"Shape Memory Nano Alloy, $Cu_{74}zn_{22}al_4$ (Wt %) Characterization and Synthesis Using Ball Milling"

Sujit Kumar Verma, Naveen Kumar Gupta

Abstract: ***This experimental work is focused on preparation of shape-memory Nano alloy using high energy ball mill (HEBM). Precise ball to powder proportion, working medium, and ball mill speed are cardinal factors which determine effectively of milling operation. In present work select material is micro size powder Zn, Cu, and Al of determined proportion of size 326 mesh and purit~99.5%, ball / powder ratio= 3/1 and rpm of planetary ball mill kept 300. In first step powder was dry milled up to 24 hours and samples were taken for X- ray diffraction, scanning electron microscopy, differential scanning calorimetric analysis. In presence of liquid nitrogen milling time drastically reduced with fine particle size reduction and feature. To get required characteristics, control of particle size is the most crucial phase in operation. Alloying by HEBM is an innovative technique, this technique facilitate adequate and effective control over changes at grain boundary level and external morphology by precise control over milling variables.***

Keywords : **SEM, DSC, HEBM, XRD.**

I. INTRODUCTION

Recently , Cu based SMAs are emerging as potential alternative to widely used Ni-Ti alloys, due to their appreciable recovery force, low cost material, and comparative ease in preparation. The target area applications of Cu based SMAs are various electrical, biological and electronic devices, as sensors and actuators in green house windows. Many researchers have done pioneer work in synthesis techniques and characterizations. Kenneth et.al[1]performed experimental investigation on micro-structural phase transformation and mechanical behavior of Cu-Zn-Al alloys with Fe, B modification. Authors observed that with modification, hardness decreases in the range of 32.4 to 51.5%. Shivasiddaramaiah et.al [2]performed experiment on quaternary alloy Cu-Al-Be-Mn. Authors pointed out that damping limit of an alloy increases with increase in manganese content.

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It also indicate that damping limit is more prominent in martensitic phase than austenite one. Prashantha et al.[3] performed experimental testing of shape memory effect of Cu-Al-Be alloy and wear properties with the help of Taguchi method. It has been observed that sliding distance and load applied are imminent factor in wear loss. As sliding distance and load increases, wear loss also increases. Karthik et al.[4] performed experimental and theoretical study. Authors explained shape memory effect of Ni-Ti-Fe alloy on the basis of DSC curves and crystallographic orientations. Alkan et al.[5] performed experimental investigation to study transformation stresses in shape memory alloy CuZnAl alloy. This alloy expresses low transformation stress varying from 25 to 60 MPa. Depending on crystal orientations. Authors established an atomic-informed model to predict non-Schmidt characteristic martensitic phase transformation in CuZnAl alloy. Kim et al.[6]performed experimental investigations on effect of plastic deformation induced by HEBM on SMAs Fe-13.5 Mn4.82 Si-8.32 Cr-3.49 Ni-0.15C. Experimental findings reveal that there is an optimum grain size for the maximum difference in recovery strain and plastic strain. Khalid and Abbas [7] focused on characterization aspect of SMA Ni-Mn-Ga for use in actuators and sensing device. Authors demonstrated that 400ppm strain was measured in the alloy with 7M martensitic structure at room temperature. Wu et al.[8]performed experimental analysis to find role of HCP martensite in CoAl and CoNi SMAs. Findings confirm that it gives much higher yield strength in solution treated Co-Al alloy. Lindija et al.[9]performed Muaggianu model and experimental approach to study thermodynamic, mechanical and electrical properties of ternary SMAs Cu-Al-Zn. Analysis reveals that structure consists of large and polygon grains. Aldirmaz et al.[10]fabricated diode of Cu-Al-Mn SMAs. An experimental finding shows that diode displays photoconductivity behavior. Marattukalam et al.[11]investigated effect of heat treatment on the microstructure and SME on equi-atomic NiTi alloy.

Heat treatment decreases upward and downward transformation temperature. Many researchers have done their work in manufacturing and characterization of SMAs and their effect. They have adopted conventional methods to of synthesis. Till now powder methods and severe plastic deformation through HEBM to develop Nano-crystalline structure is not widely reported and area is wide open to focus upon. Our approach is to optimize the factors, weight of ball and powder in chamber, proper speed of mill, medium of chamber, in order to achieve desired results.

II. EXPERIMENTATION

2.1 XRD of sample used for experiment

Experimentation is comprise of procurement of micro-size powder of copper, zinc and Al, its characterization to ensure authenticity of material, then weighing and mixing in required proportion for ball milling. Materials for alloy synthesis were procured from Loba Chem. pvt. Ltd. Purity of materials were ~ 99.4% and particle size of ~105µ. Sample size was taken 50 gram. Constituents of mixture taken as $C_{u74}Zn_{22}Al_4$ (wt %) was alloyed mechanically by HEBM (Retsch 400 PM) using Ni-Cr steel balls as grinding media. Mechanically induced alloying was performed at disc and vial speed of 350 rpm, where ball to powder ratio being kept 3by1 for every run. Liquidated nitrogen was used to cool the mixture and to enhance brittleness so that milling time can be drastically reduced. Milled samples selected at different intervals for characterization in order to see phase changing features by XRD,DTA/TGA and SEM.

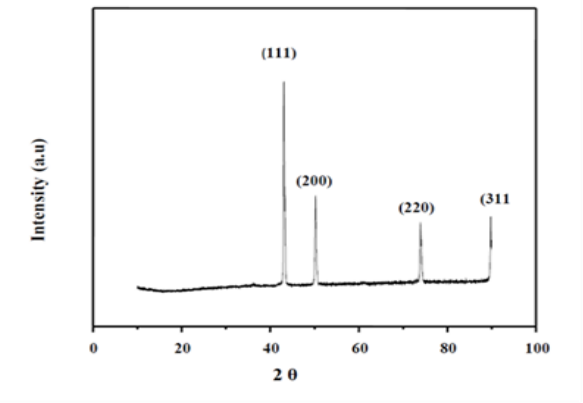

Fig: 1(a) XRD of Copper

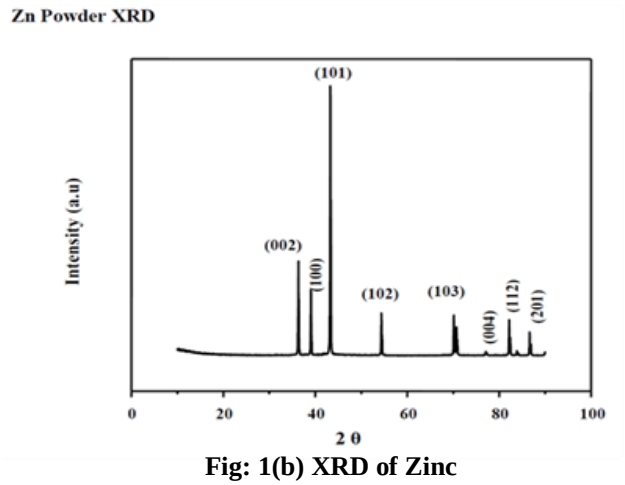

Fig: 1(b) XRD of Zinc

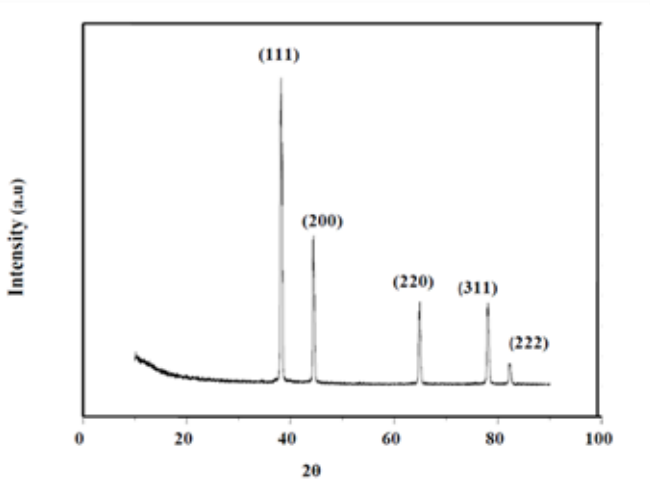

Fig: 1(c) XRD of Aluminum

2.1 stacked XRD of samples milled for different time

Analysis:

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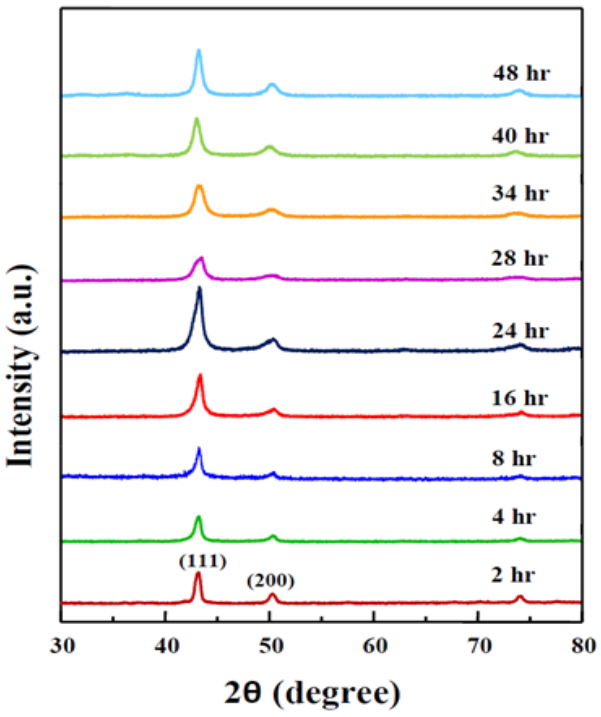

Fig: 2 XRD of samples $Cu_{74}Zn_{22}Al_4$ at varying milling time

III. MATHEMATICAL FORMULATION FOR LATTICE STRAIN DETERMINATION

(3.1). Grain Size Analysis: Scherer's Formula

$$B = \frac{0.9\lambda}{t\cos\theta} \quad (1)$$

B= width of diffraction peak observed at half of its maximum intensity

t= maximum length of the crystal particle

λ=wavelength of X-ray K_α line, for Cu $K_{\alpha\lambda}$= 1.54 A^0

(3.2). Lattice strain formulation

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

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

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

$$2d\sin\theta\cos\Delta\theta + 2d\cos\theta\sin\Delta\theta + 2\Delta d\cos\theta\sin\Delta\theta + 2\Delta d\sin\theta co$$

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

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

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

$$\Delta d/d = -\Delta\theta/t\epsilon, \quad (2)$$

here $\Delta d/\epsilon$ strain in lattice and Δθ is angular width at half of max. intensity, by above relation lattice strain can be determined milling time exposure.

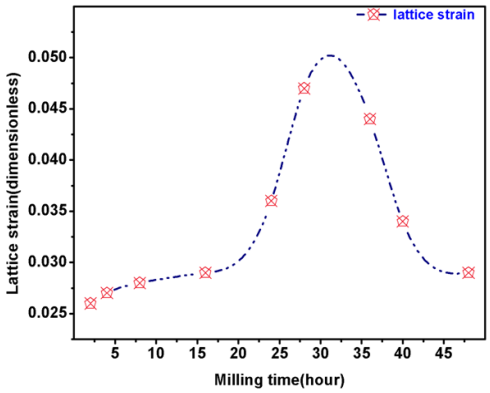

Fig: 3 Lattice strain v/s milling hours for Cu Zn Al

IV. RESULT ANALYSIS

4.1 Scanning Electron Microscopy (SEM) and analysis of features:

SEM features shown in fig: 4 indicates porous aggregation, reflect layered structure. Prolonged milling resulted in acute plastic deformation into small aggregation. Gradually features turns into particles of elongated flaks, fragmented into small particles. An experimental finding reveals that that reduction in size is maximum in interval of 24 hrs to 28hrs milling exposure, fig: 5&6. No significant size reduction is observed after 28 hr. Though heterogeneous features surfaced beyond 34 hr. Agglomeration stars due to metallic bodings of particles with smaller one. Energy releases due to refinement of grains, enhances the temperature. It resulted in agglomerated growth by welding, increase of ductility, and particle diameter recorded in extended milling exposure.

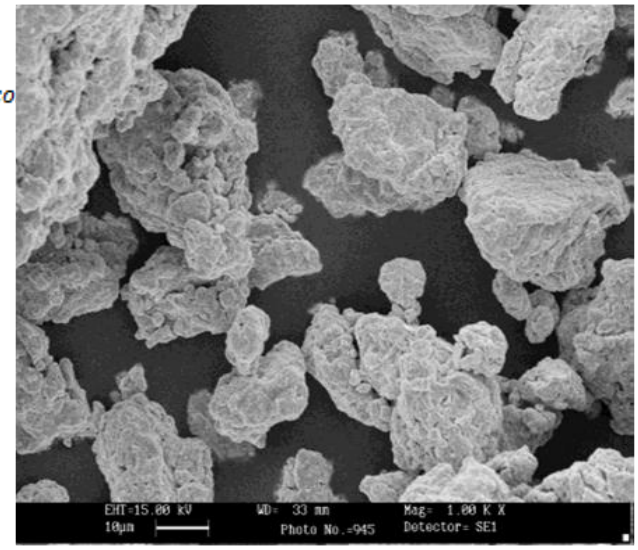

Fig: 4 SEM pictures of 2 hr milled samples 1X

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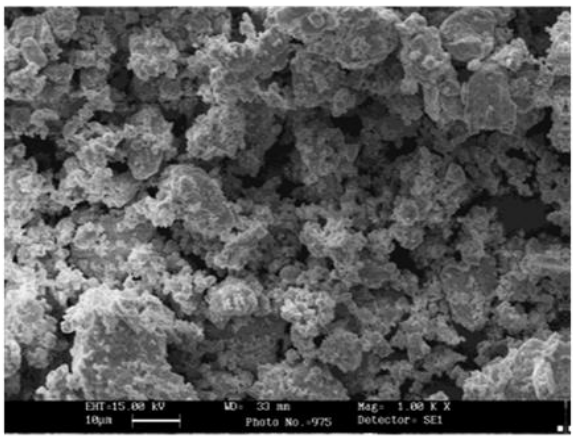

Fig: 5 24 hr samples 1X

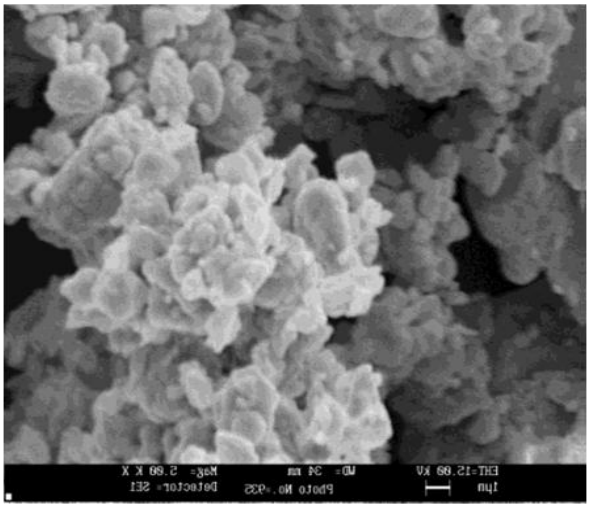

Fig: 5 24 hr samples 5X

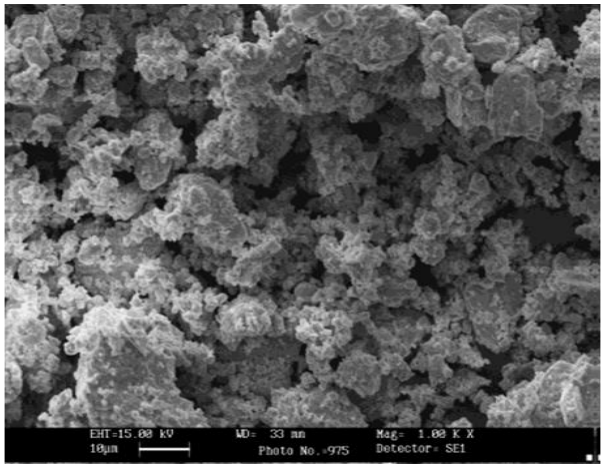

Fig: 6 28 hours milled samples 1X

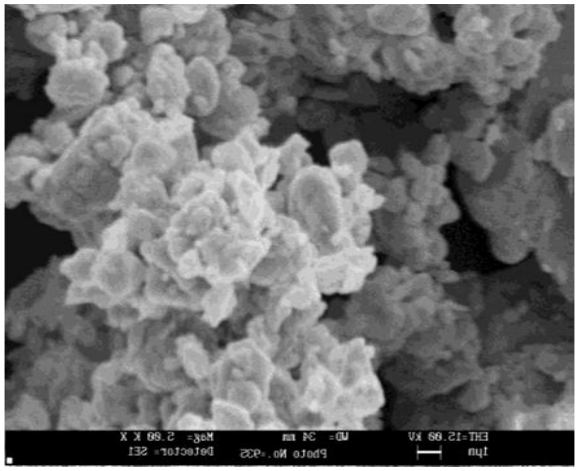

Fig: 6 28 hours milled samples 5X

4.2 Analysis of mechanical properties

Variation in density of sintered pellets observed with exposure in milling time. This observation can be clarified on the basis of steep rise in aspect ratio as particle size decrease Fig: 7, all pellets are prepared under similar pressure and surroundings, particles having more aspect ratio exhibits less density.

Fig: 8: heat treated sintered pellets at 550°C exposed in hydrogen atmosphere for 30 min minutes

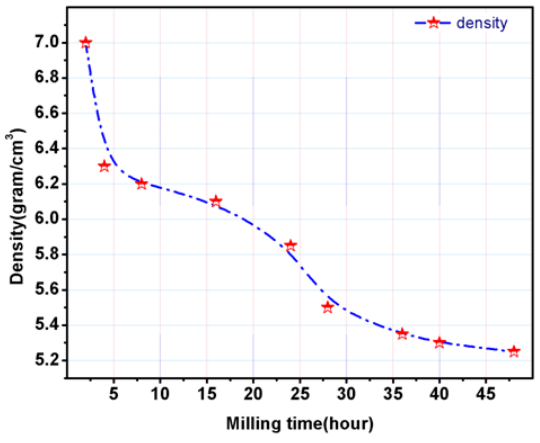

Fig: 9 milling time versus density graph

Fig: 9 exhibits decrease in density of milled alloy with hours of milling. As time of milling increases size of crystalline powder decreases and surface to volume ratio enhances significantly, this is the reason behind decrease in density. Fig: 10 shows increase in micro hardness

with development of nanofeatures, which appeared with milling time up to 28 hours. Further reduction in grain size, micro hardness decreases due to reverse Hall-Petch effect as governed by equation (3)

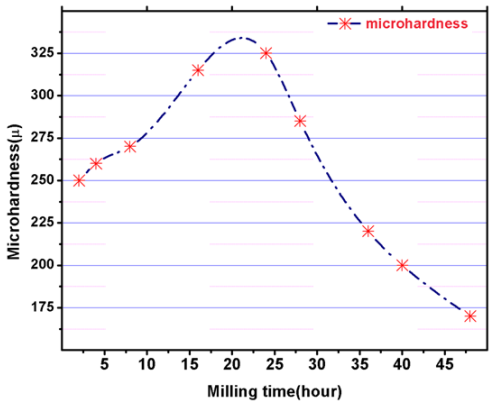

Fig: 10 milling time versus micro- hardness of material

Micro hardness behavior with milling exposure can be interpreted with help of Hall Petch & inverse Hall Petch effect.

$$\sigma_{0} = \sigma_{I+} kD^{-1/2} \quad (3)$$

Above equation can be applied to determine material hardness with incorporation of constant. Enhancement in hardness can be observed up to particle size 12nm capped by Hall-Petch limit, beyond that limit there is onset of material weakness defined by reverse Hall-Petch effect caused by GB sliding of small particles.

5.0. CONCLUSION AND FUTURE SCOPE

HEBM is highly versatile processing technique to develop nano-crystalline materials, relatively new for producing shape memory alloys. Experimental findings reveal that both Nano-features and SME do not co-exist. SME phenomenon is macro and micro level phase changing process in which significant change in volume undergo in thermo-dynamic cycling. It is highly complex and difficult to handle Nano-crystalline material for fabrication of a device to be used for engineering applications. Hot forging and rolling further destroy nano-crystalline features. Enhancement in mechanical properties i.e. hardness, thermal stability does not remain steady this certainly a drawback of ball milling approach. Notwithstanding to negative features appears HEBM facilitate us wide range of transforming temperatures. In the light of experimental observations and constraints devices can be fabricated for divergent working situations, i.e. at varying temperature ranges. Appropriate mechano-thermo training and milling exposure have significant impact on transition temperature and SME. Mechanical properties are function of milling exposure time. material hardness is inversely proportional to particle size till particle size reaches minimum dia 12nm then further reduction have adverse impact on material hardness. Further focused Research in this regard is required.

Mechanics of excessive plastic deformation through HEBM is highly unpredictable in nature; in-situ probe to record changes in material while process in operation will make this technology highly effective to control material design according to need.

Nomenclature:

HEBM: high energy ball milling
XRD: X-ray diffraction.
SEM: Scanning electron microscopy
SME: Shape memory ally
TWSME: Two way shape memory alloy
FE-SEM: Field electron scanning electron microscopy
DTA: Differentia thermometric analysis
TGA: Temperature gravimetric analysis.
GB: Grain boundary
Symbols:
$\sigma_{0} =$ The yield stress
$\sigma_{I} =$ Friction stress
K = locking parameter
D = grain diameter

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