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Design of Porous Structures in Shape Memory Alloy Systems

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Abstract. The fabrication of porous shape memory alloys is analyzed based on the particularities of the alloy families and the spacer materials potentially to be used for pores generation. The analysis is made for two distinct set of shape memory alloy families Cu-based and Ti-based, taking into account solid state sintering technologies. Sodium chloride, magnesium and carbamide are comparatively analysed for the use in the fabrication of the porous shape memory materials. Particularities in using spark plasma sintering technique for the fabrication of porous shape memory alloys is discussed. Experiments performed on alloys belonging to the shape memory system are analyzed from macro and microstructural point of view in order to assess the influence on the resulting functionality. The results allowed the selection of the optimal processing parameters for the fabrication of porous alloys.

1. Introduction

Shape memory alloys are materials that are known to exhibit shape recovery following a plastic deformation by heating above a certain temperature that is specific to the chemical composition of the alloy.

Porous materials are materials with possible use in the fabrication of lightweight structures, filters, damping components, heat exchanges and even biomedical applications especially due to the presence of a large volume of porosity [1-5]. Porous shape memory alloys have been manufactured via various techniques: self-propagating high temperature synthesis (SHS), conventional sintering (CS), hot isostatic pressing (HIP), metal or powder injection molding (MIM), spark plasma sintering (SPS) and the space holder technique (SHT) [6]. Sodium chloride, magnesium and carbamide are the main materials used as spacers. Spark plasma sintering is a technique that allows the rapid sintering of materials in one single process that combines pressing and sintering, thus avoiding extensive oxidation, generation of uniform structures with limited grain growth during the fabrication process and high reproducibility [7].

Porous shape memory alloys are gaining importance in practical applications especially in two fields: medical implant devices and as energy absorption structural materials. While for biomedical applications the Ti-based alloys are the one with real potential, for energy absorbing applications other alloy system can also be considered. The main target for porous NiTi remains biomedical applications because of the following properties good biocompatibility, comparable to conventional porous stainless steel and titanium (Ti) implant materials; a combination of high strength (important to prevent deformation or fracture), relatively low stiffness (useful to minimize stress shielding effects) and high toughness (essential to avoid brittle failure); and shape-recovery behavior facilitating implant insertion and ensuring good mechanical stability within the host tissue [8].

Copper based shape memory alloys are among the materials with very high damping capacity, especially in martensite and in the martensite austenite transformation range. Among copper based shape memory alloys the mostly used ones are CuZnAl and CuAlNi alloys. CuAlNi alloys are more expensive, but they are more resistant to degradation of functional properties due to undesired aging effects [9].

The aim of this paper is to present our work on the fabrication and characterization of porous shape memory alloys using spark plasma sintering. The focus is on CuZnAl shape memory alloys that could be used for damping and filtering applications.

2. Experimental details

The samples of CuZnAl were made by sintering following mechanical alloying of the powders using a planetary ball mill. The milling was realized for 8 hour with a speed of 300 rpm. After this the powder was mixed with salt (NaCl) of tow granulation (fine and coarse) with a proportion of 2/3 powder -1/3 salt. The mixing was made in a cylindrical recipient with a rotation speed of 50-60 rpm for 5 hours. The sintering was realized with a spark plasma sintering machine (FCT Systeme GmbH), (Figure 1), with a 20 mm diameter tungsten carbide (WC) mould (Figure 2).

Figure 1. Spark plasma sintering machine.

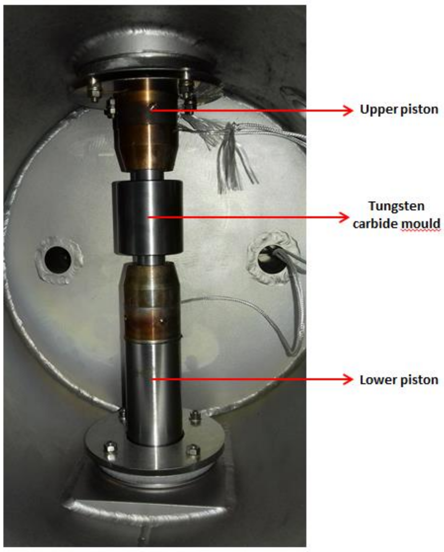

Figure 2. Tungsten carbide mould.

The sintering was made was made in two steps using 50°C/min heating speed: the first step was heating until 350°C, with a holding time of 3 minutes; the second step was heating until 450°C with a holding time of 10 minutes. The pressing force used was 20 kN. The cooling was controlled until 50°C, after that it was cooled in the chamber of the machine until room temperature. The samples were heated at 850^{o}C and maintained for 15 minutes, followed by water cooling. For the sintered samples, the salt was dissolved following the sintering process.

A Ni-Ti was also made by conventional sintering, using mechanically alloyed Ni and Ti powders and fine salt, followed by conventional sintering in a vacuum sealed quartz ampoule.

Microstructural observations of the samples was made by scanning electron microscopy (SEM) in a TESCAN Vega 3 LM scanning electron microscope (SEM), equipped with a Bruker Quantax 200 Energy Dispersive X-ray Spectroscopy (EDX) system with Peltier-cooled XFlash 410M silicon drift detector.

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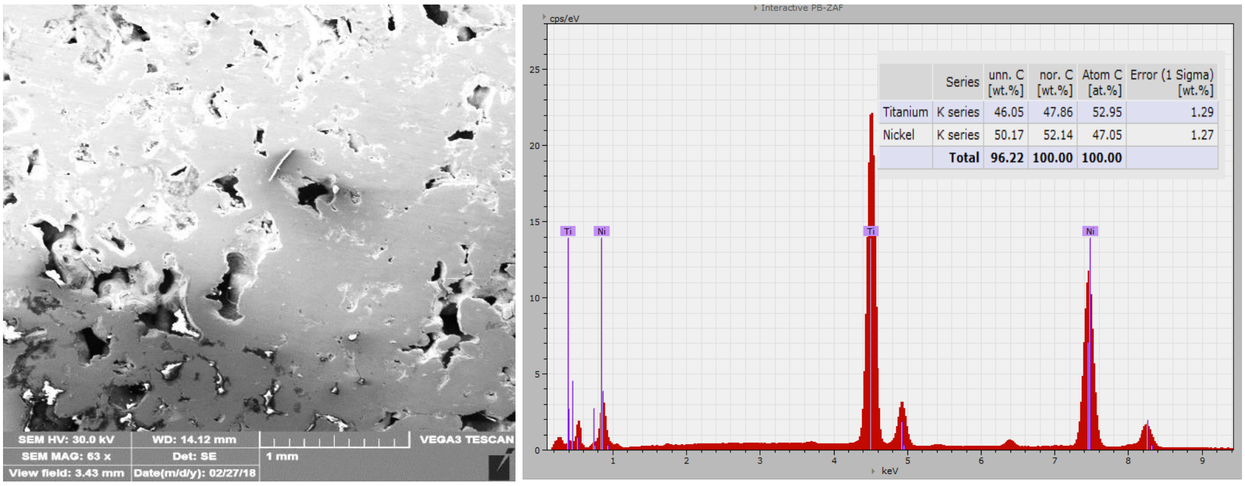
3. Results and discussions

The structure of the of the NiTi sample produced by vacuum sintering following salt dissolution shows typical pores and a very limited quantity of salt in places where it was not fully removed. The composition was analyzed and was in the compositional range of shape memory alloys, with a composition slightly higher in Ti, making it Ti-rich (figure 3).



	Series	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Error (1 Sigma) [wt.%]
Titanium	K series	46.05	47.86	52.95	1.29
Nickel	K series	50.17	52.14	47.05	1.27
	Total	**96.22**	**100.00**	**100.00**	

Figure 3. NiTi shape memory alloys produced by vacuum sintering.

The Cu-Zn-Al porous shape memory alloy produced by spark plasma sintering were of disk shape with a thickness in the range of 1-5 mm and dense (figure 4a), the SEM investigation also revealed a fine NaCl cubical particle in the structure, prior to the dissolution process (figure 4b).

a) as sintered sample b) fine NaCl particle prior to dissolution

Figure 4. CuZnAl with NaCl spark plasma sintered sample.

The composition of the manufactured alloy as it resulted from the EDX investigation is 62 at% Cu, 20 at% Zn, 18 at% Al (figure 5).

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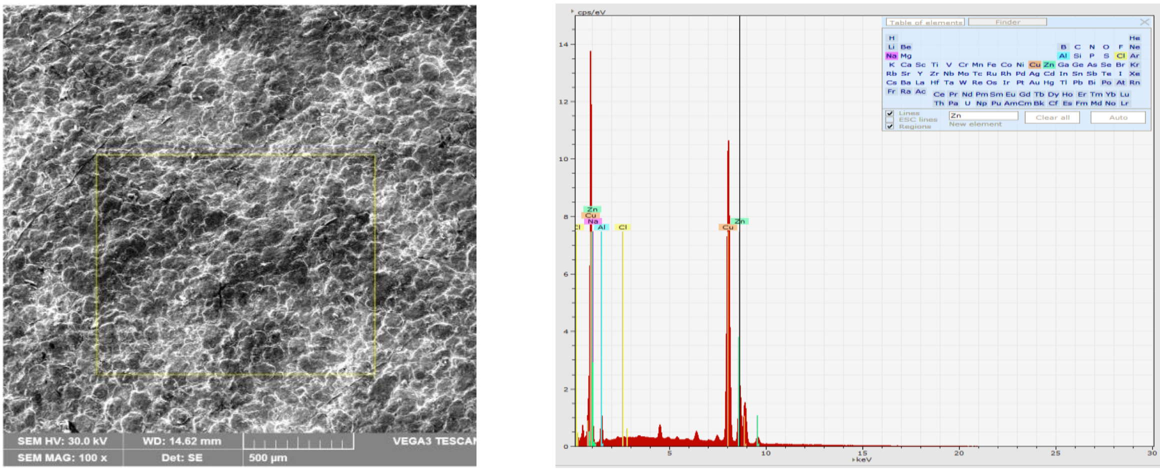
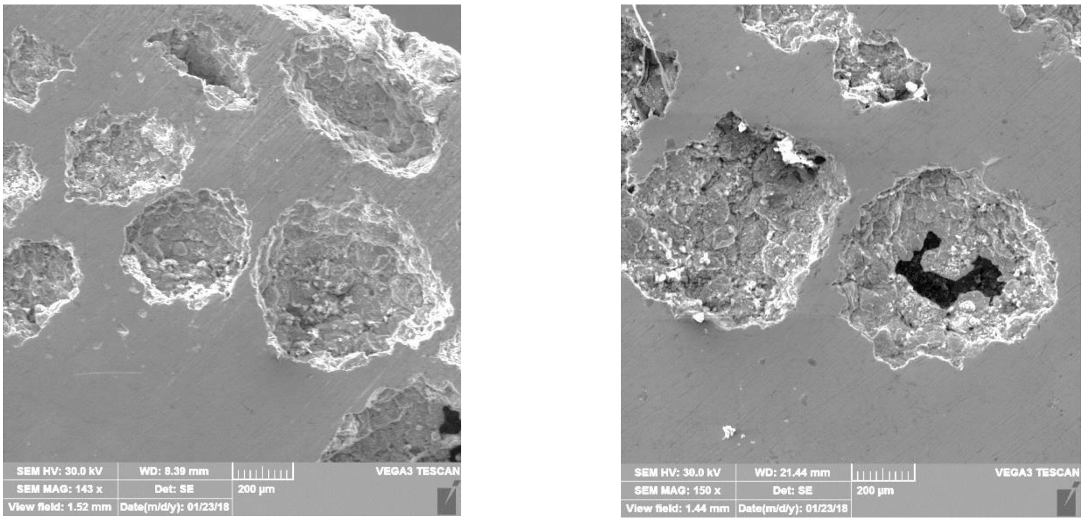


Figure 5. Surface analysis of the Cu-Zn-Al alloy sintered with fine NaCl particles.

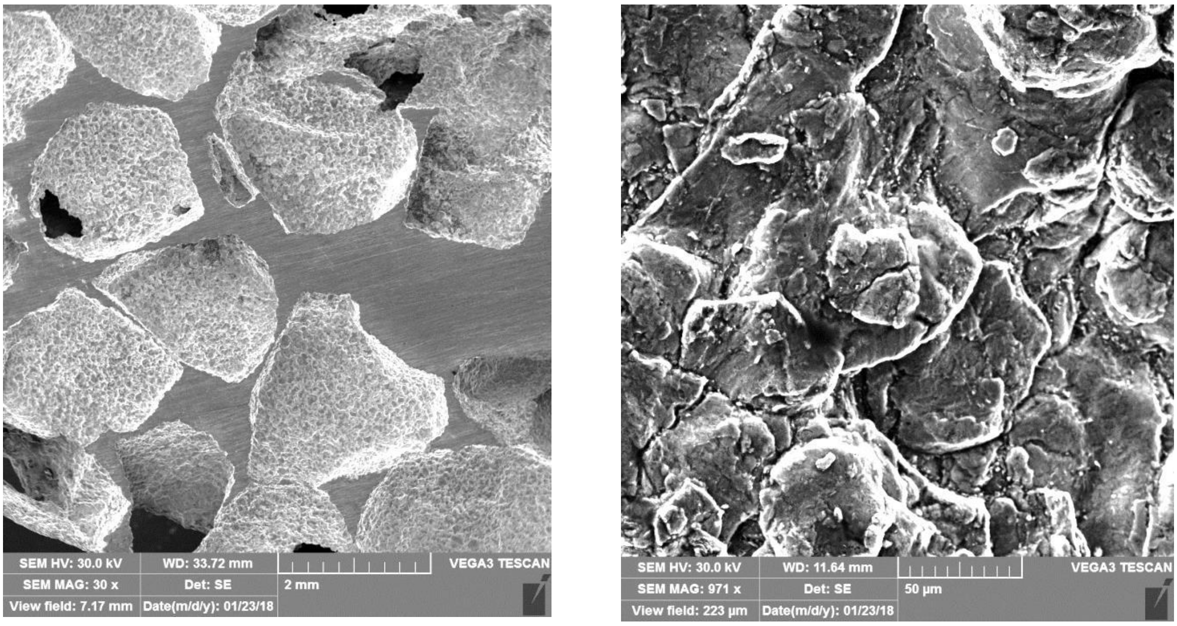
Figure 6 a, b shows the microstructure of the pores obtained after the dissolution of the Cu-Zn-Al samples sintered with fine NaCl particles. It can be seen that the pores are small and most of them have almost the same shape, this is because the NaCl particles used had the same dimensions and shape. The distribution of pores in the surface of sample is almost equal, there aren't pores agglomerated in one place.



a) b)

Figure 6. Microstructure of small pores.

For the CuZnAl porous shape memory alloy sintered with large NaCl particles, the pores have irregular shapes as it can be seen in figure 7 a, as the shape of the large particles. Because of the bigger dimensions of the NaCl particles used in this sample the pores tend to agglomerate in one place in the surface of the sample resulting in an irregular distribution of pores in the surface. On the other hand, the bottom of the pore shows that the material is well sintered.



a) b)

Figure 7. Microstructure of large pores in the Cu-Zn-Al alloy: a) -Large pores, b)- The bottom of a large pore.

The analysis of the quenched sample show the formation of a typical martensitic structure, thus confirming that the manufactured alloy belong to the shape memory system not only by composition but also by structure.

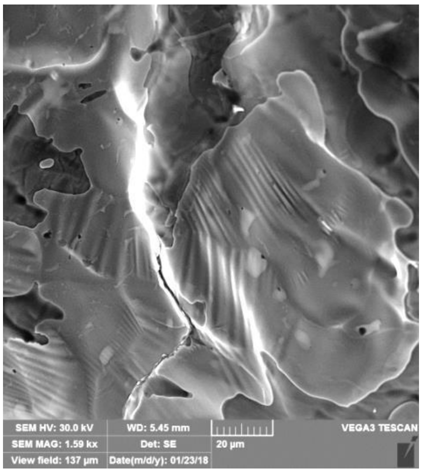


Figure 8. Martensite structure observed in the quenched Cu-Zn-Al alloy.

Further experiments are made to characterize the martensitic transformation in porous structures.

4. Conclusions

NaCl was successfully used to manufacture alloys belonging to the systems were shape memory effect and in their corresponding compositional range. It can be used in conventional as well as in spark plasma sintering, as long as the sintering temperature is lower than the melting temperature of the salt.

The resulting pores after the salt dissolution copy the features of the salt crystals. For the Cu-Zn-Al sintered alloy the large salt particles tend to agglomerate on the bottom of the sample during the sintering process in a larger amount compared to the fine particles.

The martensitic structure was observed in the Cu-Zn-Al sintered alloy following quenching.

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