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Research Article

A New Effective and Economic Sintering Technique for Cu-based Smart Alloys

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Abstract

It is well established that smart alloys prepared by powder metallurgy (P.M) techniques need to be sintered at elevated temperatures. There is Evidence that the sintering process of (Cu-Zn-Al) alloys is associated with a significant loss of zinc and the alloy may no longer behaves as a shape memory alloy. For instance, usual sintering processes if start at about 20.8%wt Zn will end up with almost 0.67%wt Zn. However, the new method ends with 20.48wt% Zn. An alternative method is available but, unfortunately, it is costly. Factors responsible for zinc evaporation are hopefully eliminated during this work. A container is specially designed and fabricated from quartz and the samples are protected by this sealed container during sintering. A pressurized argon inert gas is injected into the container before sealing. Hot isostatic pressure is also used in this research which plays an important role in this respect. An outstanding result has been obtained; there is almost no loss in zinc content after sintering. In addition to the above mentioned advantages, there is a substantial reduction in soaking time at such high temperatures.

Keywords: *Powder metallurgy, Sintering, Shape memory alloys, Porosity, Zinc evaporation.*

1. Introduction

The term “Smart Materials” describes a group of materials that react in a controlled way to external stimuli. They are capable of transforming other forms of energy to mechanical energy and, sometimes, vice versa. One of the most important categories of smart materials is the shape memory alloys (SMAs). They are a group of metallic alloys that have the special ability to `remember' or to retain a specific shape or size prior to deformation, by undergoing a heating process. This shape memorization is accomplished by the phase transformation process between two crystal structures, the higher temperature austenite phase and the lower temperature martensite phase. SMAs have already been used in a variety of applications such as robotics, biomedical engineering, vibration suppression, micro-electro-mechanical designs, etc.

Despite the fact that many alloy systems show the shape-memory effect, only few of them have been developed on a commercial scale (NiTi, NiTi-X, and Cu-Zn-Al) for engineering applications (Fugazza, 2003). Since the sixties of the previous century, where researchers at the Naval Ordnance Laboratory found the shape memory effect in Ni-Ti alloys, these alloys have been widely used due to their good corrosion resistance (Tan et al., 2003) , wear resistance (Zhang and Farhat, 2009), biocompatibility, superior engineering properties (Li and Rong, 2000) and greater shape memory strain (up to 8% versus 4 to 5% for the copper base alloys) (Xie, 2007). Unfortunately, Ni-Ti alloys are still expensive in comparison with other kinds of SMAs. This problem has led to the increase demand of the copper based alloys like Cu-Zn-Al and Cu-Al-Ni that are commercially available and 100 times less in price than Ni-Ti alloys (Hopulele et al., 2004).

Sintering is the basic method used in the preparation of the SMAs. Sintering’s variables are mostly thermodynamic variables, such as temperature, time, atmosphere, pressure, heating and cooling rates. Many previous studies have examined the effects of sintering temperature and time on sintering of powder compacts. It appears, however, that in real processing, the effects of sintering atmosphere and pressure are much more complicated and important (Rahaman, 2008). It is preferred to have minimum porosity in the material which can be obtained at high temperature and short time (Monmaturapoj and Yatongchai , 2010). Unfortunately, further increase in sintering temperature may lead to the evaporation of one of the elements that has the lowest melting point and therefore sometimes the density of the sintered samples does not show notable changes with increasing sintering temperature (Marrero et al., 2009).

Sintering atmospheres must be controlled for proper production since they affect the densification, microstructure, and the properties of the products. Padmavathi et al. (2011) found that sintering of (Al-Zn-Cu-Mn and Al-Cu-Mn-Si) alloys under vacuum gives

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better properties than sintering with nitrogen, hydrogen, and argon. The densification rate and final grain size were found to have a substantial dependence on the green density. As a function of sintered density, the densification rates were initially higher for the lower green density specimens, but the opposite behavior was observed in the final sintering stage. With increasing green density, the mean grain size was found to be smaller and the size distribution more uniform throughout the densification (Schoenberg et al., 2006).

It is well known that the sintering of the (Cu-Zn-Al) alloy is accompanied by significant loss in Zinc element as a result of evaporation at the high temperatures necessary for the copper diffusion. Because of this problem, researches had been redirected to the (Cu-Al-Ni) alloy instead of (Cu-Zn-Al) alloy. The use of spark plasma sintering leads to overcome the problem of evaporation of zinc completely (Wen et al. 2013), but unfortunately, this method is expensive. This study is intended to develop and use an inexpensive method for the purpose of producing (Cu-Zn-Al) alloy without the loss of the zinc element.

2 Materials and experimental Procedures

The elemental powders used in this study, with purity and mesh of (99.9%) and (-325) respectively, were provided by the Sky Spring nanomaterial's Inc. The powders were prepared by the electrolytic technique. The main mixture prepared in this study included (Cu +20.8%wt Zn + 5.8%wt Al). This mixture was selected because of its moderate transformation temperatures as shown below (Asanović and Delijić):

	Temperature [^{o}C]			
Alloy	M_s	M_f	A_s	A_f
Cu-20.8% Zn-5.8% Al	68	37	57	100

Green compacts of (6.14 g/cm^3) density and 25% porosity were obtained using a uniaxial compression die. Five samples were sintered with solid phase sintering process (SFS) (fig.1) and another five samples were sintered with a liquid phase sintering process (LFS) (fig.2).

Fig.1 Solid phase sintered samples

Fig. 2 Liquid phase sintered samples

Each sample was prepared with different temperatures and soaking times ((fig.3) and table-1) to investigate these two important variables. Sintering was conducted using the tubular furnace shown in (fig.4) under vacuum environment.

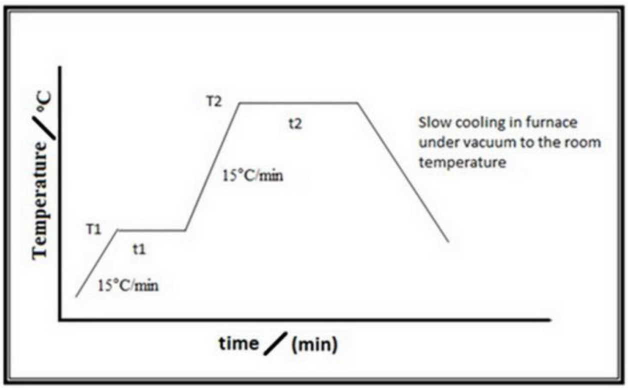


Fig.3 Heating cycles during sintering processes.

Table-1 Solid and liquid phase sintering attempts

	T_1(^{o}C)			T_2(^{o}C)		
No. of sample	SFS	LFS	t_1(hr)	SFS	LFS	t_2(hrs)
1	350	450	1	850	850	1
2	350	450	2	850	850	2
3	350	450	3	850	850	3
4	350	450	2	850	850	4
5	350	450	1	850	850	5

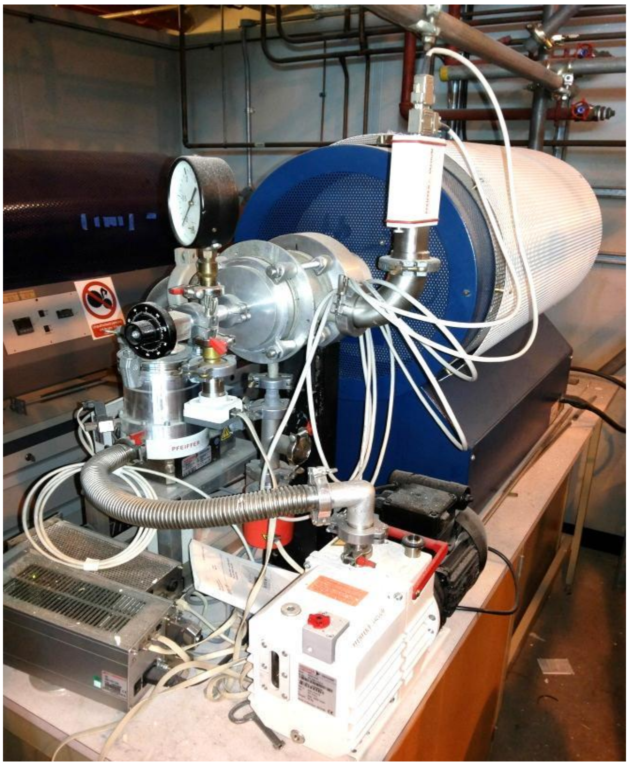


Fig.4 Vacuum tube furnace used in the sintering process.

The same tube furnace was used for sintering additional samples under inert gas environment after replacing the vacuum pump of the tube furnace with a continuous stream of argon. This was done to isolate the samples from oxygen and thus prevent oxidation at elevated temperatures during the sintering process.

In addition to this traditional technique of sintering, another creative technique was used by manufacturing a sealed capsule from quartz. It was filled with green compacts under pressurized inert gas before sealing (fig.5). This method will ensure a full isolation from the surrounding air using the least possible amount of inert gas and thus reducing the cost of the sintering process. On the other hand, the pressure inside the capsule will be higher than the atmospheric pressure without any drop during the sintering process because there is no continuous flow of the inert gas inside the capsule. It is possible to use such capsules in any traditional box furnaces. So, large quantities of samples can be sintered at one time and this is an additional economic factor.

Fig.5 Quartz capsule filled with an inert gas.

Hot isostatic pressing (HIP) was used to produce a sintered block with a dwell time of 2 hours at 820 ° C as a maximum temperature and a pressure of 150 MPa (fig.6). The heating rate was 8 ^{o}C/min while the cooling process was achieved by a jet of air. Comparisons were made among all samples which have been produced by the different methods of sintering.

Fig.6 The manufactured mild steel can used for HIP purpose.

ASTM, B 328-96 method was used in order to measure the apparent density and porosity for the sintered samples while quantitative energy dispersive X-ray spectroscopy (EDS) was used to evaluate the evaporation of the zinc content after sintering.

3. Results and discussion

Porosity is a very important parameter that affects the mechanical properties and the fatigue life of parts and structures. Figures (7 and 8) show that the densities after solid phase sintering are higher than those of the liquid phase sintering with less porosity.

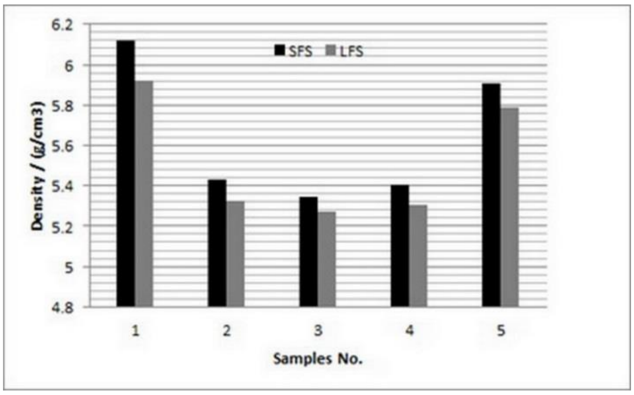


Fig.7 A comparison between densities of liquid phase and solid phase sintering samples

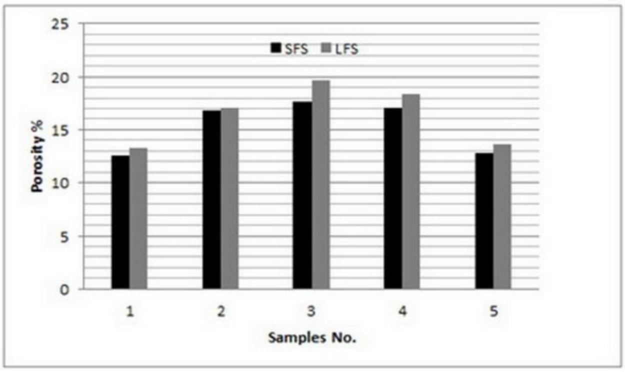
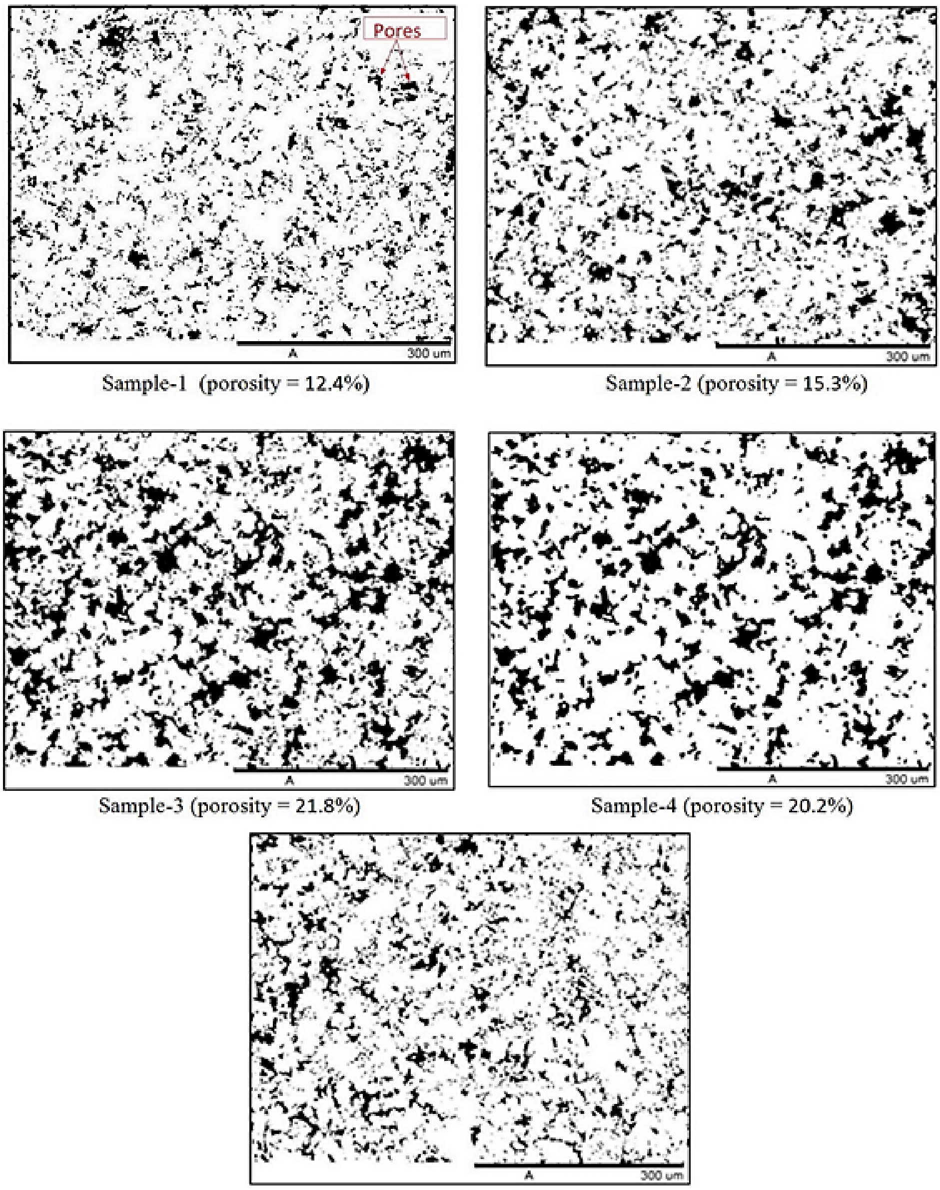


Fig.8 A comparison between porosities of liquid phase and solid phase sintering samples

To verify these results, image processing was used with the aid of an image processing package to evaluate some images taken by scanning electron microscopy. Five images were taken for each sample by choosing different areas within the same sample to calculate the average porosity for each sample. The white regions in the binary image

The distribution of porosity within the area of the tested samples is observed in figures (11 and 12). These figures give an impression about the efficiency of the powders mixing process which was done using an electrical roll mixer for a period of six hours. Table-2 illustrates the average values of porosity. It is obvious that these results are approaching the results of the previous method.



Sample-1 (porosity = 12.4%)

Sample-2 (porosity = 15.3%)

Sample-3 (porosity = 21.8%)

Sample-4 (porosity = 20.2%)

Sample-5 (porosity = 14.5%)

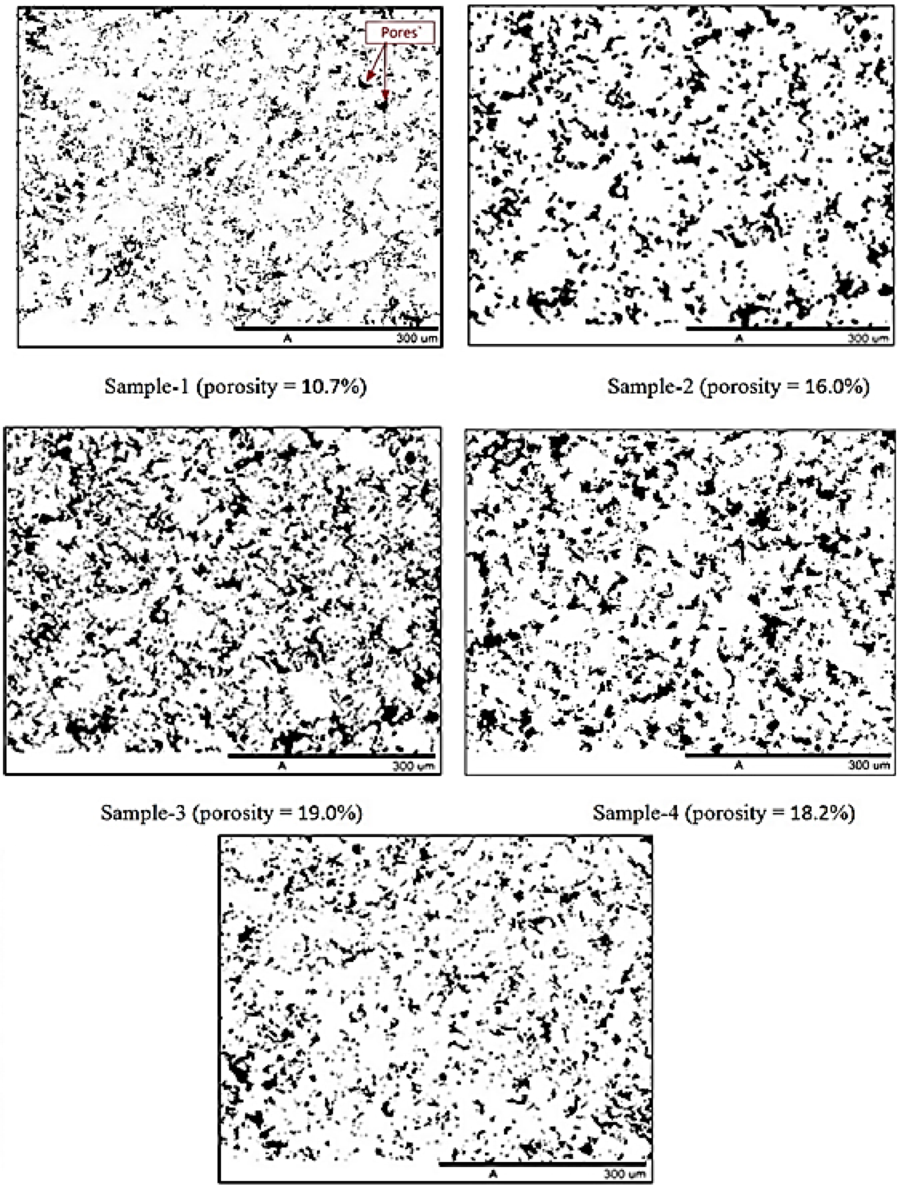
Fig.9 Selective SEM images for the five samples prepared by LFS.

Table-2 Average porosity measured by image processing

Sample No.	1	2	3	4	5
Average porosity % for liquid phase sintering	12.4	15.3	21.8	20.2	14.5
Average porosity % for solid phase sintering	10.7	16	19	18.2	12.6

By observing the results of densities and porosities of the prepared samples, it can be concluded that samples produced by solid phase sintering process were more useful (in general) than that of liquid phase sintering process. The minimum porosity and the maximum density was detected with the use of the minimum time of sintering which is one hour at 350^{o}C and one hour at 850^{o}C. The compacting pressure of 844MPa was used during the process of production of green compacts. The minimum porosity obtained was (10.7 %) which is still high in connection to the mechanical properties of samples. These voids are considered as cracks which may have an easy tendency to propagate and cause early failure.

The first stage of sintering process is the main factor which can control the final value of the porosity of the samples. Referring to the previous results, the duration of the first stage of sintering play a main role in the processof the evaporation of the zinc element. As it is known, the boiling temperature of the zinc element at (760mm Hg) is (907 degrees Celsius). This value is reduced dramatically under vacuum environment. This fact can be observed in (fig. 13).



Sample-5 (porosity = 12.6%)

Fig.10 Selective SEM images for the five samples prepared by SFS.

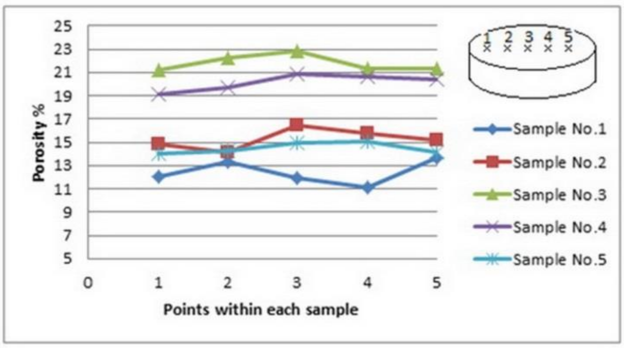


Fig.11 Porosity distribution for liquid phase sintering samples

Since the sintering process in this study has been conducted under a pressure of (-760 mm Hg), the boiling point of zinc would be less than 330 degrees Celsius. Therefore, the complete evaporation of the zinc element occurred during the first stage of sintering with a period of up to three hours as indicated in (fig.14) which represents

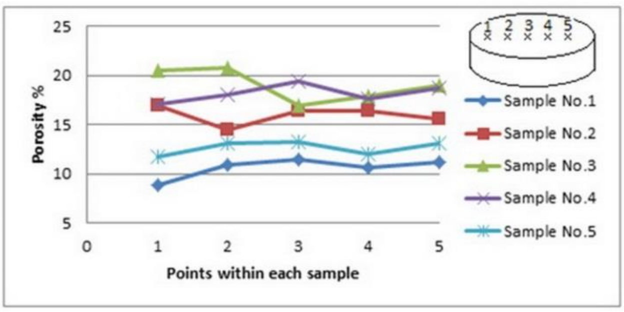


Fig.12 Porosity distribution for solid phase sintering samples

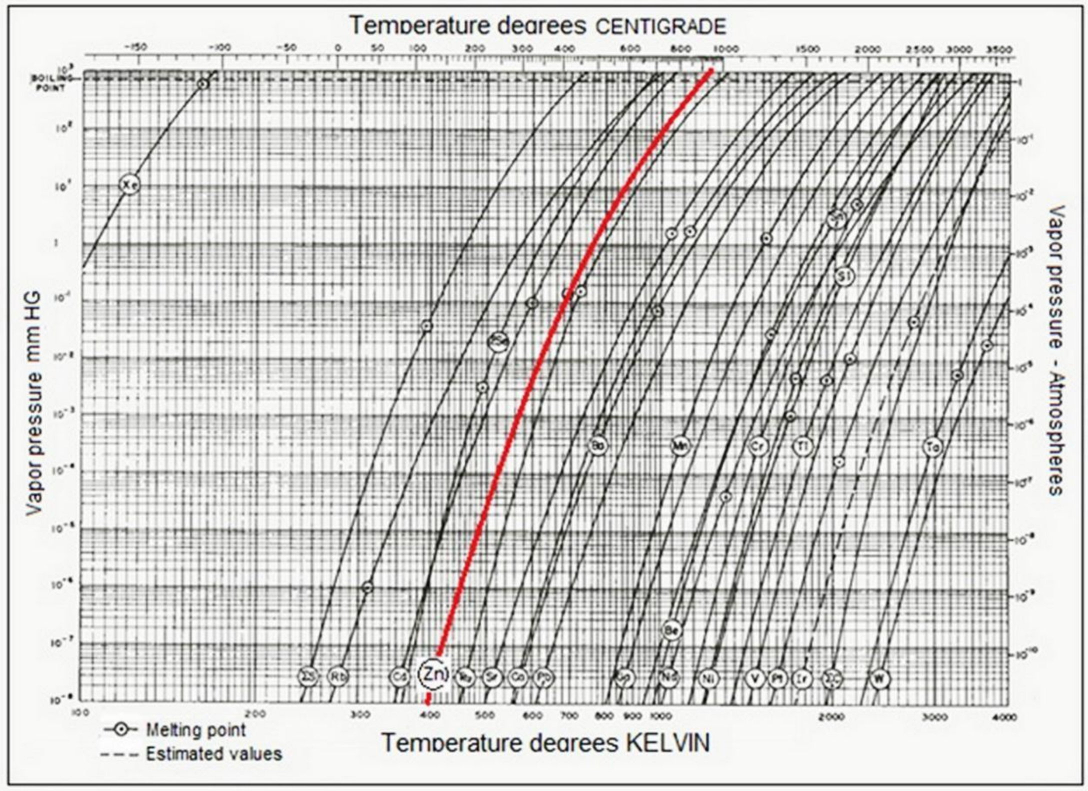


Fig.13 Vapor pressure of some elements (http://www.powerstream.com/vapor-pressure.htm)

Spectrum: Map/ Sample No.1

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	82.86	75.79
Zn	30	K-series	10.05	8.94
Al	13	K-series	7.09	15.27
		Total:	100.00	100.00

Spectrum: Map/ Sample No.2

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	88.15	79.87
Al	13	K-series	7.74	16.51
Zn	30	K-series	4.11	3.62
		Total:	100.00	100.00

Spectrum: Map/ Sample No.3

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	91.11	81.99
Al	13	K-series	8.22	17.42
Zn	30	K-series	0.67	0.59
		Total:	100.00	100.00

Spectrum: Map/ Sample No.4

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	89.63	81.58
Al	13	K-series	7.35	15.75
Zn	30	K-series	3.02	2.67
		Total:	100.00	100.00

Spectrum: Map/ Sample No.5

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	85.93	78.16
Al	13	K-series	7.47	16.01
Zn	30	K-series	6.60	5.83
		Total:	100.00	100.00

Fig.14 Spectrum EDS results for the main elements of SFS samples.

the results of quantitative EDS examination of the five solid phase sintering samples. In addition to that important factor, there is another but less influential factor which is the duration of the second stage of the sintering process.

An attempt was made to avoid the problem of the rapid evaporation of zinc under vacuum environment, and at the same time to protect samples from oxidation during sintering, an inert gas was used. By this way, sintering takes place at atmospheric pressure rather than vacuum. The same furnace was used for this purpose after replacing the vacuum pump with an argon cylindrical container to shed a steady stream of inert gas during sintering. Unfortunately, this technique could not overcome the problem of the evaporation of zinc during sintering where there is still evaporation of this element as shown in (fig.15) which represents the quantitative EDS test using the same SEM device. For this reason, most researchers prefer to use spark plasma sintering technique which ensures fully no evaporation of zinc.

Spectrum: map

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	78.85	72.43
Zn	30	K-series	14.32	12.79
Al	13	K-series	6.83	14.78
		Total:	100.00	100.00

Fig.15 Spectrum EDS result for the main elements of samples prepared under inert gas.

The evaporation of a little amount of zinc during sintering is due to some drop in pressure during the process of the flow of the inert gas. It is possible to overcome this problem by tightly isolating the environment around samples during sintering by placing the samples inside the court capsule shown in (fig.5) after filling it with an inert gas at a pressure higher than atmospheric pressure.

This new method in sintering will prevent dropping in pressure during sintering and leads to reduce the evaporation of zinc to a minimum value as shown in (fig.16) which can confirm this hypothesis.

Spectrum: Map

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	73.26	67.90
Zn	30	K-series	20.48	18.45
Al	13	K-series	6.26	13.66
		Total:	100.00	100.00

Fig.16 Spectrum EDS result for the main elements of samples prepared inside quartz capsules.

The SEM test shows a significant improvement in the porosity of samples which was produced by this way. This can be observed in (fig.17) which represents the SEM image for a sample sintered inside the protected capsule. The average porosity for such samples was (5.2%) and it is clear that it is a good value compared with the previous porous samples produced by sintering under vacuum.

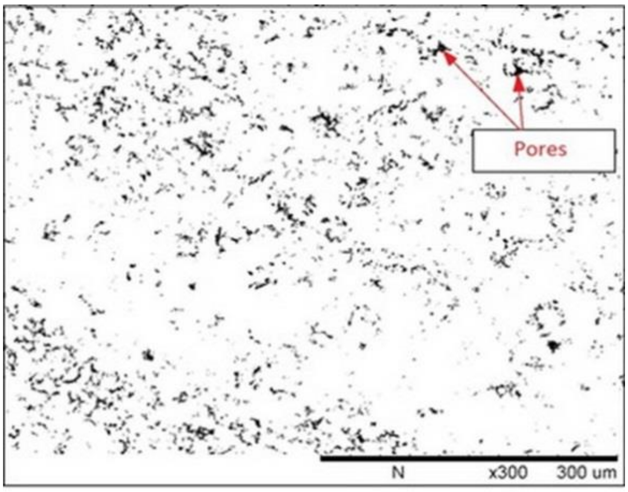


Fig.17 Selective SEM image for a sample prepared inside a quartz capsule.

With regard to samples that have been prepared using hot isostatic pressing (HIP), results showed a very significant improvement in the porosity of samples as shown in (fig.18) which was found to be equal to (0.46 %) as an average.

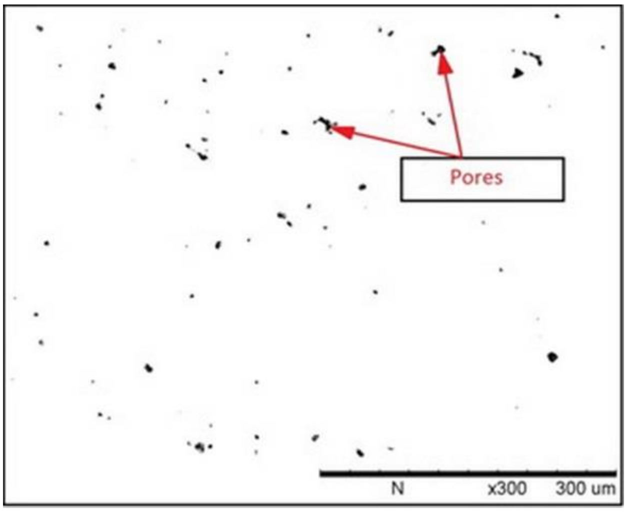


Fig.18 Selective SEM image for a sample prepared by HIP technique.

The very low porosity of the samples produced by HIP technique is due to the continuous closing of the pores under the influence of constant pressure during sintering. In addition, sealing the mild steel cylinder which contained the powders prevents the process of evaporation of zinc and thus the percentage of this element inside the alloy after sintering is almost identical to the initial content in the mixed powders as shown in (fig.19) which represents the result of the EDS test using SEM device.

Spectrum: Map

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	73.22	68.57
Zn	30	K-series	21.33	19.41
Al	13	K-series	5.45	12.02
		Total:	100.00	100.00

Fig.19 Spectrum EDS result for the main elements of samples prepared by HIP technique.

Conclusions

1. A new economic and efficient technique was used to almost eliminate completely the evaporation of zinc during sintering of (Cu-Zn-Al) shape memory alloy.
2. Usual sintering processes start with about 20.8%wt Zn and end up with almost 0.67%wt Zn. However, the new method ends with 20.48wt% Zn.
3. Some other methods are available to minimize Zinc evaporation including spark sintering or hot isostatic pressing but all of them are costly compared with the simple, economic, and straightforward new technique.
4. The new method provides provision of space surrounding the green compacts after filling with an inert gas and thus ensures no drop in vapor pressure during sintering.

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