Optical metallography and DTA/TGA Analysis of Shape memory alloy: Cu$_{74}$Zn$_{22}$ Al$_4$ (Wt.%)

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Abstract. Phase changing materials play very important role in design of actuators and sensors in many equipment. Allow of copper, Zinc and Aluminium exhibits shape memory features. In presented experimental investigation, Cu$_{74}$Zn$_{22}$ Al$_4$ (Wt.%) was prepared by mechanical alloying using high energy ball milling process. By mechanical alloying, nano-crystalline features were developed. Powder was converted into pellets and sintered and forged for optical metallography characterization. DTA/TGA analysis was performed to exhibits shape memory features. When shape memory material changes its phase, energy in form of heat either released or absorbed. Optical metallographs indicates that sintered and forged samples exhibits different features.

Key words: SMA, Phase transformation, optical metallography, nano-crystalline, DTA/TGA

Table:1 Abbreviation

| Abbreviation | Description |
|--------------|-------------|
| SMA          | Shape memory alloy |
| SME          | Shape memory effect |
| DTA          | Differential thermal analysis |
| TGA          | Temperature gravimetric analysis |
| DSC          | Differential scanning calorimetry |
| XRD          | X-Ray Diffraction |
| HEBM         | High energy ball mill |

1.0 Introduction
Optical Metallography deals with optical and electron microscopy of metals and alloys for martensitic phase transformation that undergoes during process of thermo-mechanical training. Microstructures can be defined as those material structure which can be discerned with naked eye or with the help of microscope. Microscopes have enough resolution to distinguish grain boundaries of phase transformed material. Resolution limit of microscopes is limited with wavelength of visible light (~0.5 micron). Microscopy can facilitate about in terms of changes in material structure with heat treatment training of material at various stages. Specific features of interest are changes in grain size and shape, grain boundaries variation, chemical composition changes due to thermo-mechanical processes applied on material.

1.1 Literature Review
P. Yong et al [1] investigated deformation behaviour of one and two phase CuAlMn alloy during heating stage. Authors performed tests at constant temperature with variation in strain rate from (0.001/s to 1/s) at temperature less than 500°C. Authors conclude that deformation behaviours
of alloy depends strongly on $\alpha$-phase. Strength improvement of CuAlNiMn alloy can be done by torsion at high pressure.[2, 3]. Dian et al[4] observed that appreciable improvement of shape memory effect (SMA) can be achieved for Co-Ni based alloy through alloying with Si. Zhi Zeng et al[5] fabricated and characterized innovative bionic manipulators from NiTi (SMA). Experimental observation reveals that laser processing regions of material produces distinctive phase transformation temperature and also recovery characteristics based on thermo-mechanical changes, which are necessary features of actuators. H.J Yu et al[6] investigated phase transformation temperatures in multicrystalline ferro-magnetic SMA. Authors investigated poly-crystalline Ni$_{56.5}$Fe$_{12.7}$Ga$_{26.5}$ SMA employing optical metallographic approaches, XRD and DSC for constituent’s variation and phase transformation behaviour. Decrease in transformation temperature can be caused by decrease in electronic concentration. Guobo pang et al[7] investigated relationship in martensitic transformation and super elastic behaviour of Au$_7$ Cu$_5$Al$_4$ SMA of microwires. Yu Lei et al observed Martensitic changes in CuAlMn SMA at low temp(100K) [8]. Observation also reveals the grain boundaries and crossing points may develops new nucleation sites. Paz et al studied interdiffusion of Ti coated wires of Ni to ascertain shape memory of NiTi microtubes[9]. Meng et al investigated a relation in the volumetric fraction of martensite with respect to plastic deformation in Fe Mn Si Cr N SMA. Thermal induced training have impact on shape memory behaviour of pre-strained SMA Fe-30 Mn-6 Si-5 Cr[10]. Stress induced transformation can also bring about changes in shape memory effect in polycrystalline NiTi SMA[11, 12]. These effects observed in micro and macro-mechanical test of NiTi with in-situ optical metallography[13]. Mazi and Krishnan studied effect of copper on microstructure and SME effect of copper on microstructure and shape retrieval of Fe-Mn-Cr-Ni SMAs[14]. Experimental observation reveals that Cu can be dissolved up-to 3% by weight in austenite ($\gamma$) form and can play as strong stabilizer of $\gamma$. Yu et al performed experimental investigation to interrelate between transformation of phase and magneto-caloric effect in Ni Fe Cr SMA[15]. Kannan et al characterized laser welded NiTiNol SMAs [16]. Based on observation, it can be concluded that quality of weld depends on depth of penetration, improved hardness and resistance to corrosion. Annealing temperature significantly modify SME of Fe-14Mn-5Si-9Cr-5Ni alloy as reported [17]. Authors observed that at 650°C annealing temperature, best performance in SME observed during first cycle. SME effect was induced due to formation of stress-induced $\varepsilon$ martensite. Many researchers have performed thermomechanical training to variety of SMAs and successfully achieved SME[18-20].

Functionalized nanomaterials are also getting application as smart material[21-23].

Based on above reviews one can have assumed that controlled heat treatment of SMAs in proper proportion can be trained for Shape memory effect. Cu-74-Al-22 Zn-4 (Wt.%) is innovative material which can be taken suitable thermo-mechanical training in order to develop shape memory effect.

2.0 Materials and Methods

2.1 Preparation of sample:

First sample of Cu$_{72}$Zn$_{22}$Al$_{4}$ (Wt.%) prepared for ball milling to develop nano-crystalline features. XRD was performed to measure particle size of milled sample. Pellets were prepared for sintering and hot forging. The sample is prepared to expose microstructural feature of surface. Hot forged sample were cut using diamond cutter to expose the section. Mounting of small cut section into the resin was done for ease to handle sample is small see Fig: 1. Coarse grinding on progressively finer emery paper then polishing using
alumina powder or diamond paste on rotating wheel. etching on dilute acid Washing in alcohol & drying exposes grain boundaries.

Figure 1 mounted samples in order (as mixed, 2, 20, 48 hr milled hot forged, from bottom to top

Optical microscopy was performed using Optical Microscope (Leika), see fig:2

Figure 2Optical Microscope (Leika) System at Metallography Lab MMED I I T Roorkee.
Figure 3 Perkin Elmer Thermal Analyzer (Pyris Diamond) at I I C Roorkee.

TGA/DTA 6300, max Temp 1500°C, inert gas H₂, N₂.

2.2 DTA/DSC DTG Analysis of the sample

Thermo-gravimetric analysis (TGA) involves thermal analysis technique that measures changes in weight% with variation in temperature and time in specified insitu condition. It further helps us to measure structural and phase stability of material and how material will behave in atmospheric and inert condition. This analysis is suitable applied for all types of material, solids, organic or inorganic. An another very useful technique, is differential thermal analysis (DTA). It is actually calorimetry recording of temperature variation with heat flow associated with thermal and phase transition in material. Phase transitions can be easily seen through graphs (melting point, glass transition temperature, crystallization).

2.3 Hot Forging and Rolling

Hot forging and rolling process are applied on sinters pellet material in order to develop stable martensite phase which is responsible for SME in SMAs. During experimental observation, it has been noticed that selected material exhibits high order of brittleness to deform into this sheet which can be demonstrated for shape memory effect. So it is simply very difficult to develop SME in SMA prepared through mechanical alloying. it is also not possible to retain nano-features after hot forging.

3.0 Mathematical formulation

3.1 Calculation of Lattice Strain:

According to law of X-ray diffraction pattern

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

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

\[ 2d \sin \theta \cos \Delta \theta + 2d \cos \theta \sin \Delta \theta + 2\Delta d \cos \theta \sin \Delta \theta + 2 \Delta d \sin \theta \cos \Delta \theta = n \lambda \]  

\[ 2d \sin \theta + 2d \cos \theta \Delta \theta + 2 \Delta d \Delta \theta \cos \theta + 2 \Delta d \sin \theta = n \lambda \]
\[ 2d \sin \theta = n\lambda, \quad \text{and} \quad 2\Delta d \Delta \theta \cos \theta = 0, \text{equivalent to zero} \]

\[ 2d \cos \theta \Delta \theta + 2d \sin \theta = 0 \]

\[ \Delta d/d = -\Delta \theta / \tan \theta \tag{2} \]

\[ \sigma = \sigma_0 + kd^{-1/2} \tag{3} \]

Here, \( \sigma \) stand for yield stress of deformation, \( \sigma_0 \) and \( k \) are constant

### 4.0 Results analysis

![Figure 4](image)

**Figure 4** From top to bottom two in groups: (1.) as mixed sintered and forged sample. (2.) 2hr sintered and forged. (3.) 20 hr sintered and forged

#### 4.1 Optical Metallography: An Analysis

Optical Metallographs above as shown, (a), (b)&(c) Fig:4 difference in morphology of grain structure and alignment of grains for milled sintered sample and hot forged sample. In as mixed
sample Metallographs shows that material is in two phase, grains are elongated along the length and perpendicular to the direction of applied force in forging process. In 2hr and 20 hr milled sintered and hot forged sample grains are finer, agglomeration of small particles into bigger one also takes place but in forged sample, it is difficult to trace two phase system, grains are elongated like thin strips. Some stabilization of martensitic phase also takes place in hot forging and rapid cooling process. In 48 hr milled hot forged sample, grain boundaries are distinct, overlapping takes place, morphology is heterogeneous but martensitic β is stabilized, as it is evident in DTA test.

4.2 DTA/TGA Analysis

An analysis of stacked heat flow curves, Fig:5 of differing samples undergone through increasing milling time exhibits that there has been specific phase transformation temperature for 24, 28, and 48 hr milled material. observed particle size for 28 hr milled material exhibits lowest size and magnitude of heat flow was highest for this material sample also. There was highest shift in peak temperature for this sample(236°C). T3-T1 (variation in temperature of beginning and end of peak is highest for 28 hr sample. This phenomenon observation is indication of onset of nano crystallization effect. For 28 hr milled sample sharpest heat flow peak recorded also range of heat flow minimizes. Exothermic transformation associated with flow of heat in this range. Some re-crystallization process also happens in phase-transformation process

4.3 TGA Plots for various samples, heating only

TGA (Thermo-gravimetric 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 graphs, Fig:6 exhibits that variation in weight change is highest for 28 hr milled and sintered material sample. For 48hr milled material sample, temperature for highest weight loss occurs is highest (263°C), all transition temperatures for selected sample are higher. DTA and DTG analysis indicates that phase transformation brings about change of weight (gain or loss) for
each material sample. Gain or loss in weight preceded phase transformation for each material sample. Rate of heat flow per unit mass is maximum for 28 hr milled sample. Range of temperature is minimum for which transformation takes place for this material sample. For 28 hr milled sample particle size is minimum and grain distribution is homogeneous in size. This material sample results offer 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.

![Graph](https://via.placeholder.com/150)

**Figure 6** Weight loss versus variation in temperature (heating)

5.0 Conclusion and future scope:
Optical metallography is highly useful when heat treatment of shape memory alloy material performed. Mechanical alloying is the most appropriate technique to prepare shape memory alloy of Copper Zinc and Aluminium powder. Though DSC/TGA test confirm shape memory effect of alloy in powder form. In order to observe SME in solid stage, pellet sintering and hot gorging is required. Grain boundaries formation of hot forged samples exhibits variation in grain sizes and dislocation of strain boundaries. Cycling heating and cooling of hot forged samples develops shape memory effect. By precise selection of material distribution and controlled thermo-mechanical training, shape memory effect can be established in specific alloys. Materials having shape memory effect can be used for actuators in electronic equipments and sensors. More research is needed to maintain nano-features in materials during hot forging.

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