AlMg35.8	High reactivity	Moderate reactivity	Moderate reactivity
ZnMg46.3	Very low reactivity	Very low reactivity	Very low reactivity
Al68.5Cu26.5Si5	Moderate reactivity	Moderate reactivity	Moderate reactivity

Table 2: General behaviour of the investigated PCM alloys in contact with the three different steel encapsulation materials.

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