

The Adsorption Ability Of Powders Obtained By Pulsed Electrical Discharge In Cryogenic Liquids



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Motivation

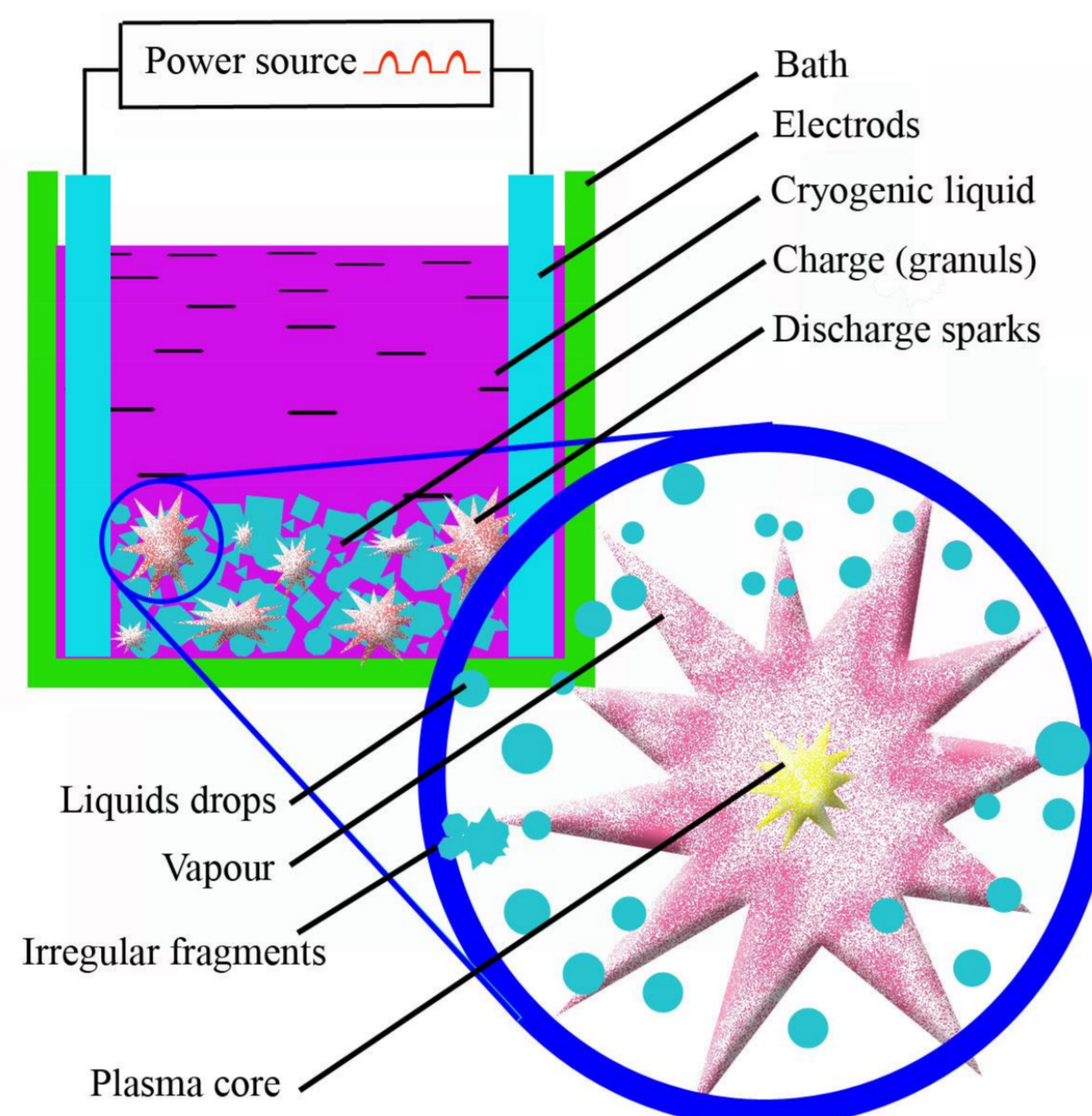
Significant heat realize has been observed during the heating in DSC calorimeter the micron-sized and nano-sized powders B2 alloys Ti-Ni [1], Ni-Al [2], Ni-Mn-Ga [3], Cu-Al-Ni [2], glass-forming alloy Zr-Ni-Cu-Ti-Al and pure Ti and Ni. Powders were obtained by electrical pulse discharge or so-called spark erosion (SE) method in liquid nitrogen and argon. This effect masked the effect of heat realize associated with martensitic transformation, which some of the powders of shape memory B2 alloys Ti-Ni, Ni-Al, Ni-Mn-Ga, Cu-Al-Ni undergoes.

Objectives

- To elucidate the effect of heat realize in SE powders
- To study the nature of this effect
- To determine the relationship between the structure of SE powder particles

Spark erosion method

- Heavy current applies between two electrodes, made from the pre-alloyed materials, that are immersed in a cryogenic liquid (argon or nitrogen).
- Small chunks of the pre-alloyed materials loaded in container between two electrodes from this materials.
- A lot of arc columns are formed between electrodes and pieces of materials.
- Melted droplets and/or vapor are quenched into solid powder particles by the surrounding coolant.



Experimental

- Differential scanning calorimetry (DSC)
- Thermal gravimetry analysis (TGA)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)

Morphologies of SE powder particles

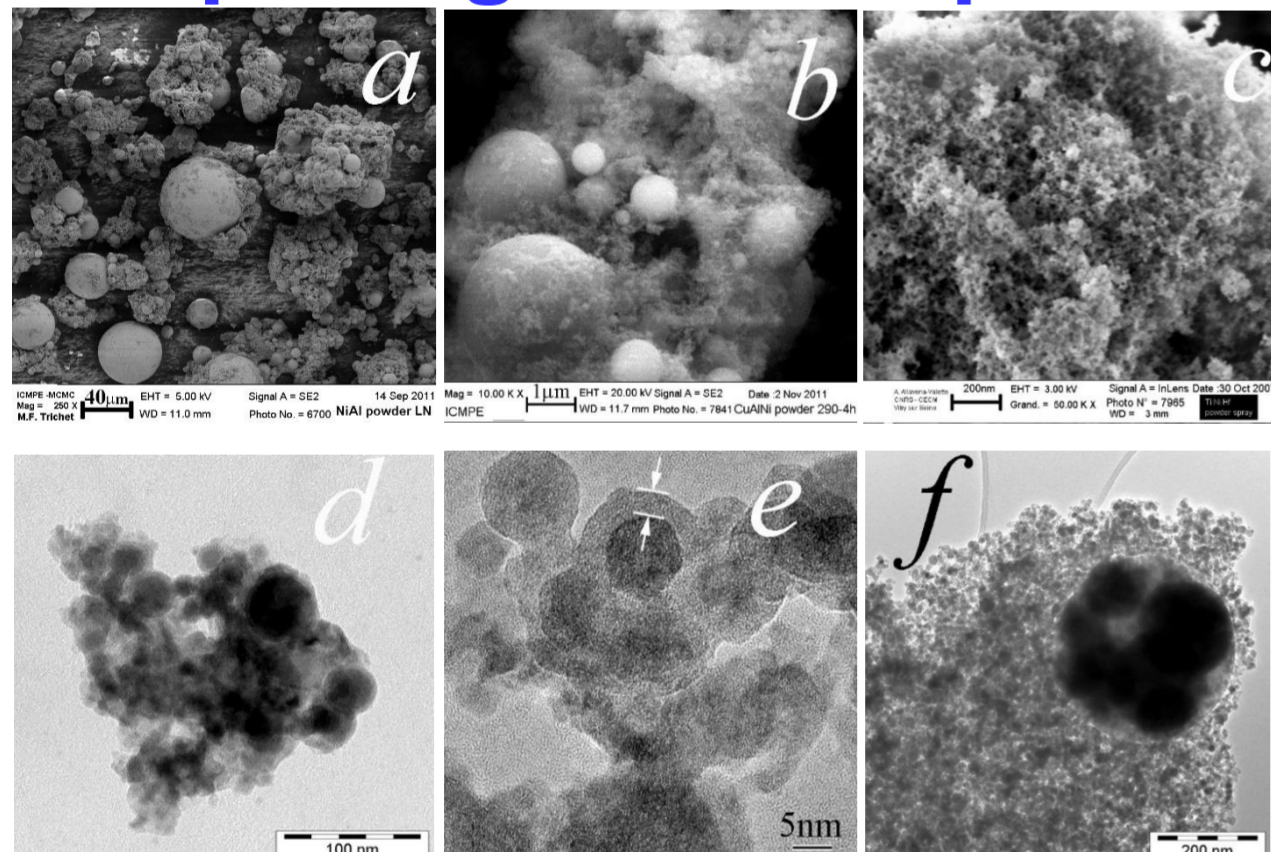


Fig. SEM 1. a) individual and agglomerates of Ni-Al particles; b) micron and submicron Cu-Al-Ni particles in the foam agglomerate; c) foamy agglomerates of Ti-Ni-Hf powder formed by nanofraction.

Fig. TEM. d) Zr-Cu-Ni-Ti-Al; e) Ti-Ni-Hf; f) Ni-Al. d) agglomerated particles are covered with an oxide layer. On e) the arrows indicate the oxide layer on the particle of the polyhedron. On f) a composite nanoparticle.

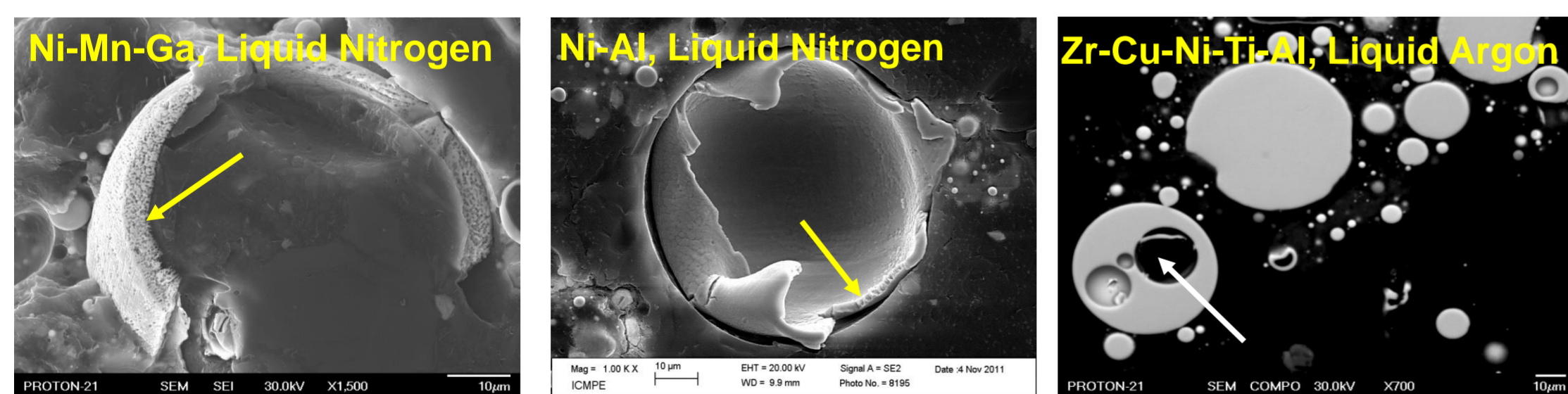


Fig. SEM 2. Hollow and porous particles obtained by spark erosion method.

Summary observations and discussion

- In all powders the spreading and powerful endothermic peak at the first heating in a calorimeter is observed. This peak disappears in the second cycle (**Fig. DSC analysis**).
- Because the position of the heat flow peak coincides with intense weight loss of the sample (**Fig. TGA&DSC**), it is associated with desorption processes.
- Estimation of the amount of desorbed water and the shift of the desorption temperature indicate the easy absorption of water by SE powders from the environment.
- When cooled to -50°C, the water vapor contained in the carrier gas atmosphere (nitrogen) sublimated on the surface of the particles, and when heated evaporated. (Sharp peak on **Fig. DSC analysis** c, d). This process is repetitive.
- The sequence of the main elements that formed the basis of the studied powders, in order of increasing their reactivity is as follows: Ni and/or Cu → Al → Ti and/or Zr (Hf).
- Assuming that the gas desorption is mainly related to H₂O, we obtain that the specific heat of desorption is 3.4 kcal / mol. These are too small to be explained by the desorption of chemically adsorbed gases, but the interval of intensive desorption is too high for the desorption of physically adsorbed gases. This is explained by the simultaneous course of two processes: desorption - endothermic, and oxidation - exothermic.

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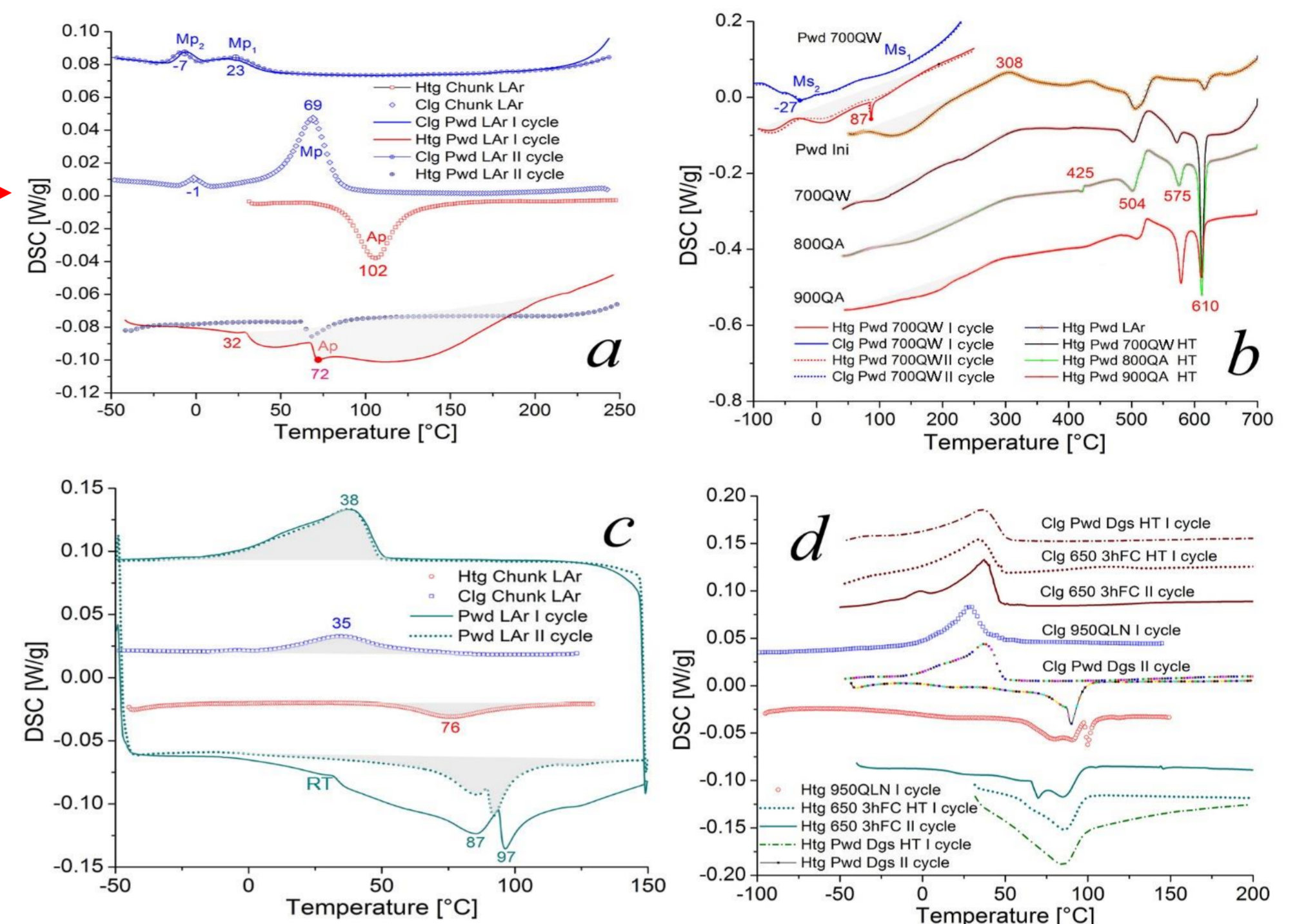


Fig. DSC analysis: a), b) - Cu-Al-Ni. a) - Chunk Ar (Pwd Ar) – a piece of alloy (powders obtained in liquid Ar after SE); b) low- (-100÷250°C) and high-temperature cycles (HT - heating up to 700°C). Gray filled region is the heat realize, which mask the reverse martensitic transformation. 700 (800,900) QA (QW) – quenching in air (water) at the corresponding temperature. Htg (Clg) - heating (cooling) on the first (second) cycle (I (II) cycle). c), d) - Ti-Ni-Zr-Cu. Htg (Clg) - heating (cooling) on the first (second) cycle (I (II) cycle). Numbers near the curves - temperature features. Mr, Ar - temperature of martensitic, austenitic transformation peaks. DGS – powders after preliminary ageing at about 200°C during several hours in vacuum. ### 3hFC – powder after ageing at temperature ###°C in vacuum followed by slow cooling in furnace

Weight loss of the powder during the heating

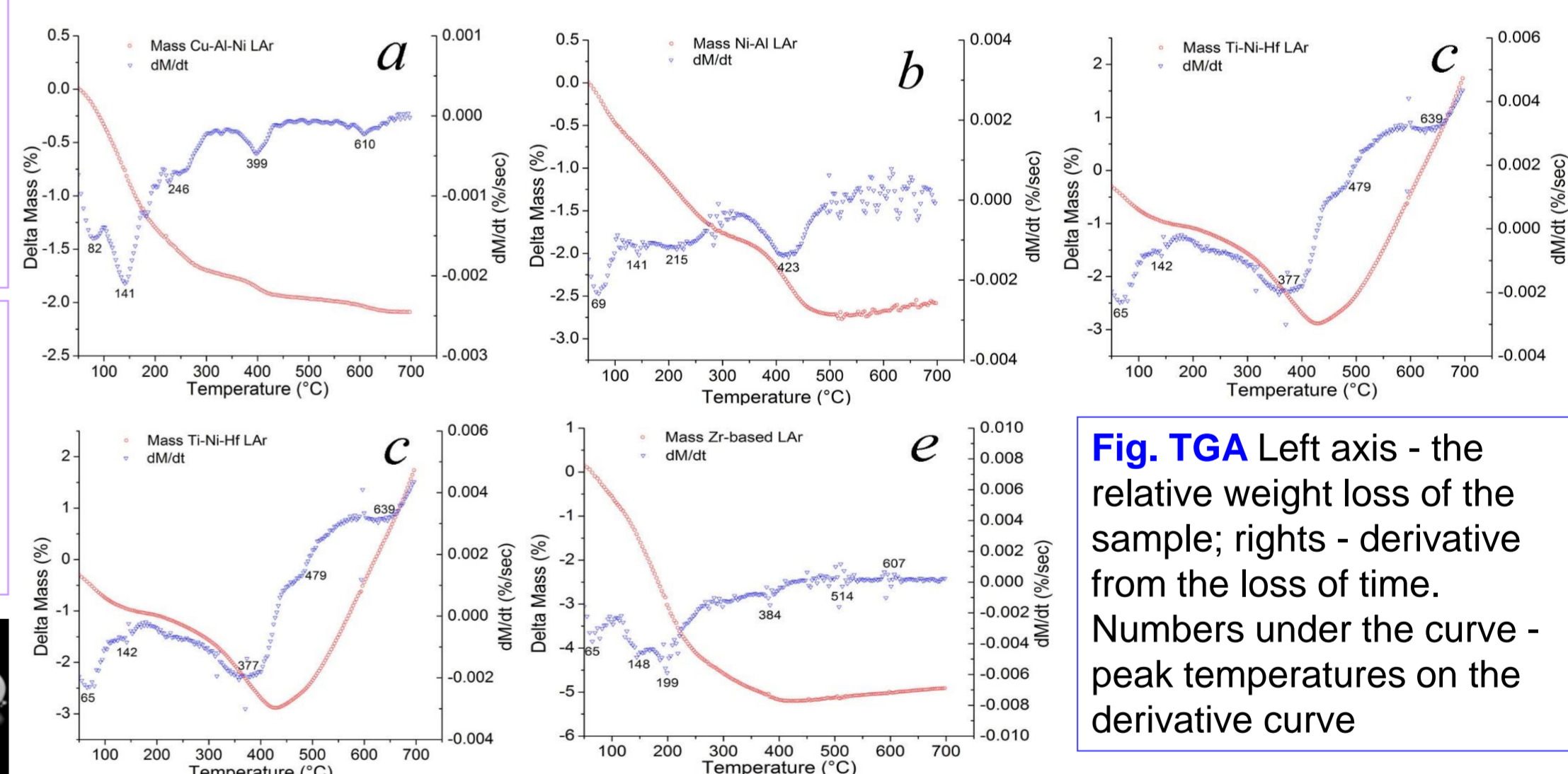


Fig. TGA Left axis - the relative weight loss of the sample; rights - derivative from the loss of time. Numbers under the curve - peak temperatures on the derivative curve

Weight loss and heat realize

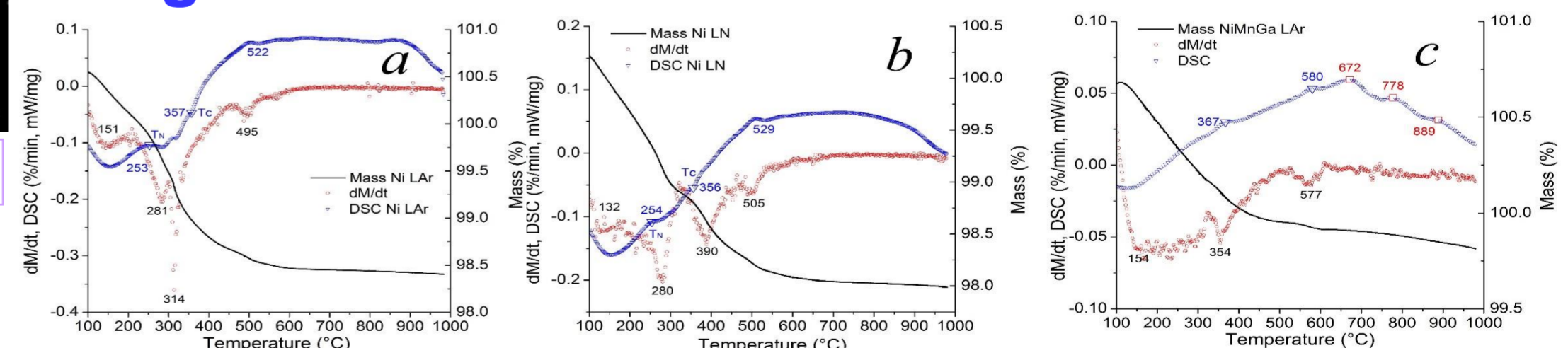


Fig. TGA&DSC Left axis is derivative from the loss of mass over time and heat flux from the sample; rights - relative weight loss. The numbers next to the selected peculiarities on the curves dM/dt and DSC - are the corresponding temperatures. T_C, T_N - Curie and Neel points.

Conclusions

During the spark erosion of alloys and metals and following storage the powders are adsorbed of up to several weight percent of water vapor and other gases. In addition repetitive sublimation of water vapor is observed when cooling powders below 0°C. When heated to ~450°C, gases are released with heat release, which is the result of desorption of chemically adsorbed gases and oxidation and reduction reactions of alloy components.

References

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2. Monastyrsky G.E., Ochinnik P., Gilchuk A.V. et al. The role of nano-sized fraction on spark plasma sintering the pre-alloyed spark-erosion powders // Journal of Nano- and Electronic Physics, -2012.-4:1.P.1007-1-7