



Synthesis and characterization of shape memory Nano alloy, Cu₇₄Zn₂₂Al₄ (wt %) using high energy ball milling.

Sujit Kumar Verma¹, B.S.S. Daniel^{1,2}

¹Department of Mechanical Engineering GLA University Mathura, U.P., India.

¹Centre of Nanotechnology, ²Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India

Abstract: Present work is based on synthesis of shape memory nano alloy by mechanical alloying using high energy ball mill (HEBM). Shape memory alloys are very useful in various applications, especially in actuators and smart systems, these materials recognize their shape due to pseudoelastic property, they exhibit. Pseudoelastic transformation itself is not naturally occurring property; instead it can be achieved by Thermomechanical training. Method of preparation has been most important aspect for shape memory alloys for achieving desired SME (shape memory effect). Earlier works done by most of the authors on shape memory effect were based on conventional method of synthesis. We have focused on synthesis of shape memory alloy by mechanical alloying using high energy ball mill. Ball to powder ratio, milling medium, and speed of ball mill are important parameters which influence effectiveness of milling process. By selecting proper ball to powder ratio, rotational speed, medium we can optimize the process. In our work we have chosen powder Cu, Zn and Al of known proportion of size 325 mesh and purit~99.7%, ball to powder ratio 3/1 and rpm of planetary ball mill was 300. In first case we milled the powder up to 24 hours dry milling and taken out samples for XRD, SEM, DSC analysis in order to know about physical and morphological changes occurring with milling time and phase transformation changes can be analyzed by Xrd and DTATGA test.

When liquid nitrogen used at 24 hour milled state there has been drastic fall of particle size, earlier up to 24 hour milling decrease in particle size has small and gradual. From 24 to 28 hour milling with liquid nitrogen, reduction in particle size was max, no further reduction of particle size was observed, and in fact there has been increase of grain size observed due to agglomeration and grain growth due to evolved heat. In second set of sample we added liquid nitrogen at 16 hour stage and milled up to 20 hour and found that reduction of particle size was same as it was in earlier sample. FE-SEM .AND DSC analysis also conforms the results. Particle size reduction up to 7 nanometers was observed in optimize state. Micro hardness test shows increase of hardness and yield strength with decrease of particle size up to 15 nanometers and then reverse effect observed. To achieve desired property, particle size control is most important aspect. Mechanical alloying by HEBM is the most competitive technique because we have complete control over morphological changes by controlling over milling parameters.

Key words: HEBM, SME, XRD, DSC

I. Introduction:

In recent years, Cu based shape memory alloys have emerged as a replacement of widely used Ni-Ti alloys, due to their comparable recovery force, lower material cost, and relative ease of processing. The potential application area of Cu based shape memory alloys has been identified in various electrical equipment, green houses windows as actuators and sensors. Among Cu based shape memory alloys, Cu Zn Al alloy have been found to be promising candidate. At an international scale the shape memory alloys (SMA) used mainly for commercial purposes belong to the Ni-Ti or copper based (Cu-Zn-Al) and (Cu-Al-Ni) systems. The Cu-Zn-Al alloys stay on the second place due to the higher characteristics of Ti based alloys in different applications. Yet taking into account the very high price (about 1\$/g) of Ni-Ti alloys, the Cu based alloys remain a good economic alternative, due to their price 100 times lower [1,2] in addition to above economic advantages, Cu-Zn-Al alloys exhibits, about 6% shape memory effect or 2% two way shape memory effect (TWSME) [3,4]. A 1 j/g mechanical work developed by heating, as well as pseudo elastic change. However, Cu-Zn-Al alloys produced by conventional casting route are quite brittle, which limits its applicability. It has been pointed out that high brittleness of Cu-Zn-Al alloys is primarily related to the large elastic anisotropy and large grain size, which enhance the susceptibility of alloys to intergranular fracture [5,

6]. In pursuit of improving mechanical properties, several attempts have been made to refine grain size of Cu-Zn-Al alloys by adding various alloying elements, such as Ti, Zr, V and boron [7, 8]

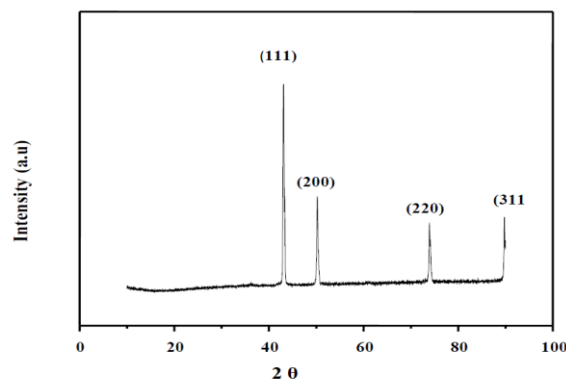
Grain size refinement exhibited significant improvement in the mechanical properties as compared to coarse-grained alloys. However, the problem of composition control during casting, which is crucial for controlling the transformation temperature and desired level of grain refinement, has hindered its further development. It is well established that the grain size and composition can be controlled in materials produced by powder metallurgy route in better way. In particular mechanical alloying has emerged as a promising method to produce a variety of nanocrystalline and ultra fine grained powders. Alloy powders produced by mechanical alloying have shown to possess better control over composition and chemical homogeneity as compared to their conventionally produced counterparts. In recent years few attempts have been made to develop Cu-Zn-Al alloys by a powder metallurgy route involving mechanical alloying followed by consolidation of milled powder via hot extrusion or isostatic pressing at elevated temperature [9, 10]. Since micro structural evolution in consolidated material is derived from the mechanically alloyed powders, it is extremely important to acquire an in-depth understanding of the structural evolution in the Cu-Zn-Al powder during mechanical alloying. However very little attention has been focused to this aspect in the literature.

The present work describes the experimental results related to micro structural evolutions, such as particle size, and phase evolution during different stages of mechanical alloying of $\text{Cu}_{74}\text{Zn}_{22}\text{Al}_4$ (Wt %) powder mixture. A detailed analysis of the milled nano-crystalline powder was carried out by TEM for observing the nano-scale features present inside the mechanically alloyed powder particles. The mechanism related to shape memory effect (SME) are essentially governed by the occurrence of preferred microstructure constitution of martensite and parent phase involved in the reversible transformations cycles [11, 12]. It has been established that Cu-based shape memory alloys (SMAs) conform to many of the commercial and technological necessities like affordable cost, favorable deformation behavior and better electrical and thermal conductivities [13]. However repetitive transformation cycles in such alloys results into accumulated chemical and topological changes resembling the attributes of isothermal ageing process [14, 15]. Moreover formation of the precipitate phases during the ageing treatment significantly contributes to the profile of the hysteresis loop [16] as well as appearance of two-way shape memory effect [17]. Moreover, the accumulated interface migration during the reversible transformation cycling in SMAs, particularly in the presence of precipitate phase, may significantly influence the value of the percent recoverable strain yielded by the subsequent transformation cycle [13,14]. This may reasonably be attributed to the pinning of the migration interphase boundaries by precipitate phases [15, 16].

II. Experimental details and results

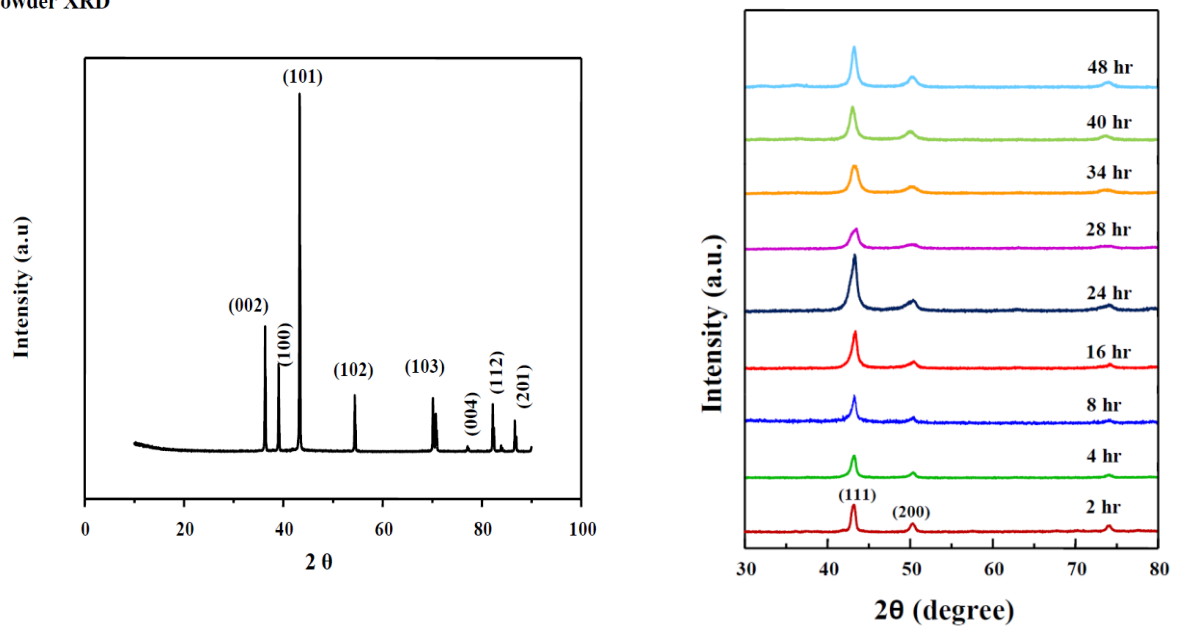
We have started from procurement of Cu, Zn, and Al powder from Loba Chem Ltd. Powder were pure $\sim 99.5\%$ and particle size of $\sim 100\mu$. We prepared sample by taking weight of each constituent and mixed it in container. Weight of prepared sample was 50 gram. Composition of mixture taken as $\text{Cu}_{74}\text{Zn}_{22}\text{Al}_4$ (wt %) was mechanically alloyed in a high energy planetary ball mill (Retsch 400 PM/2) using Ni-Cr steel balls as grinding media. The mechanical alloying was carried out at disc and vial rotation speed of 300 rpm, whereas ball to powder ratio was maintained 3:1 for each run. Liquid nitrogen was added to cool down the mixture and make material brittle so reduce the milling time significantly. Powder samples were collected at various stages of milling for various analyses such as XRD, FE-SEM, and DTA/TGA.

A. XRD Analyses

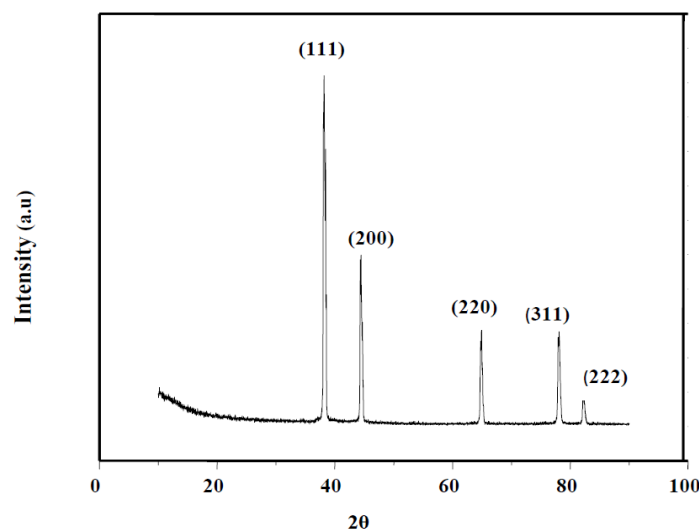


XRD of Cu Powder

Zn Powder XRD



Al Powder XRD



B. XRD of various samples milled for progressively increasing time:

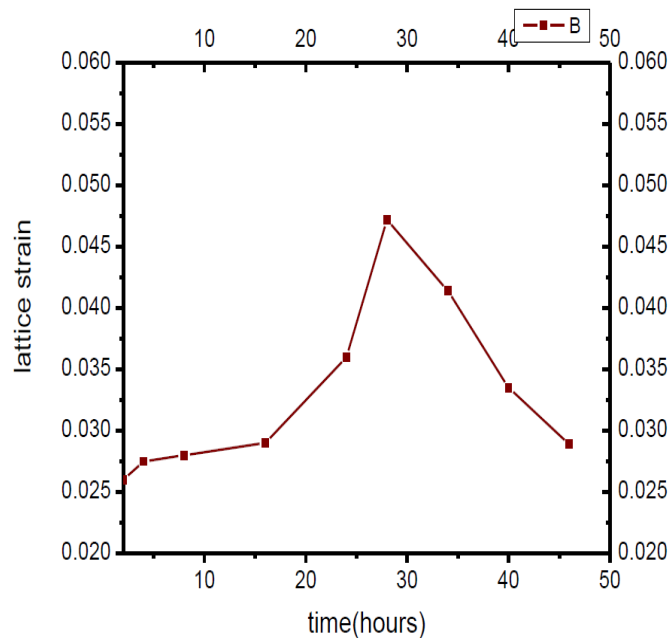
Analysis

XRD pattern of prepared samples shows dominant (111) diffraction peak along with low intensity (200) diffraction peak. A reduction in particle size with increase of milling time has been observed. Rate of particle size reduction is maximum. For first 2 hr of milling. After that moderate size reduction observed. Grain (particle) size reduction was calculated by using Scherer formula. Another phenomenon which observed is decrease of gradual relative intensity of secondary peaks with respect to milling time. It is obvious outcome because some part of Zn and Al dissolves in Cu. Dissolution of Zn in copper is not complete due to structural constraints (Cu is face centered and Zn is hexagonal). dissolution of Zn and Al is maximum up to 28hrs of milling stage. At 24 hr milling stage liquid nitrogen introduced to cool down the material substantially and enhance particle reduction and optimize lattice strain. During 4hr of milling in liquid nitrogen medium, there has been maximum particle size reduction and maximum lattice strain, in fact it is optimized condition observed.

Table: 1 variation of lattice parameter of Cu with milling time.

Time(hr)	2hr	8hr	16hr	24hr	28hr	34hr	40hr	48hr
Lattice Parameter								
Cu Zn Al	3.6258	3.6196	3.6120	3.6158	3.6305	3.6248	3.6376	3.6225
Lattice Parameter(Å)								

Lattice strain v/s milling hr graph



a. Grain Size Analysis: Scherer's Formula

$$B = 0.9\lambda / t \cos\theta$$

B = Broadening of diffraction line measured at half its max. Intensity

t = diameter of the crystal particle

λ = wavelength of X-ray K_{α} line for Cu K_{α} = $1.54 \text{ \AA}$

b. calculation of lattice strain

$$2 d \sin\theta = n\lambda$$

$$2(d + \Delta d) \sin(\theta + \Delta\theta) = n\lambda$$

$$2(d + \Delta d) (\sin\theta \cos\Delta\theta + \cos\theta \sin\Delta\theta) = n\lambda$$

$$2d \sin\theta \cos\Delta\theta + 2d \cos\theta \sin\Delta\theta + 2\Delta d \cos\theta \sin\Delta\theta + 2\Delta d \sin\theta \cos\Delta\theta = n\lambda$$

$$2d \sin\theta + 2d \cos\theta \Delta\theta + 2\Delta d \Delta\theta \cos\theta + 2\Delta d \sin\theta = n\lambda$$

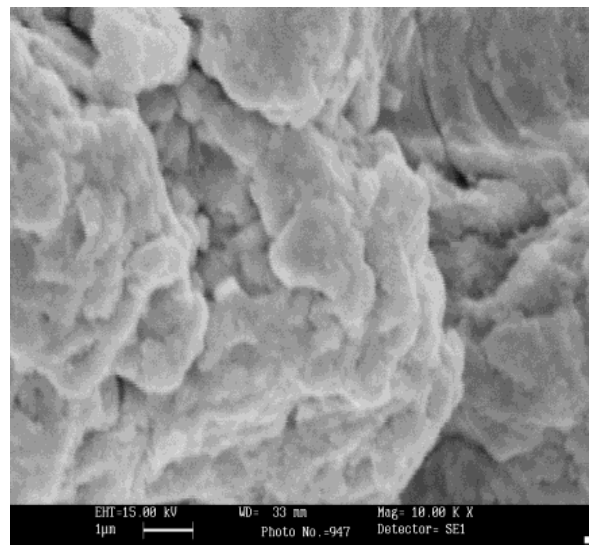
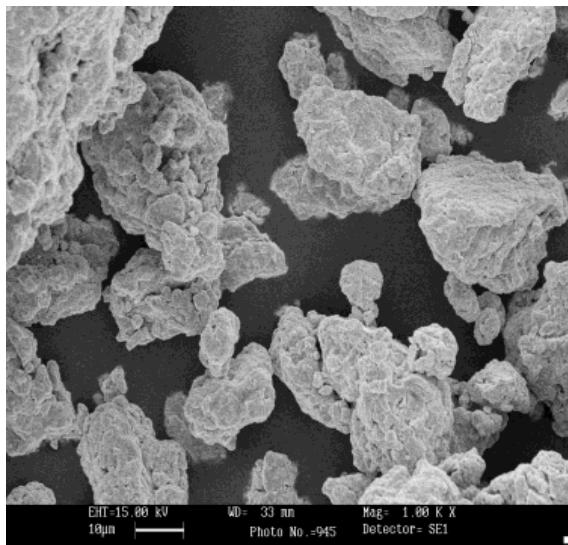
$$2\Delta d \Delta\theta \cos\theta \text{ is negligible } \sim 0$$

$$2d \cos\theta \Delta\theta + 2\Delta d \sin\theta = 0$$

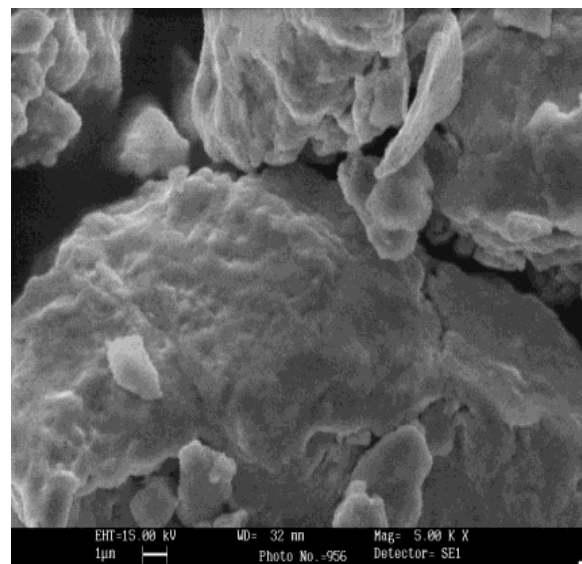
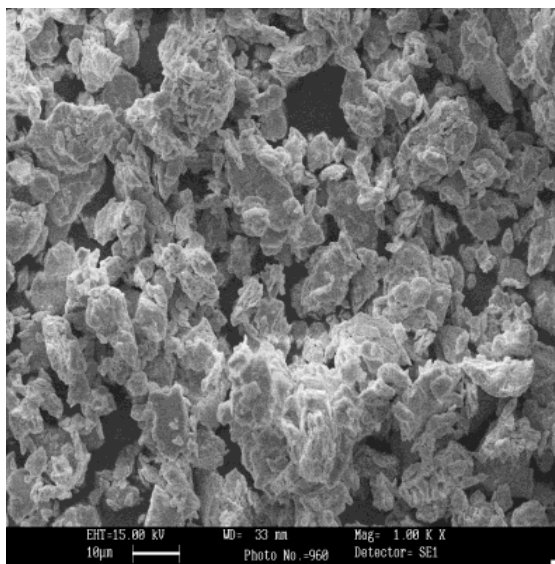
$\Delta d/d = -\Delta\theta/\tan\theta$, here $\Delta d/d$ is lattice strain and $\Delta\theta$ is angular width at half maximum, using this relation we can calculate lattice strain with respect to milling hours of sample.

C. Scanning Electron Microscopy (SEM)

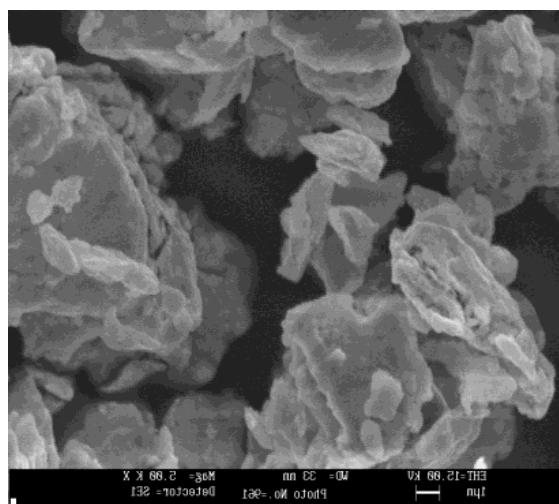
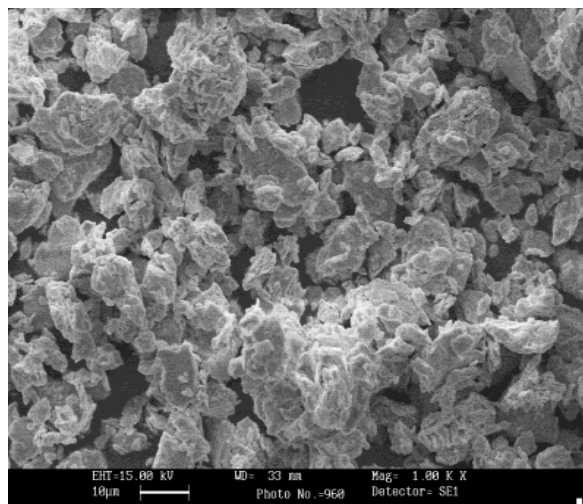
Morphology of two hr milling stage shows porous aggregation, in layered structure. Further milling causes severe plastic deformation to small aggregates. Further severe plastic deformation causes elongated flaky particles, fragmented to small particles. Results show that size reduction around 24 hrs to 28hrs is maximum. Further size reduction is not observed after 28 hr of milling. More heterogeneity observed beyond 34 hr of milling. Bigger particles embedded with smaller one. Heat releases due to restructuring of grain boundaries, increases the temperature, causing agglomeration, welding, increase in ductility, and increase of particle diameter observed in prolonged milling. Morphology of two hr milling stage shows porous aggregation, in layered structure. Further milling causes severe plastic deformation to small aggregates. Further severe plastic deformation causes elongated flaky particles, fragmented to small particles. Results show that size reduction around 24 hrs to 28hrs is maximum. Further size reduction is not observed after 28 hr of milling. More heterogeneity observed beyond 34 hr of milling. Bigger particles embedded with smaller one. Heat releases due to restructuring of grain boundaries, increases the temperature, causing agglomeration, welding, increase in ductility, an increase of particle diameter observed in prolonged milling.



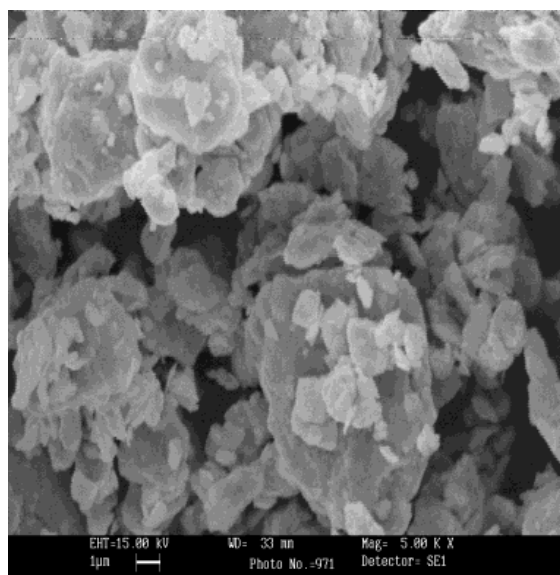
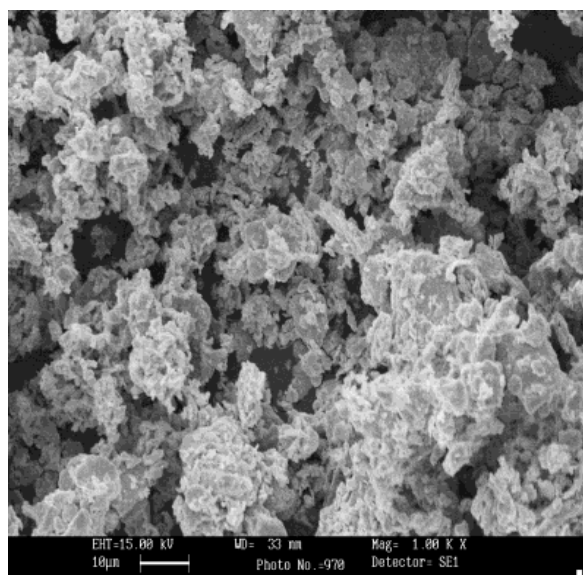
Picture: 1 SEM 2 hr milled sample (1X, 10X)



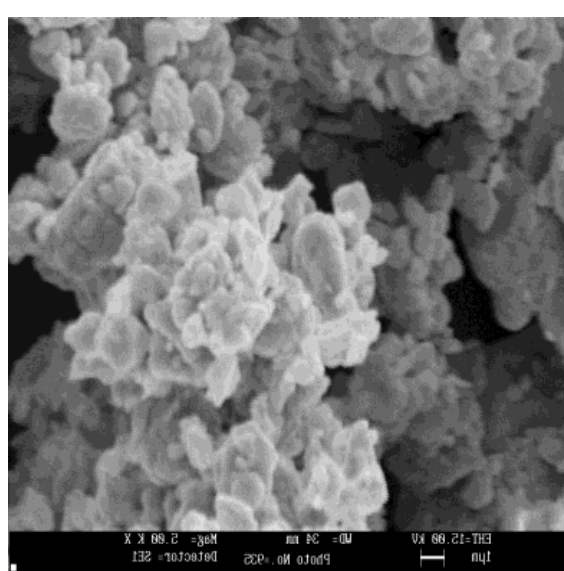
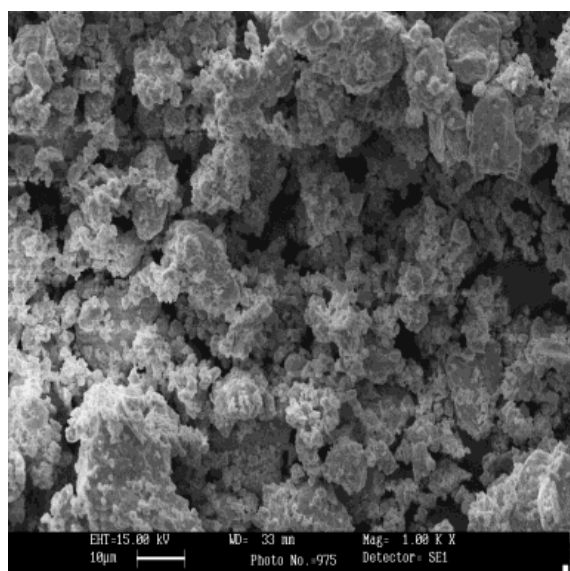
Picture: 2 SEM 4hr milled sample (1X, 5X)



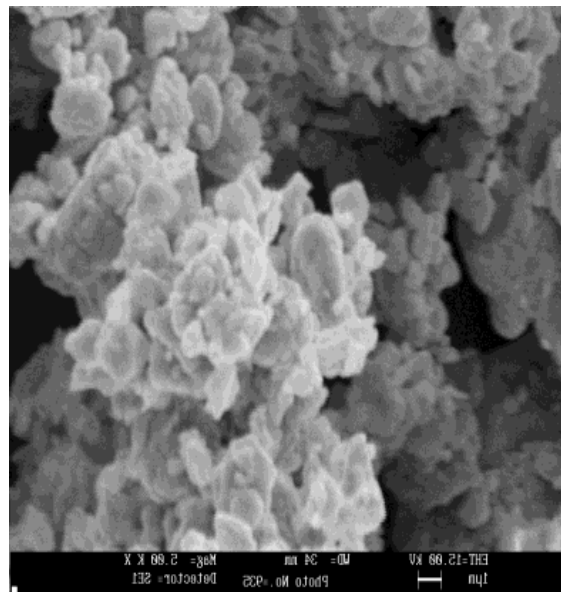
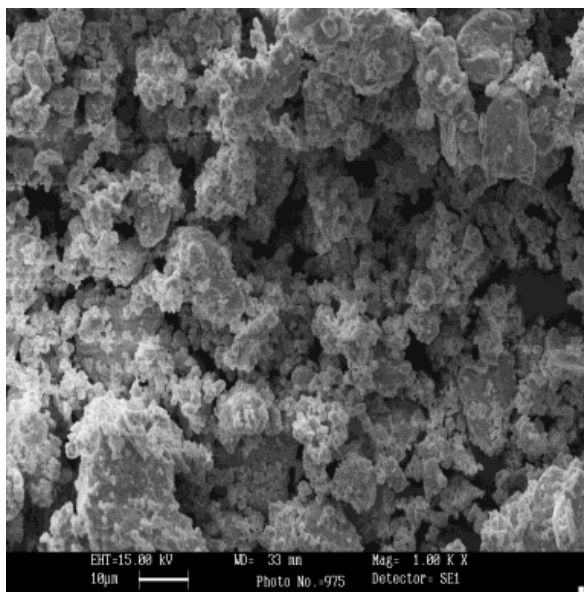
Picture: 3 SEM 8hr milled sample (1X, 5X)



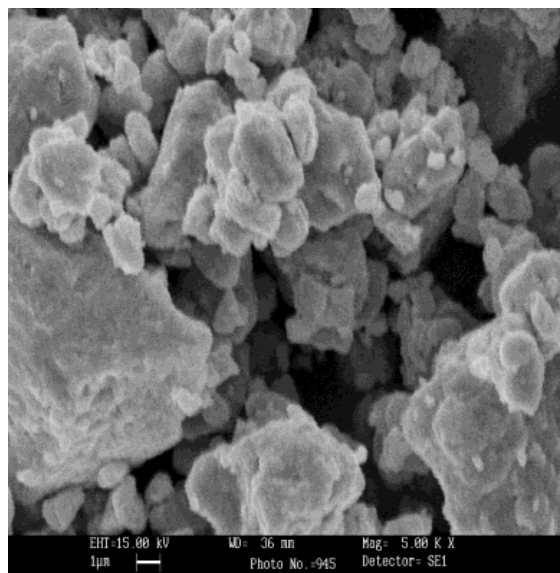
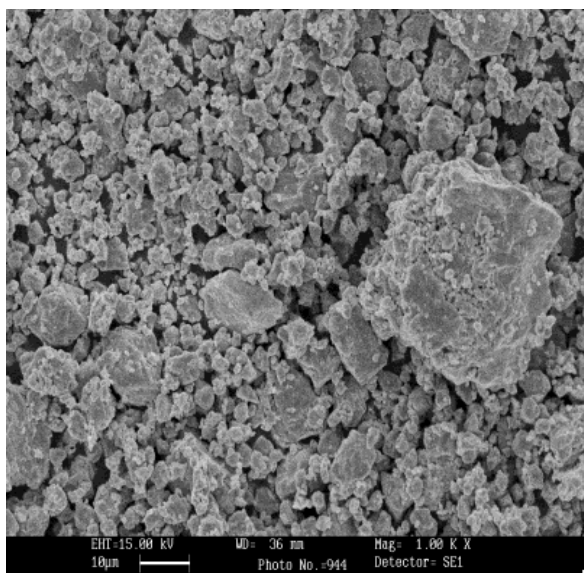
Picture: 4 SEM 16 hr milled Sample (1X, 5X)



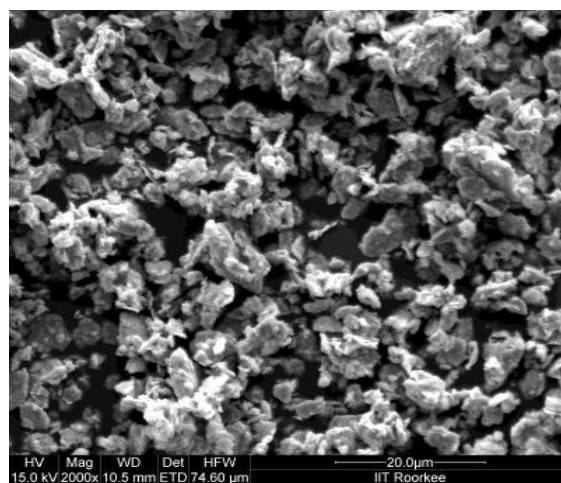
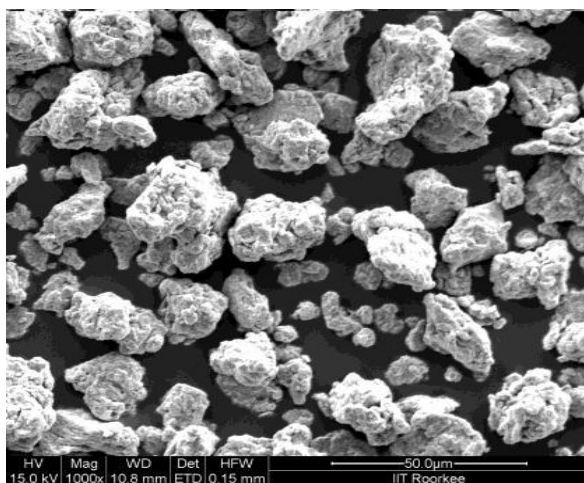
Picture: 5 24 hr milled sample (1X, 5X)



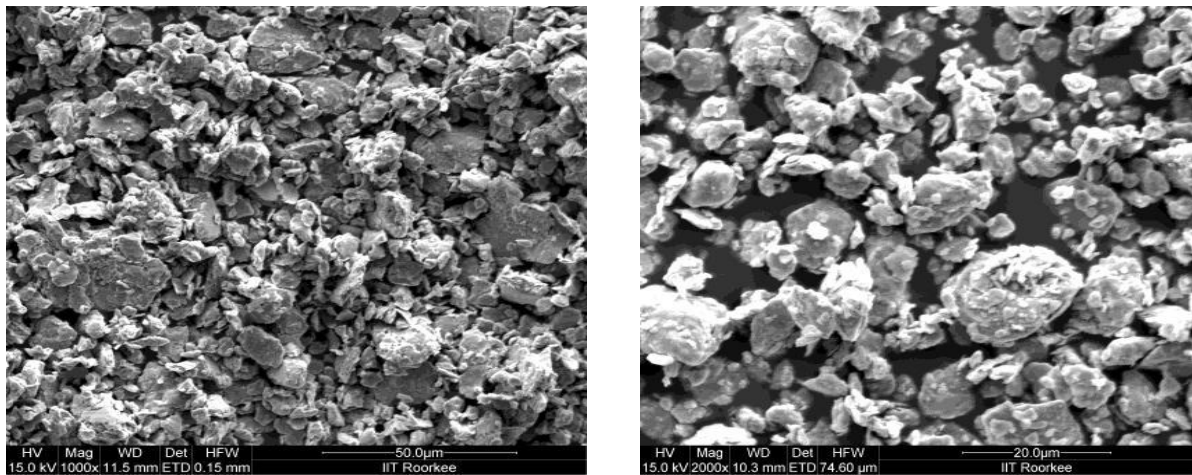
Picture: 6 28hr milled sample (1X, 5X)



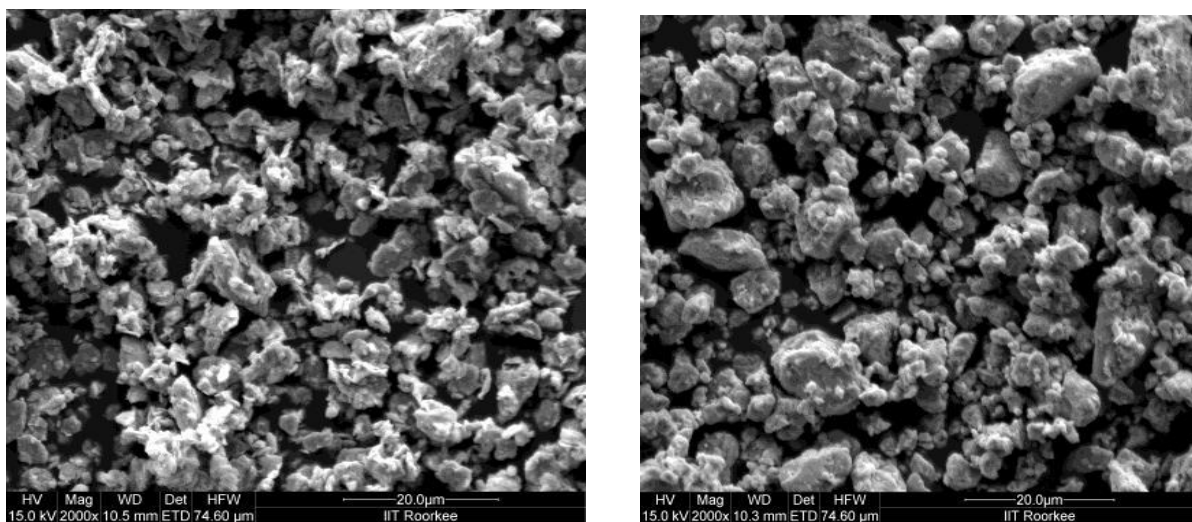
Picture: 7 48 hr milled sample (1X, 5X)



Picture: 8 From left to right 2, 8 hr milled FE-SEM Images



Picture: 9 From left to right 16, 24 hr milled FE-SEM Images



Picture: 10 From left to right 28 and 48 hr milled FE-SEM Images

D. Mechanical Properties



Picture: 11 Green pellets (as mixed, 2hr, 20hr and 48 hr milled samples) prepared in hydraulic press with application of 5 ton load)



Picture: 12 Sintered pellets heat treated at 500°C in hydrogen atmosphere for 30 minutes.

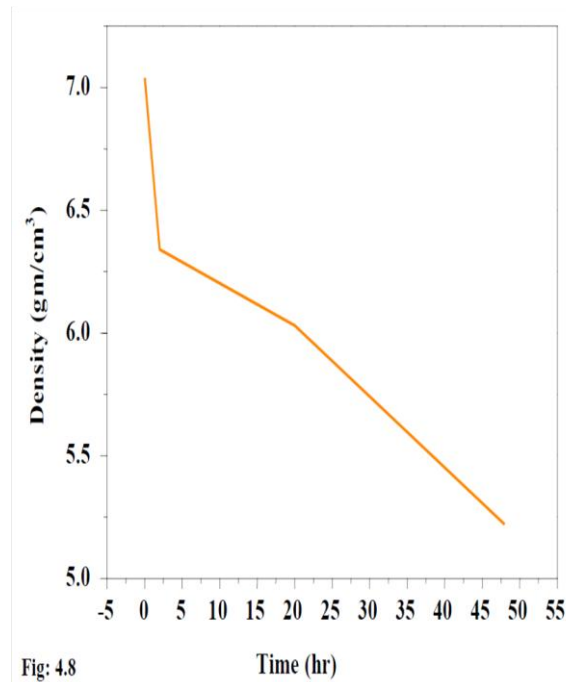


Fig: 4.8

Analysis: density of sintered pellets decreases with milling hr. this phenomenon can be explained on the basis of increase of surface area per unit volume with decrease in particle size. Since pressure applied is same for making all pellets density is lowest for that sample which was milled for maximum time, its particle size is lowest.

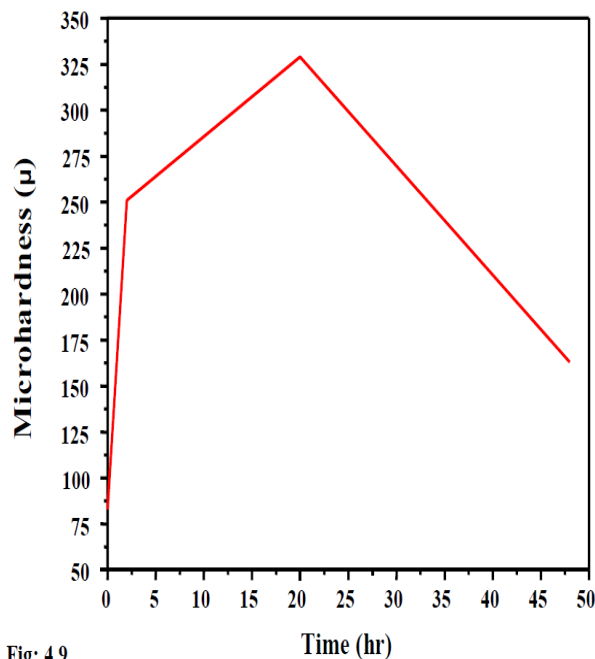


Fig: 4.9

Micro hardness v/s milling time graph

Analysis:

Variation of micro hardness with milling time in hrs can be explained on the basis of Hall-Petch & reverse Hall-Petch effect.

$$\sigma_0 = \sigma_I + kD^{-1/2}$$

Where σ_0 = the yield stress

σ_I = the “friction stress,” representing the overall resistance of the crystal lattice to dislocation movement.

K = the “locking parameter,” which measures the relative hardening contribution of the grain boundaries

D = grain diameter

This equation also applicable to measure hardness of the material with adjustment of suitable constant. As particle diameter decreases, hardness increases and max for Hall-Petch limit, that is about 12nm. The weakening of the material, due to the shift in the dominant mechanism of plastic deformation in the coarse-grained materials to GB sliding in the case of ultra-small grain sizes, is referred to as the inverse Hall-Petch behavior.

E. Differential Temperature and Temperature Gravimetry Analysis (DTA/TGA) for Shape Memory Effect Transformation Temperature.

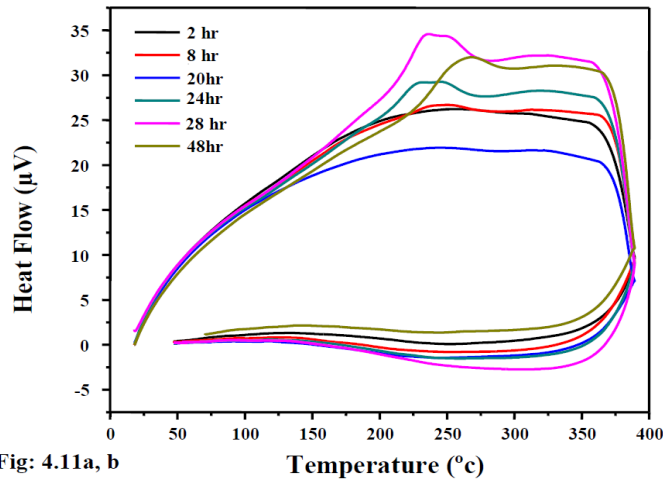
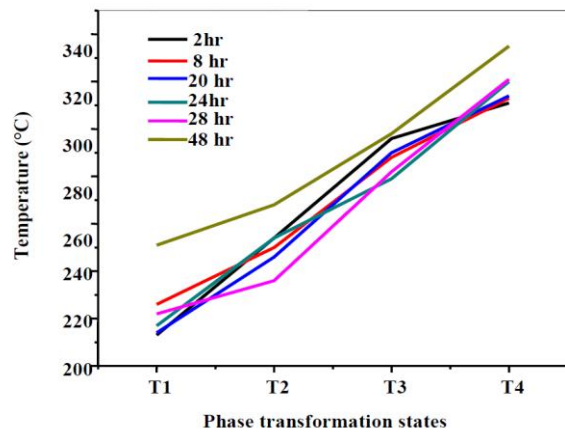
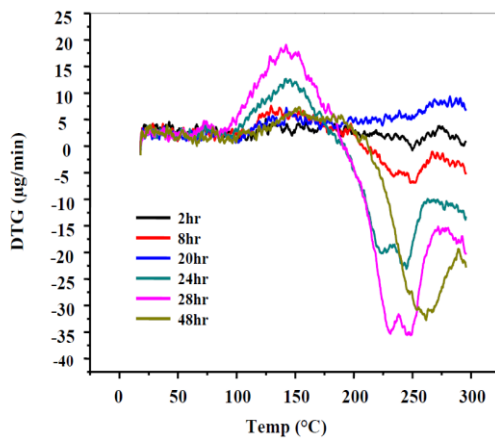
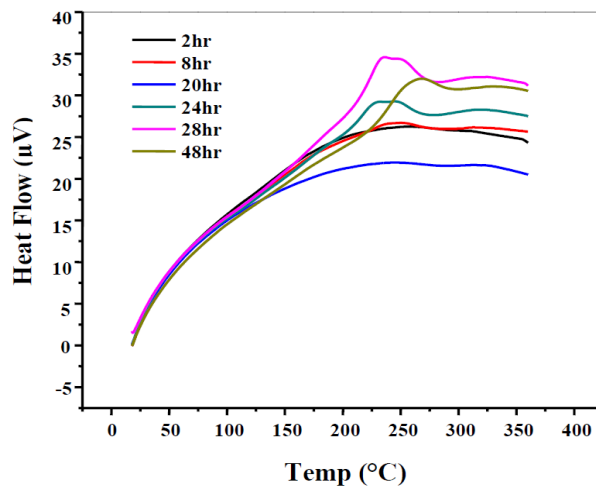


Fig: 4.11a, b



Milling time v/s transformation temperatures

	2hr	8hr	20hr	24hr	28hr	48hr
T1	213	226	214	217	222	251
T2	254	250	246	254	236	268
T3	296	288	290	279	282	298
T4	311	313	314	320	321	335

Table: 2 for transformation temperatures

Analysis of heat flow curves for different samples having varying milling time shows that there is distinctive phase transformation temperature for 24, 28, and 48 hr milled samples. Particle size observed for 28 hr milled sample is minimum and quantity of heat flow is maximum for this sample also. There is maximum shift in peak temperature for this sample (236°C). T3-T1 (difference of temperature of peak initiation and end of peak is minimum for 28 hr sample. this phenomenon is in accordance with nano crystallization effect. Heat flow peak is sharpest; temperature range of peak is minimum and overall decrease of peak occurring temperature. Transformation occurs in this range of temperature and peak is exothermic, heat is evolved due to phase transformation, some recrystallization process also occurs in transformation process. TGA (Thermogravimetric Analysis) is a thermal analysis technique, which measures the weight change in a material as a function of temperature and time, in a controlled environment. In above graphs variation of weight change is maximum for 28 hr milled sintered sample. For 48hr sample, temperature at which maximum weight loss occurs is highest (263°C), all transition temperature for this sample are higher. DTA and DTG analysis.

Time(hr) milled Temp(°C)	24hr	28hr	48hr
T1	93	92	106
T2	143	142	145
T3	174	185	198
T4	225	232	263
T5	235	240	289
T6	245	248	310

Table: 3 for transition temperatures DTG Curves

Specifications of transformation temperatures:

T1 (initiation of weight gain), T2 (peak of weight gain), T3 (end of weight gain), T4 (peak of weight loss), T5 (reverse of peak weight gain), T6 (end of weight loss).

Shows that phase transformation leads change of weight (gain or loss) for each sample. Weight gain or loss preceded phase transformation for each sample. Heat flow rate per unit mass is maximum for 28 hr sample, range of temperature for which transformation takes place is minimum for this sample. For 28 hr milled sample particle size is minimum and grain distribution is homogeneous in size. This sample may be better choice for application as shape memory alloy to fabricate devices for actuation purposes, provided grain size and distribution remains almost same in fabrication and further processing.

III. Conclusion

HEBM is a versatile processing method to fabricate nanocrystalline materials, relatively new for fabricating shape memory alloy material. No illustration has been found in this area to develop material by using HEBM method and process it further for fabricating devices which would exhibit enhanced SME. Here we have to face paradoxes regarding shape memory effect and nanocrystalline material. Shape Memory Effect is bulk transformation process where large change in volume takes place in thermodynamic cycling. Nanocrystalline powder is difficult to be handled for fabrication purpose in order to make a device which can be used for commercial purposes. In hot forging and rolling process nanocrystalline features lost significantly, enhanced mechanical properties, hardness, thermal stability does not remains invariant with further processing., this may be negative aspect for a specific case, otherwise this route of fabrication provides us variable range of transformation temperatures, based on this we can fabricate devices which can be used for different working conditions, i.e. at different temperature range. Variation in transformation temperature range observed for various sample milled for different time periods. Thermomechanical training and milling time both have effect on transformation temperature and shape memory effect. Mechanical properties also changes with milling time. Hardness of material increases with reduction of particle size, governed by Hall Petch relation, to a certain point up to ~12nm size beyond that it decreases rapidly, this phenomenon is due to reverse Hall-Petch effect. Materials which are difficult to process by conventional means can be processed by HEBM method and solubility limit can be increased beyond theoretical limit in this process. Limitations are also there. We cannot have control in process parameters. We cannot have in-situ observation of mechanism of grain formation, refinement and atomic level movement in this process. HEBM needs further automation, incorporation of sensors along with high speed computing device to get control over process parameters so that we can get desired features.

IV. Future work

We have observed difficulty to consolidate nanocrystalline powder material into solid device and retain nanofeatures simultaneously by hot forging and rolling process. Research in this area is needed. Mechanism of severe plastic deformation in ball milling is highly statistical in nature; we don't have in-situ observation while process is going on. Automation is needed to have precise control over parameters during the milling process

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