

## Metallic form-stable phase change materials for thermal energy storage and management: general features and effect of manufacturing process on thermal response and stability

C. Confalonieri, Z. Li, E. Gariboldi

Phase Change Materials (PCMs) can be applied for thermal energy storage and management. During a thermal cycle, the most diffused class of PCMs, latent heat PCMs, can store the latent heat associated to an endothermic phase transition and release it when the transition is reversed. If a solid-liquid transition is exploited, leakage of the molten phase above the transition temperature must be avoided: a possible solution is to embed the active phase (the actual PCM) in a passive phase, obtaining a Form-Stable (FS) PCM. In the case of high-thermal conductivity passive phase, there is also the advantage of an increased thermal conductivity of FS-PCM compared to the active phase and this allows a faster thermal response of the system. In the present paper, an Al-Sn alloy is presented as metallic FS-PCM manufactured by two powder metallurgy processes and by different Sn powders.

Thermal and mechanical behaviour of the material were analysed considering the effect of particle size distribution of initial powders and powder mixing technique.

**KEYWORDS:** METALLIC PHASE CHANGE MATERIALS – FORM-STABLE – THERMAL ENERGY STORAGE – POWDER METALLURGY – BALL MILLING

### INTRODUCTION

Phase Change Materials (PCMs) are materials whose application is based on a phase transition occurring in certain conditions. The phase transition causes the variation of at least one material property every time that the conditions are met. Concerning thermal applications, PCMs can be used to store and manage thermal energy, exploiting the energy associated to the phase transition. In fact, when an endothermic transition occurs (e.g. melting), the energy is stored and when the transition is reversed (e.g. solidification) the energy is released. During a phase transition, the material temperature does not increase, allowing heat storage at almost constant temperature. Therefore, a PCMs stores sensible heat as its temperature increases, then, when transition occurs, it stores latent heat at constant temperature and finally it can still store sensitive heat as the new phase heats up. PCMs can thus be applied in Thermal Energy Storage systems to store surplus of heat to be released later or as heat sinks to avoid too high temperatures during heating or cooling. Practical examples are climatization systems in buildings, cooling systems for electronic devices, solar thermal storage systems, solar power plants, heat exchangers and smart textiles [1–3].

### PCMS CLASSIFICATION

Many materials belonging to different classes have been studied and applied as PCMs in the last decades [2–4]. The clas-

sification of PCMs can be firstly based on the type of phase transition involved, i.e. gas-liquid, solid-gas, solid-liquid, solid-solid [2–4]. The large volume change associated to gas transitions makes them generally unsuitable for PCMs applications, even if the latent heat is relatively high [2,3]. This issue is less significant for solid-solid and solid-liquid transitions, in which volume change is usually lower than 10% [2]. The advantage of exploit a solid-liquid transition is the higher latent heat; on the other hand, solid-solid transitions do not have issues regarding leakage of the liquid phase from the container [2,3].

Further classification of PCMs is based on the material. Focusing on solid-liquid PCMs, they can be organic, i.e. low molecu-

**Chiara Confalonieri,  
Ziwei Li,**

**Elisabetta Gariboldi**

Politecnico di Milano,  
Dipartimento di Ingegneria Meccanica,  
Via La Masa 1, 20156 Milan (Italy)

lar compounds and polymers, or inorganic materials, like salts, inorganic compounds and alloys [2,4]. Commercially, organic materials and salts are the most spread PCMs.

### Selection principles and properties of PCMs

The selection principles of PCMs are based on several requirements related to thermodynamics, physics, kinetics, chemistry and economics, summarized in Tab. 1 [2,5,6]. The most important thermophysical properties to be considered are latent heat and transition temperature. The transition temperature defines the application range of the material: organic and salt-based PCMs have relatively low transition temperatures (below 120÷150°C), which are higher for inorganic compounds and alloys [3,7,8]. Considering the latent heat, metallic PCMs have

the lowest value [7]; however, thanks to their high density with respect to other materials, they achieve relatively large heat per unit volume [2,3].

Specific heat and thermal conductivity of PCM are additional thermophysical properties of interest for thermal management systems [2,5,8,9]. High specific heat helps the thermal storage to be increased by sensible heat, so that in some cases sensible heat PCMs have been proposed [9]. High thermal conductivity is beneficial for most of the Thermal Energy Systems since it fastens the PCM response both during heat storage and its release [9]. Low amounts of high-conductivity metallic phases or graphite are thus added to organic materials to increase their thermal conductivity [10].

**Tab. 1** – Main requirements for PCMs related to thermodynamics, physics, kinetics, chemistry and economics (based on [2,5,6])

THERMODYNAMICS	PHYSICS	KINETICS	CHEMISTRY	ECONOMICS
Phase change temperature	Good phase equilibrium	Fast crystallization	Good chemical stability	Readily available raw material
Large latent heat	Low vapour pressure	No supercooling	Minimal corrosiveness and anti-oxidation	Low cost
Relatively large thermal conductivity	Low volume change in phase transition		Completely reversible freezement cycle	Good industrial utility
Large specific heat	High density		Non-flammable	
Congruent melting			Non-explosive	
			Non-toxic	
			Safe to use	

### ENCAPSULATED AND FORM-STABLE PCMS

As already mentioned, the drawback of using a solid-liquid PCM is the possible occurrence of leakage of liquid phase after transition and, thus, usually these materials need a container [3]. However, most of inorganic and metallic PCMs are corrosive for the container, while organic materials often have low conductivity, poor thermal response and flammability [3]. These problems can be faced in two ways: encapsulating the PCM or using a form-stable PCM [2,3]. An encapsulated PCM consists of an active phase enclosed in a milli-, micro- or nanometric capsule made of a passive material, i.e. a higher-melting material. However, the encapsulation process can be expensive and

complex, as well as PCM conductivity can be still too low [2]. On the other hand, in a form-stable material, the active phase is embedded in a higher-melting passive matrix without any encapsulation; since the matrix is solid throughout the service temperature range, it should prevent leakage and keep the structural properties [2,9]. Moreover, the passive phase combined to the PCM, e.g. organic PCM in metallic matrix, can significantly affect the thermal response of the hybrid material and in particular enhance thermal conductivity [11,12]. In both cases, the material can be considered as a composite in which the actual PCM is the active phase.

## METALLIC FORM-STABLE MATERIALS

Metallic PCMs are the less applied class of PCMs. The most probable reason is related to their relatively low latent heat, even if they have many interesting features: high transition and maximum temperatures, high thermal conductivity, large latent heat per unit volume, good thermal stability and reliability [5,6,8,13]. The high application temperatures make metallic PCMs suitable for medium- and high-temperature applications, ranging from 120°C to more than 1600°C; space heating, steam turbine electricity generation, high temperature industrial processes could benefit from the application of these PCMs [7–9,13]. Usually metallic PCMs are obtained through encapsulation (i.e. mechanical process or electroplating); however, oxidation and degradation occur often at high temperatures, reducing material durability and thermal energy performance [8,9]. Therefore, the use of alloys to obtain form-stable PCMs has been considered more and more promising [8]. To ensure geometrical stability, two approaches can be followed: the active phase can be embedded in the passive matrix (i.e. Cu in Fe, Sn in Al) [14] or it can have just a good wettability on the matrix (e.g. Bi in Cu) [15]. A further requirement to keep microstructural and compositional stability is that there must be no interaction between the two phases. To achieve these goals, Sugo et al. [13] suggested to apply specific Miscibility Gap Alloys (MGAs), i.e. systems whose elements are immiscible in both liquid and solid state, keeping a stable composition over time and thermal cycles. In fact, the formation of intermetallics and solid solutions is prevented, due to the low solubility of the high-melting alloy also when the active phase is liquid. The issue of this approach, which can be extended also to ternary systems, also considering intermetallic phases, is that the natural cooling of MGAs gives a microstructure consisting of grains of the high-melting phase surrounded by the low-melting active phase, which is the opposite situation with respect to the desired one. A possibility to overcome this limitation is to apply a powder metallurgy process (powder mixing, compaction,

sintering) [13,16].

Our research group is studying an Al-Sn alloy with a 40% mass of Sn, which corresponds to about 20% in volume. Al-Sn alloys were suggested as possible MGAs candidates as PCMs by Sugo et al., as well as Fe-Cu, Fe-Mg and Al-Bi [13]. Actually, this alloy has a metastable miscibility gap, since an eutectic transition occurs at 228°C; however, since the eutectic composition corresponds to almost pure Sn (99.8% mass Sn), the presence of eutectic phase can be neglected [17,18]. So, the following assumptions were made [13]: the alloy consists only of pure Al and pure Sn and the activation temperature is the melting temperature of pure Sn, i.e. 232°C. Moreover, the solubility of Al in Sn and vice versa is minimal between room temperature and 300°C, which can be the service range of the material. In the present paper, a comparison between different production processes of this alloy, all based on powder mixing and compaction, is presented. The main feature that will be highlighted is the effect of powder size distribution. In particular, some results obtained in a previous study on the same alloy [19], in which the manufacturing process was closer to that proposed in [13], will be compared with new samples. If in the previous study two different Sn powders were simply mixed to Al ones before compression, in the second one they were mixed in a ball mill, with the purpose of size reduction and hardening of powders.

## MATERIALS AND METHODS

The two set of samples of Al-40% Sn alloy were produced by powder metallurgy using the same type of powders. Only one Al powder was used, while two Sn powder types were chosen with different powder size distribution. Powder specifications are summarized in Tab. 2. Powder 106 has low homogeneity, since it contains both relatively high quantity of fine particles (< 20 µm) and coarse particles (anyway, generally smaller than 100 µm). On the other hand, SN powders has very fine particle-size distribution and good homogeneity.

**Tab. 2** – Powder specifications

ELEMENT (COMMERCIAL NAME)	PRODUCER	COMPOSITION	POWDER SIZE (OVER SIEVE GRAIN SIZE)	TYPE OF DISTRIBUTION
Al	ECKA Granules GmbH, Germany	Al > 99.7 m%	<45µm	
Sn (106)	Metalpolveri S.r.l, Italy	Sn > 99.7 m%	<45µm: 55-85% >45µm: 15-45% >106µm: 0.1%	inhomogeneous
Sn (SN)	Metalpolveri S.r.l, Italy	Sn > 99.9 m%	<25µm: 64÷71% 25µm<OSGS<45µm: 20÷26% 45µm<OSGS<75µm: 5÷11% >75µm: <0.3%	homogeneous

Two mixtures consisting of Al and 40 mass% of Sn (20% volume) were prepared by simple mixing (SM) and ball milling (BM) of powders. Simple mixing was performed at 25°C for 1 h in a tumbler mixer at 20 rpm [19]. The other powder mixture was ball-milled using a planetary mill (Retsch PM 400 Planetary Ball Mill) with ball/powder mass ratio 5:1, for 24 h at 250 rpm. All the further production steps were the same for both mixtures. Blends were compressed at room temperature in a cylindrical steel mould, giving samples with diameter and height of about 15 mm; the maximum applied pressure was 300 MPa (53 kN) for 1 minute. Then, samples were sintered for 1 h at 500°C in Ar atmosphere.

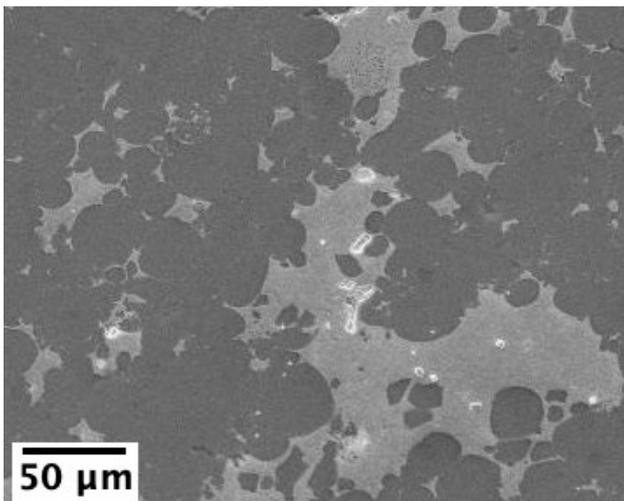
Characterization investigated microstructural, thermal and mechanical properties. Microstructure was analysed through Optical Microscopy and Scanning Electron Microscopy (SEM, Zeiss EVO 50). Differential Scanning Calorimetry (DSC, Setaram TG/DSC Labsys 1600) was used to study thermal response of the material and, in particular, to measure transition temperature and latent heat. DSC test consisted in two cycles around activation temperature, i.e. Sn melting temperature (~232°C): the

sample (55 mg) was heated at 20°C/min with a holding time of 5 min at 320°C, then cooled at 20°C/min to 40°C, repeating the cycle after 5 min holding. Finally, Vickers micro-hardness tests with load of 4.9N and dwell time of 15 s were used to evaluate mechanical properties.

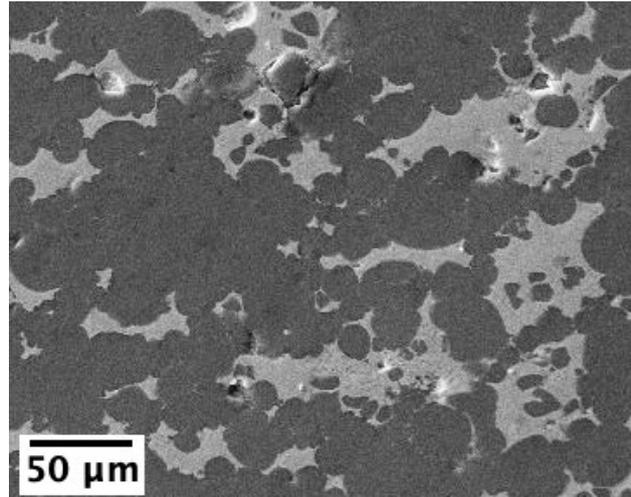
## RESULTS AND DISCUSSION

### Microstructure

Secondary electron (SE) SEM micrographs of simple-mixed samples produced with different Sn powders are shown in Fig. 1 and Fig. 2 (compression direction vertical, as in all the microstructures shown in the present paper). The white phase is Sn and the grey one is Al, while darker spots are pores. Gariboldi and Perrin [19] observed that inhomogeneous Sn powders (Figure 1) result in a more inhomogeneous structure, characterized by larger Sn particles; on the other hand, there are less pores with respect to the other powder blend, since small Sn particles present in the inhomogeneous Sn powder can fill better the voids.



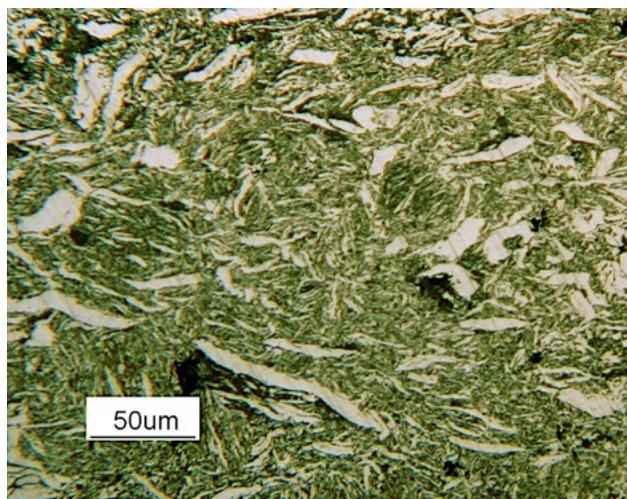
**Fig. 1** – SE-SEM image of sample obtained from SM inhomogeneous Sn powders at low magnification



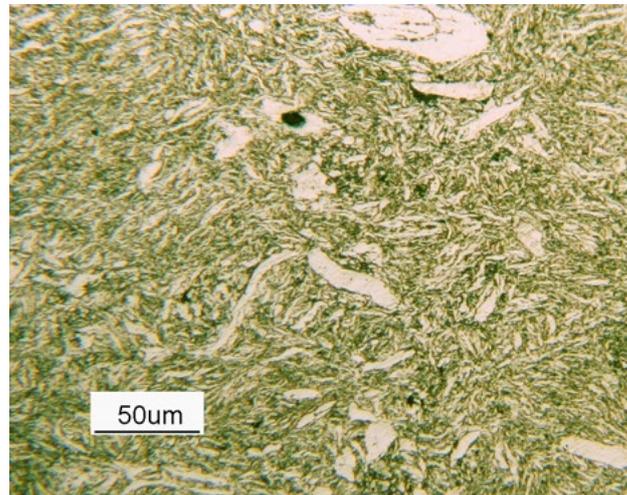
**Fig. 2** – SE-SEM image of sample obtained from SM homogeneous Sn powders at low magnification

Comparing SEM images of SM samples with OM micrographs of BM samples at the same magnification (Fig. 3 and Fig. 4), it is evident that BM of powders allows the formation of a significantly finer microstructure. In the case of BM, OM micrographs highlight better the presence of the three phases: Al particles

(white), Sn regions (grey areas) and pores (black spots). The microstructure is so fine, that it is not possible to distinguish clearly Sn particles. The sample obtained from homogeneous Sn powder has a more homogeneous final microstructure, with less pores and coarse particles.



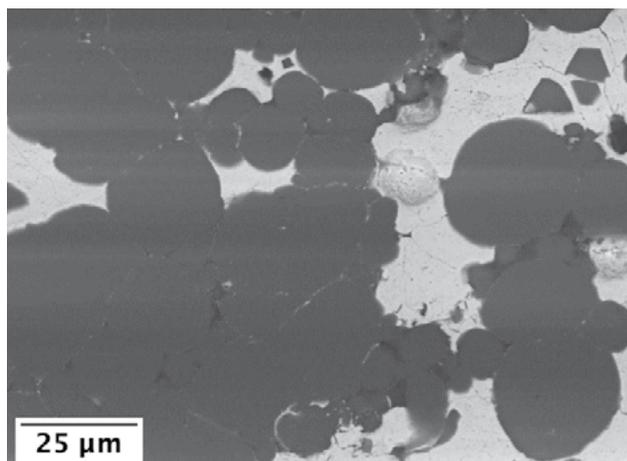
**Fig. 3** – OM micrograph of sample obtained from BM inhomogeneous Sn powder



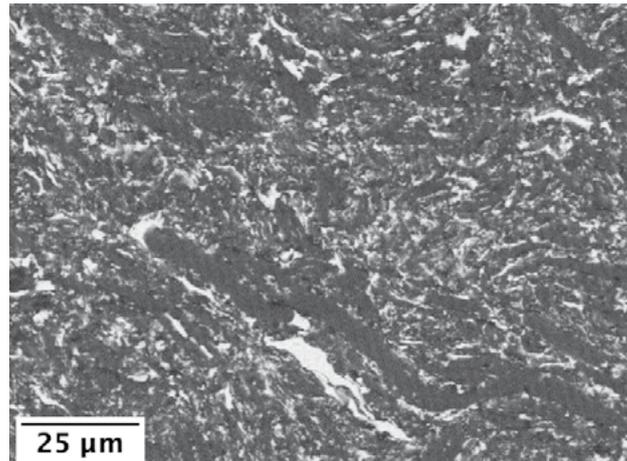
**Fig. 4** – OM micrograph of sample obtained from BM homogeneous Sn powder

Backscattered (BSE) SEM micrographs of a simple-mixed and a ball-milled sample obtained with the same Sn powder (homogeneous) are shown in Fig. 5 and Fig. 6. In both images there are almost no pores. In BM sample, there are both coarse particles ( $50\div 70\mu\text{m}$ ) and small particles ( $100\div 200\text{ nm}$ ); the latter are generally at the boundary of Al particles and are so small that it is not possible to distinguish them clearly, even at higher magnification. As observed by Gariboldi and Perrin [19], the structure obtained from SM powders was finer than

those obtained by Sugo et al, [13], but is not exactly the desired “inverse microstructure” which is considered necessary to avoid leakage of the active phase [13] and, in facts, they observed leakage during thermal cycles. The same observation can be made for BM microstructure; however, apart from some relatively coarse Sn regions, Sn particles are generally isolated. Therefore, the microstructure of BM samples is considered by the authors to be less critical as far as leakage of Sn during service is concerned.



**Fig. 5** – BSE-SEM image of sample obtained from SM homogeneous Sn powders at high magnification



**Fig. 6** – BSE-SEM image of sample obtained from BM homogeneous Sn powders at high magnification

## Thermal response

V-shaped melting peak was observed for all samples (Fig. 7). The difference between BM and SM samples is in the peak size: BM samples have smaller peaks and, so, lower energy is stored (about 14 J/g for BM, about 28 J/g for SM). However, the transition occurred at the same temperature in all samples (onset temperature at 228/230°C, peak temperature at 239/240°C). At present, the reason for the lower stored energy in BM samples is not clear and it will be further investigated. A simple lower content of Sn due to losses in production steps seems to be not enough to explain such reduction. More differences between samples obtained by different

powders and/or manufacturing processes are observed in solidification (Fig. 8). The common feature for all samples is the presence of multiple peaks. The difference is in the shape of peaks. Both SM samples show the main peak at the beginning of transition (~228°C) and some secondary small peaks at lower temperatures (one peak for inhomogeneous powders, three peaks for homogeneous powders). BM samples display at least four small peaks and the main one could be considered the one occurring at about 150÷160°C, even if the actual temperature range changes for the different Sn powders used in the process; both DSC cycles confirm this behaviour.

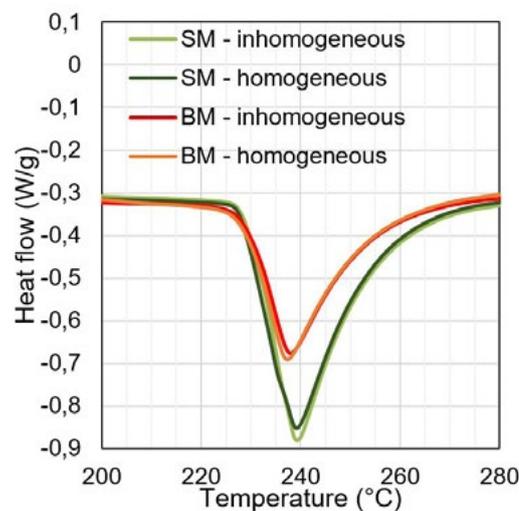


Fig. 7 – DSC curve in correspondence of melting peak

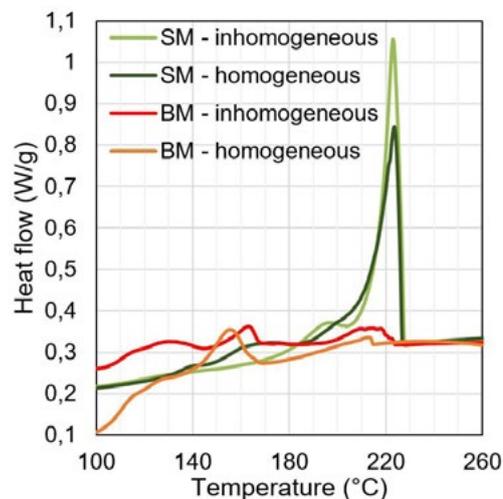


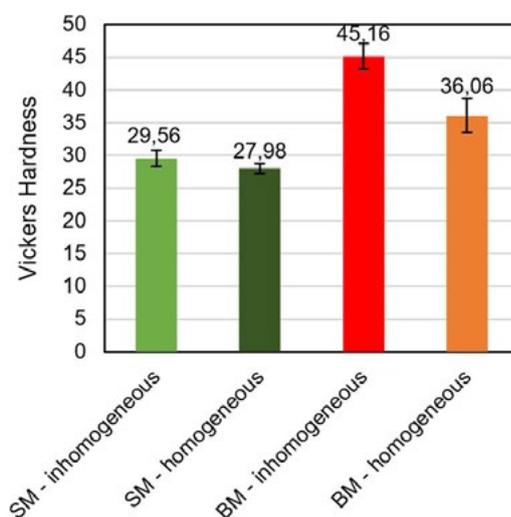
Fig. 8 – DSC curve in correspondence of solidification peak

Explanation of the solidification behaviour could be ascribed to the Sn particle size distribution inside the material. In fact, smaller particles with dimension below 1  $\mu\text{m}$  solidify at lower temperatures [20] and, since the particle size distribution is quite wide, more than one solidification temperature can be observed. Anyway, this phenomenon will be further investigated. The practical consequence of these peak shapes is that SM PCMs can both store and release heat relatively fast, while BM PCMs can provide quick storage and gradual release.

## Mechanical properties

Results of Vickers micro-hardness tests are summarized in Fig. 9. Hardness values for BM samples are higher than values for

SM samples. This fact was expected since BM causes hardening of powders. Moreover, also the dispersion of the soft sub-micrometric Sn particles in the Al matrix could contribute to hardening [21]. Higher-hardness material are beneficial for applications where FS-PCMs require structural properties for the material, to be retained at least after thermal cycles and, if possible, as the active phase is molten. No data are at present available on the stability of microhardness after thermal cycles for the BM samples, nor its changes with temperature. Nevertheless, its correlation to the fine submicrometric, well separated Sn particles suggest that good hardness levels should be retained after thermal cycles and structural properties can be considered for the material at temperatures up to 250-300°C.



**Fig. 9** – Results of Vickers micro-hardness tests on samples produced with inhomogeneous and homogeneous powders mixed by SM or BM

## CONCLUSIONS AND OUTLOOK

Ball milling applied as powder mixture technique in production of PCMs based on MGAs proved to give finer microstructures with respect to simple mixing. Sn particle size distribution has a significant effect on the thermal behaviour of the material, especially when very small particles are present. This result suggests that, if Sn particle size can be controlled, also the thermal response of the material during thermal cycles can be tailored. Moreover, this microstructure has a beneficial effect

on hardness, which is higher than the value for FS-PCM obtained by compaction of simple-mixed powders. Considerations made on the correlation between different hardness and microstructure suggest that a control of Sn particle size could also be beneficial for the stability of structural properties and for the structural response during thermal cycles. Further investigations will be carried out to investigate the effect of thermal cycles simulating service and check the role played by Sn particle size distribution.

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