

Effect of (Al-Ni) & (Cu-Ni) Concentrations Ratios on the Hardness and Porosity of Ternary (Cu-Al-Ni) Smart Alloys

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Abstract

In this research, the newly achieved results determined the best ratio of (Cu-Ni) and (Al-Ni) in the smart (Cu-Al-Ni) alloys since these values achieved the best results in terms of, hardness and porosity. Their mechanical properties have great commercial and technological importance in many applications: industrial, aerospace & biomedicine and also in high damping composites, filters, prosthetic hands, sensors, actuators, self-lubricant applications, automobile industry, electronic industry...etc. (Cu-Al-Ni) smart alloys samples were produced using powder metallurgy technique with vacuum system. In this experimental setup, five weight percentages Cu-Ni & Al-Ni of ternary (Cu-Al-Ni) smart alloys were selected. Vickers micro-hardness and porosity properties of these alloys were studied using a digital Vickers micro-hardness tester, X-ray diffraction device (XRD), Optical microscopic device, Scanning Electron Microscope device (SEM) & Porosity testing in accordance to the ASTM B328-(1996) so as to show the effects of (Cu-Ni) & (Al-Ni) concentrations ratios on hardness & porosity of (Cu-Al-Ni) smart alloys. The analysis results proved that when there is an increase in Al and Ni concentration in alloy lead, it will automatically increase the hardness and porosity, but the increase in Al ratio shows more effect than the increase in Ni ratio. It is preferred to select the weight percentages of aluminum and nickel so that we get smart alloys that possess single martensitic phase (β'_3) because when it increases the aluminum weight percentage above 14%. It leads to the production of single martensitic phase (γ'_3). This type of martensitic is brittle and causes heavy increase in its hardness, which makes it lose its ability to recover its original shape and confines it to limited use in applications at high temperatures. Finally, the best smart alloy is S₅ (82.4%Cu,14%Al, 3.6%Ni), especially for applications such as (high damping composites & self-lubricant applications) because it gives the highest hardness (155.73 HV) and highest porosity (6.853% by volume) among the five samples studied.

Keywords: (Cu-Al-Ni) Smart Alloys, Hardness, Porosity, Powder Metallurgy method, XRD, SEM.

INTRODUCTION

The objective of this study is to know the influence of (Al-Ni) & (Cu-Ni) concentrations ratios on the hardness and porosity of ternary (Cu-Al-Ni) smart alloys. The weight percentages of the alloying elements can be selected on the basis of comparison with the application of new material CN-250X Nimesis alloy which contains Cu 82.4wt.%, Al 13.5wt.% and Ni 4.1wt.% where its shape recovery (8 to 10%) at 150MPa for transformation temperature below 200°C seems to be better than (NiTi) (6 to 7%) when the temperature is lower than 100°C, (Hautcoeur A., *et al.*, 2015). As illustrated in the figure 1.

The smart alloy possesses the ability to remember its original shape when stimulated by an external effect if any source increases its temperature upward its transformation temperature, even after severe plastic deformations (Shahadat H., *et al.*, 2017). As a result of its unique properties, it has been used in many applications: industrial (Ming H. Wu., *et al.*, 2000), aerospace (D J Hartl, *et al.*, 2007), biomedicine such as sensors, actuators, high damping composites (Gabriel L., *et al.*, 2009), prosthetic hands (Konstantinos A., *et al.*, 2010), self-lubricant applications, etc.

Selection the weight percentages of the alloying elements (Cu-Ni), (Al-Ni) for ternary (Cu-Al-Ni) shape memory alloy.

For the β_3' martensites: $M_s(^\circ\text{C}) = 2660 - 187 \text{ pct Al} - 16 \text{ pct Ni (wt pct)}$ -----(3)

Nimesis application New Material (CN-250X).

- 1- Cu 82.8%, Ni 3.7%
Al=const.=13.5%
 - 2- Cu 81.8%, Ni 4.7%
Al=const.=13.5%
 - 3- Al 13.5%, Ni 4.1%
Cu=const.=82.4%
 - 4- Al 13%-Ni 4.6%
Cu=const.=82.4%
 - 5- Al 14%-Ni 3.6%
Cu=const.=82.4%
- 1- $M_{s1} = 76.3^\circ\text{C}$
 2- $M_{s2} = 60.3^\circ\text{C}$
 3- $M_{s3} = 69.9^\circ\text{C}$
 4- $M_{s4} = 155.4^\circ\text{C}$
 5- $M_{s5} = -15.6^\circ\text{C}$

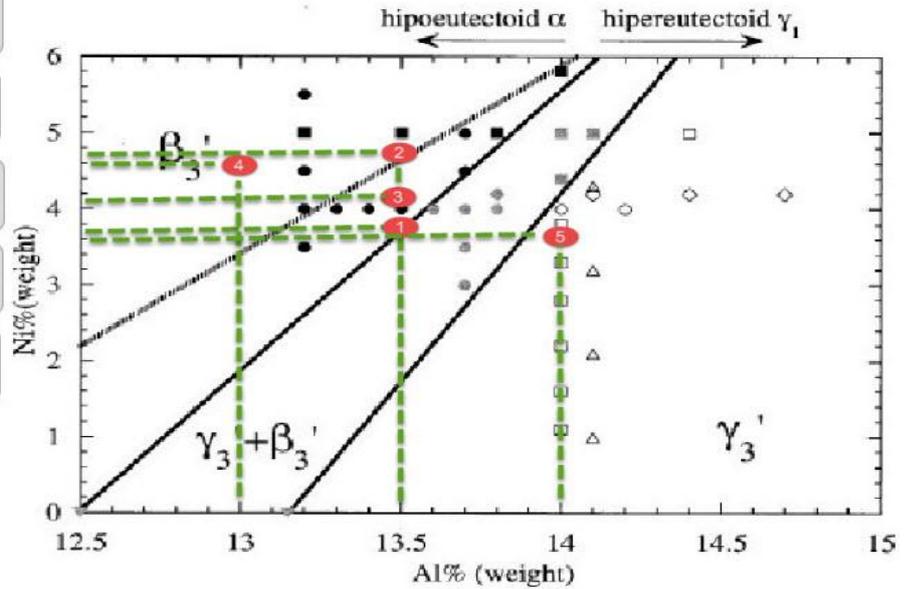


Fig. 1: The four weight percentages of Cu-Al-Ni smart alloys to be studied with the weight percentage of the application (CN-250X), (Recarte V., *et al.*, 2002 & Hautcoeur A., *et al.*, 2015).

There are several types of smart alloys are present. Of them, the alloys which are applied the most and the widely used ones are (Ni-Ti) smart alloys, but as a result of their high cost, their need for non-traditional machining process and low transformation temperature (restricted to 100 °C) there is a need arise here for the best alternative especially at the high transformation temperature i.e., Ternary Cu-Al-Ni smart alloys because they are less expensive, easier for manufacturing and has high transformation temperature (-200°C to 200°C). But they are some limitations such as brittleness and poor corrosion resistance. In order to overcome these problems, the ratio of alloying elements needs to be changed or otherwise the conditions of heat treatment to be modified or the addition of new elements to be changed and the above said actions lead to refined grain size, increased strength and improvement thermo-elastic characteristics of the alloy (Darel H., *et al.*, 1990 & Dr.T. Vigraman E., *et al.*, 2014).

The best concentrations of Al & Ni can be used for smart applications i.e., 1 to 6 weight percentage of Nickel and 13 to 14.5 wt. pct. of aluminum is to be added in the right mixture. When the concentration of aluminum increases above 14%, then it results in single brittle phase γ_3' . The appearance of this phase causes heavy brittleness in the smart alloy and results in failure of shape restoration. The smart alloys possess a single $\beta_3 \Rightarrow \beta_3'$ martensitic transformation which should be selected especially for high temperature applications, because these alloys are thermally more stable and highly thermoelastic as shown in the figure 1 (Recarte V., *et al.*, 2002).

Experimental work:

The experimental work was performed according to the following procedures:

1. The pure powders of Cu, Al & Ni with 99 % purity was imported from Sky Spring Nanomaterials, Inc. USA and prepared with an average particle size of 44 microns (-325 mesh) Groover M., 2013). To verify the purity, the chemical composition of the powders was checked using emission spectrometer device after compacting the Cu, AL and Ni powders to produce disc samples of 14mm diameter & 5 mm thickness using the uniaxial press machine as shown in the figure 2.



Fig. 2: Emission spectrometer device & uniaxial press machine.

2. The powder metallurgy method was used to manufacture the ten Samples of (5mm thickness & 11mm diameter). These samples included two disc samples for each weight percentage from five weight percentages which was chosen as shown in the figure 1. The powder metallurgy method includes: -

- a) Mixing process at a constant speed of 72 rpm for 6 hours until all the samples were mixed using sensitive balance (4-digits) & Horizontal two rotating drums mixing device. One can achieve the best if the container is between 20% and 40% full (Groover M., 2013), as illustrated in the figure 3.

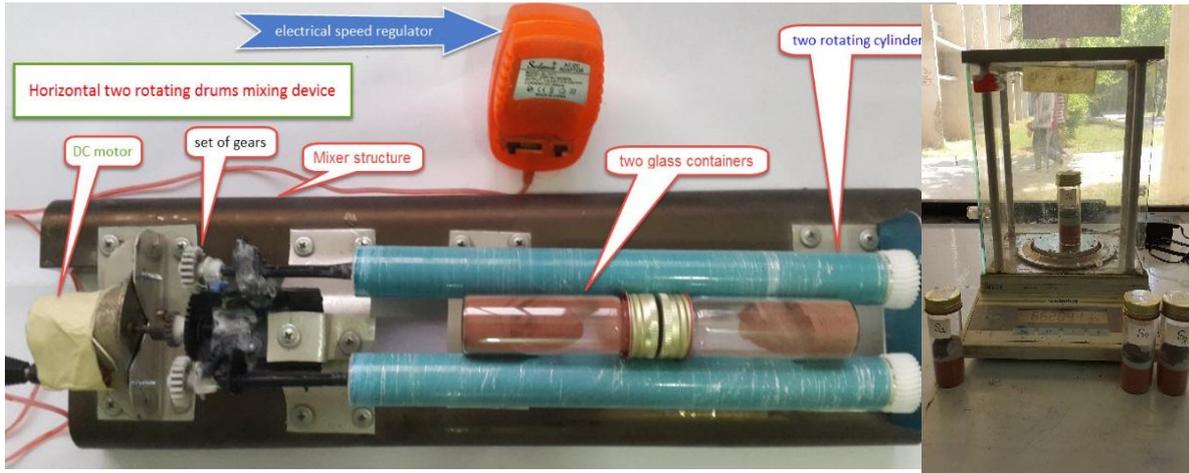


Fig. 3: Mixing device & sensitive balance (4-digits)

b) Compacting process was performed for all the samples in order to attain the desired part shape $D \times t = (11 \times 5 \text{ mm})$ under constant pressure 650 Mp at the displacement rate of 1 mm/min & holding time of two minutes using a computerized uniaxial press machine with a load capacity of 100 KN as shown in figure 4.

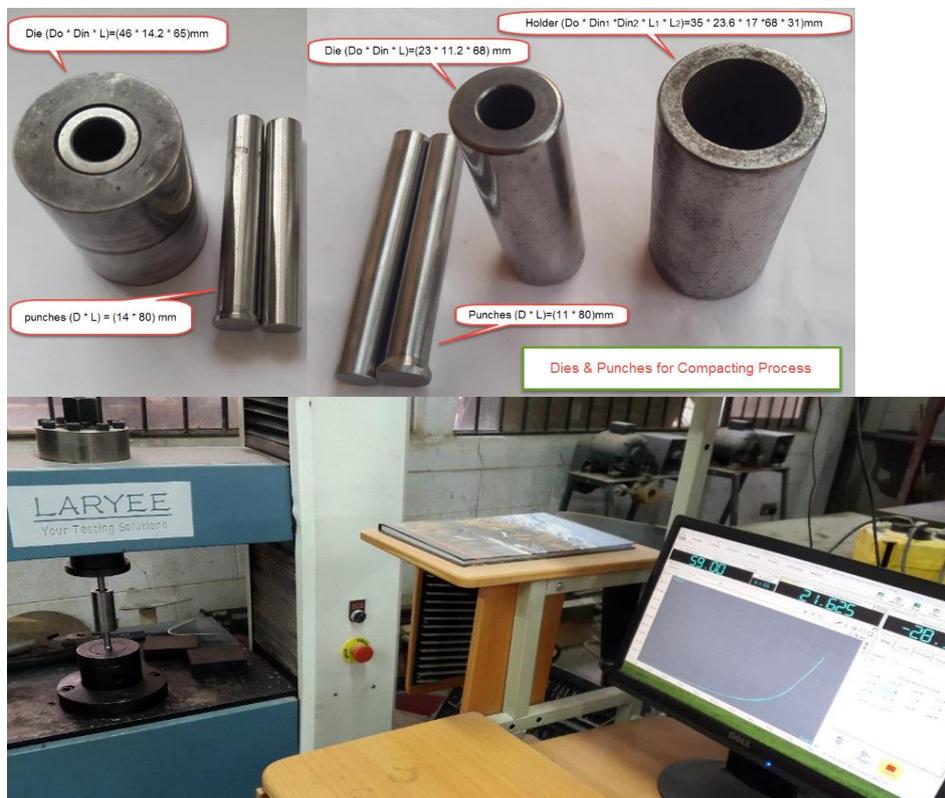


Fig. 4: Computerized uniaxial press machine & dies & punches

c) Two stages of sintering process occurred in which the first stage is, at constant temperature 500°C and one hour holding time and the second stage is, at constant temperature 850°C and five hours holding time. With 0.7-0.9 melting temperature (Groover M., 2013& Hasan A., 2016) to produce solid-state bonding of the particles and strengthening of the part using electrical tube furnace with a vacuum system to prevent the oxidation of the samples & voltage stabilizer as shown in figure 5.



Fig. 5: Electrical tube furnace with vacuum system & voltage stabilizer

d) Two stages of heat treatment were followed quenching process is by heating to 800°C with one hour holding time, followed by rapid cooling through ice water to get martensitic phase (Shafeeq M., et al., 2016). Aging process is by heating up to 100°C with two hours holding time followed by keeping it aside to cool in furnace to ensure martensitic stabilization (Nevin B., et al., 2012) as shown in figure 6.



Fig. 6: Quenching & aging processes of 10 samples

3. To conduct physical and mechanical tests, the grinding, polishing & etching for each weight percentage of samples must be performed to investigate the apparent phase is austenite before heat treatment. This is also done to make sure that the apparent phase is martensitic after heat treatment, because one need to ensure the unique characteristics of smart alloys and their special reversible transformation, called thermoelastic martensitic transformation are retained (Prof. Luca L., et al., 2011). These tests were conducted using Optical microscopic device, X-Ray Diffraction (XRD) device & Scanning Electron Microscope (SEM) device as shown in the figures 7 & 8.





Fig. 7: Grinding, Polishing, Etching processes & Optical microscopic device



Fig. 8: X-Ray Diffraction device & Scanning Electron Microscope device

4. Vickers micro-hardness testing was conducted on five samples using a digital micro-hardness tester as shown in figure (9) at applied load of 200 mg and a holding time of 20 seconds in order to investigate the effect of (Cu-Ni) and (Al-Ni) alloying elements on hardness values of smart alloys. Micro-hardness measurement was used because most of the applications in which these smart alloys operate are small in size and are subjected to low loads such as wires.



Fig. 9: Digital Vickers micro-hardness tester

5. Conduct porosity testing on five samples according to the ASTM B328-(1996) using sensitive balance (4-digits) as shown in the figure (10) to weigh each weight percentage of samples in three different cases. The first is it should be weighed in the air and the second one is when it is immersed in the closed container that contains oil, and using vacuum system for 30 min inside the closed container, final one is through opening the container and leaving it aside for ten minutes after which it has to be weighed in air after cleaning the sample from excess oil. In the third case, the oil saturated sample should be weighed in water using bin with hock. The apparent porosity can be determined from Eq. 1:

$$P = \left[\frac{(B-A) \times 100}{(B-F) \times D_o} \right] * D_w \tag{1}$$

P = interconnecting porosity by volume, %,
 A = mass in air of oil-free sample, g,

B = mass of oil-impregnated sample, g,
 F = mass of oil impregnated specimen in water with mass of wire tared, g,
 D_w = density of water at the immersion temperature, (0.9984 g/cm³ at 19°C).
 D_o = density of the oil, 0.88 g/cm³.



Fig. 10: Porosity testing

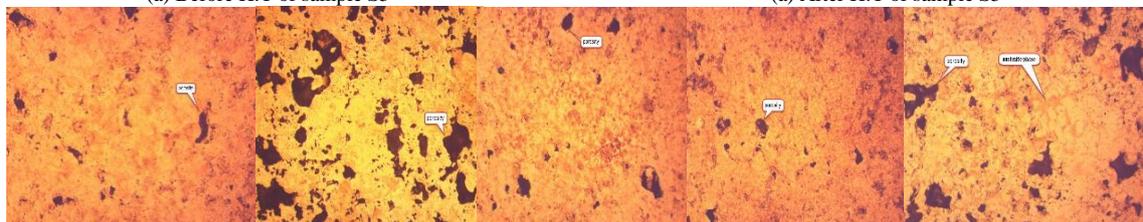
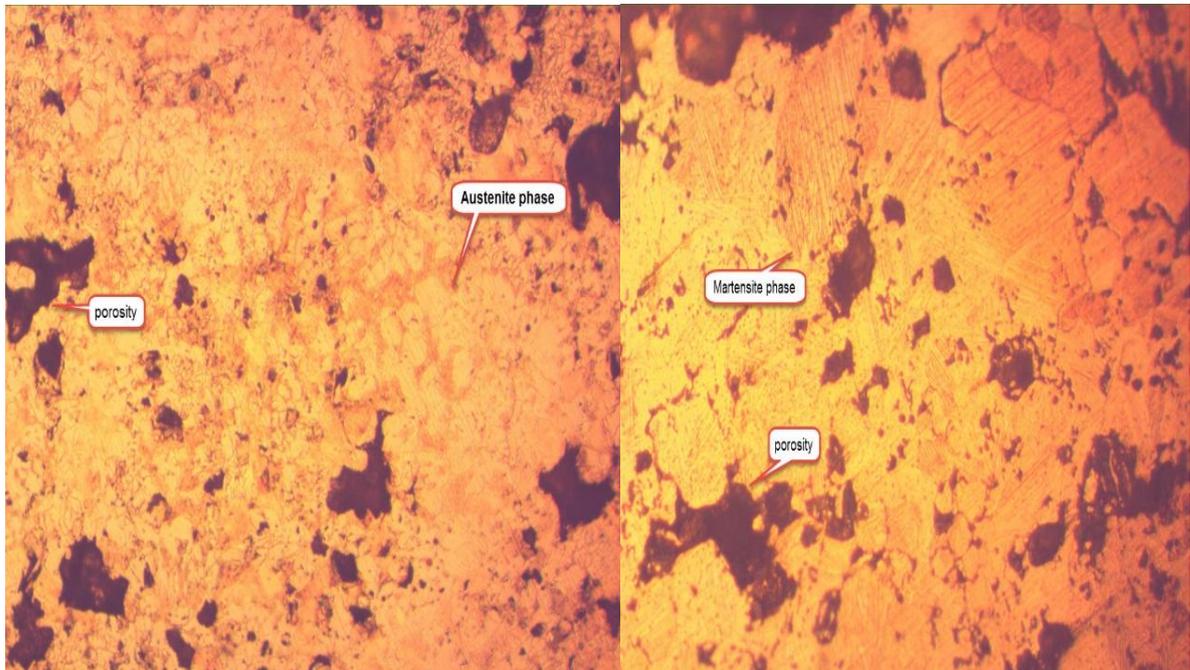
RESULTS AND DISCUSSION

In the figures (11), (12) & (13) the examination results of five samples using the Optical Microscopic device and Scanning Electron Microscope (SEM) device before heat treatment were shown, in which these images show pores and austenite layers. The second group of images represents the examination results of five samples after heat treatment, where the pores appeared with twinned-martensitic layers (V-shape or Zig-Zag shape), which are caused by heat treatment.

In figures (14) & (15) shown below, the images of the examination results of five samples using X-Ray Diffraction (XRD) device before heat treatment were shown. These results show austenite phase (for S1, S2, S3 & S4 are Al4Cu9, but for S5 is Cu9Al4) while the second group of images represents the examination results of five samples after heat treatment, where these results shows martensitic phase (for S1, S2, S3 & S4 are AlCu3, but for S5 is AlCu4) caused by heat treatment.

In the tables (1) & (2) below, the Vickers micro-hardness test results & the porosity test results of three samples were shown. In figure 16, the results were compared and represented through graphs. The results showed that the hardness and the porosity increases with the increase in the weight percentage of nickel and decrease in copper when the aluminum proportion was constant.

In the tables (3) & (4) below, the Vickers micro-hardness test results & porosity test results of three samples were shown. In figure 17, the results were compared and represented as a graph. The results showed that the hardness and the porosity increases with the increase in the weight percentage of aluminum and decrease in nickel when the copper proportion was constant. This denotes that the effect of the increase in aluminum overcomes the effect of the increase in nickel.



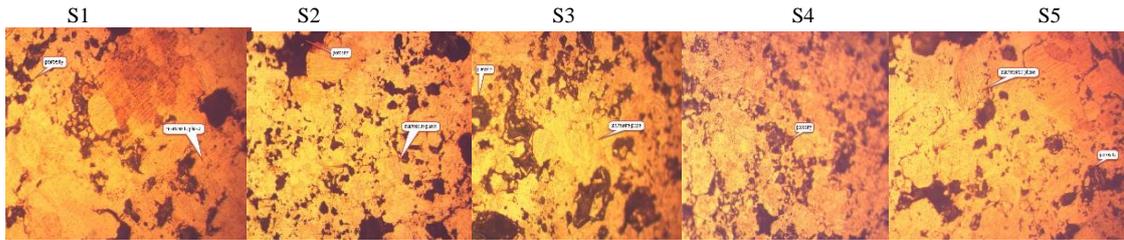
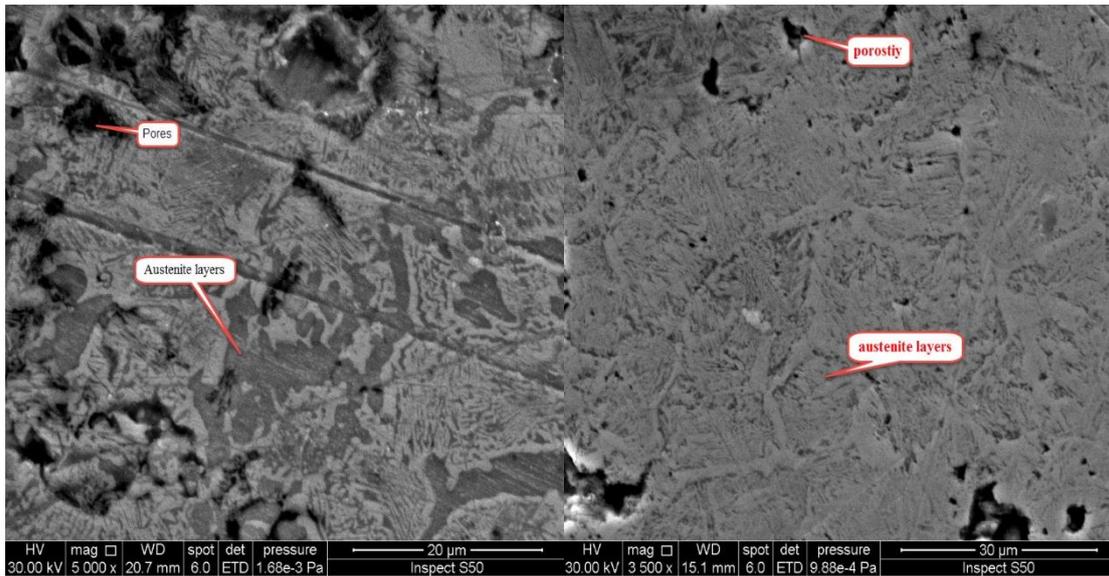
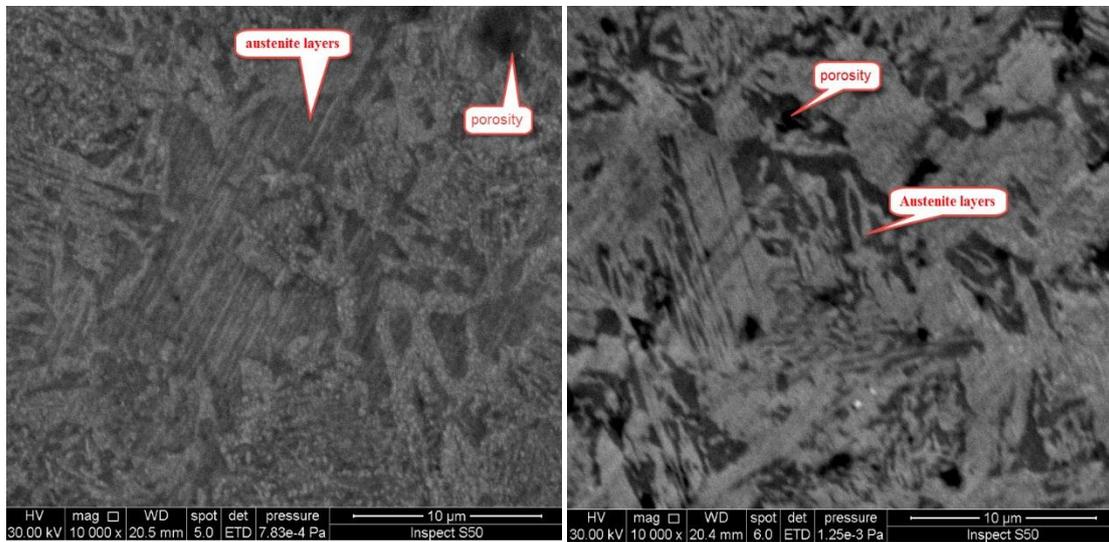


Fig. 11: Microstructure images of each ratio before & after heat treatment by optical Microscopic device (40x)



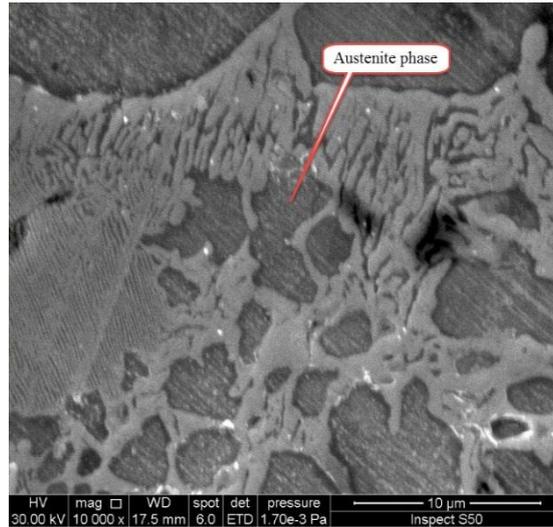
S1

S2



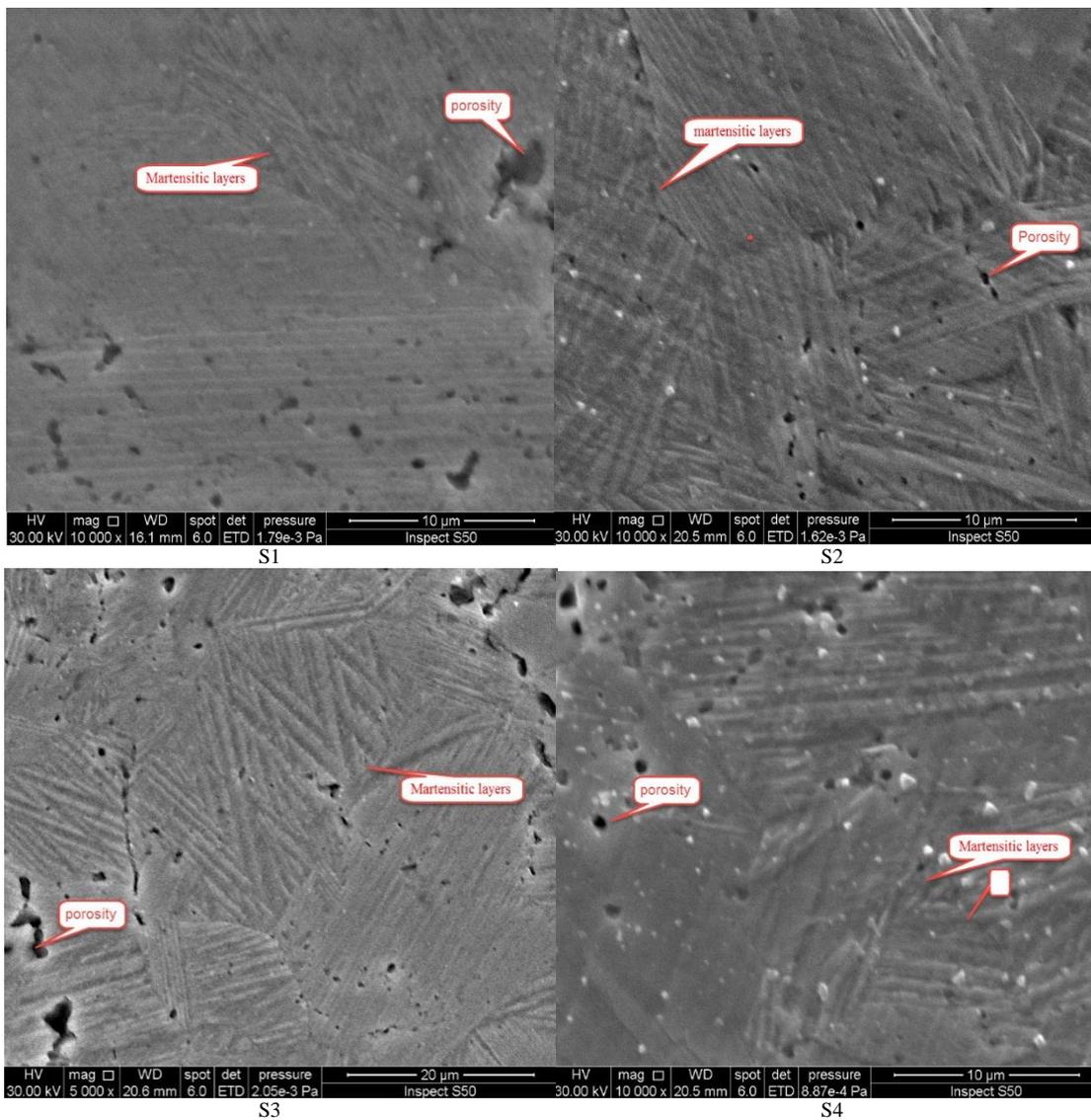
S3

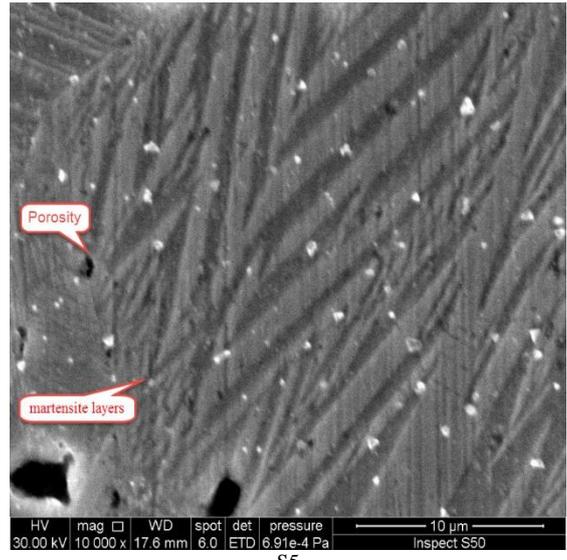
S4



S5

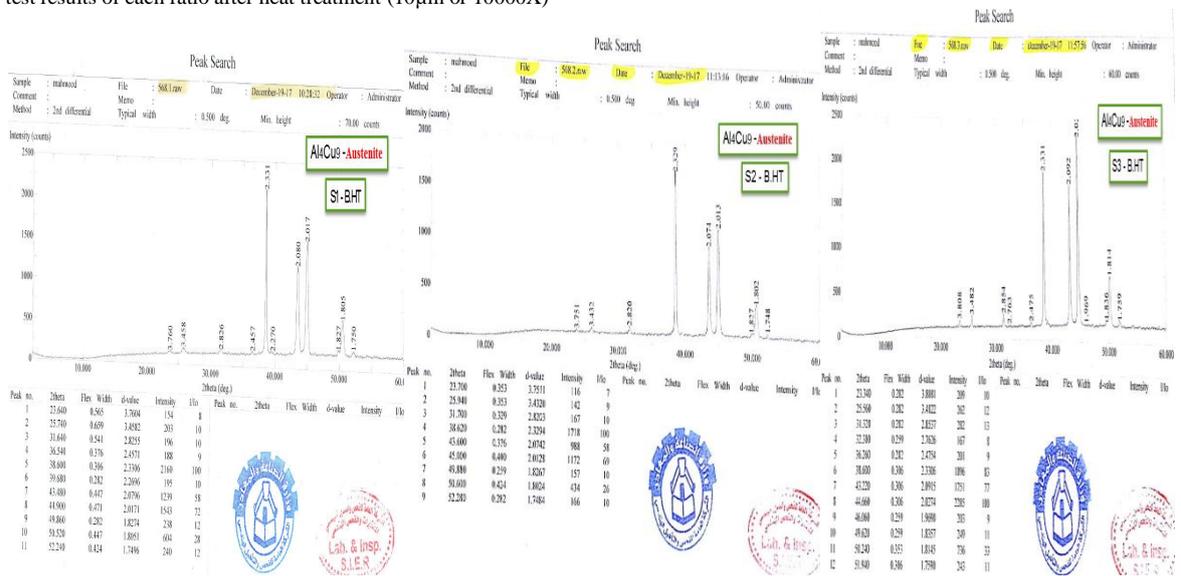
Fig. 12: SEM test results of each ratio before heat treatment (10μm or 10000X)





S5

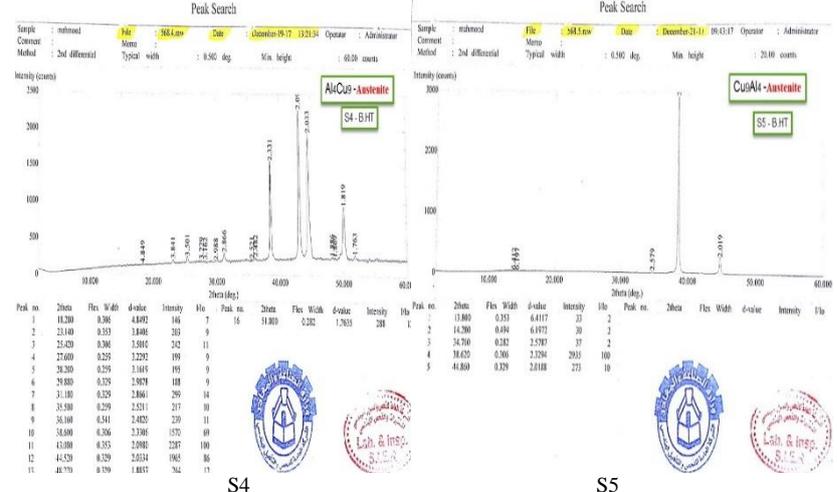
Fig. 13: SEM test results of each ratio after heat treatment (10μm or 10000X)



S1

S2

S3



S4

S5

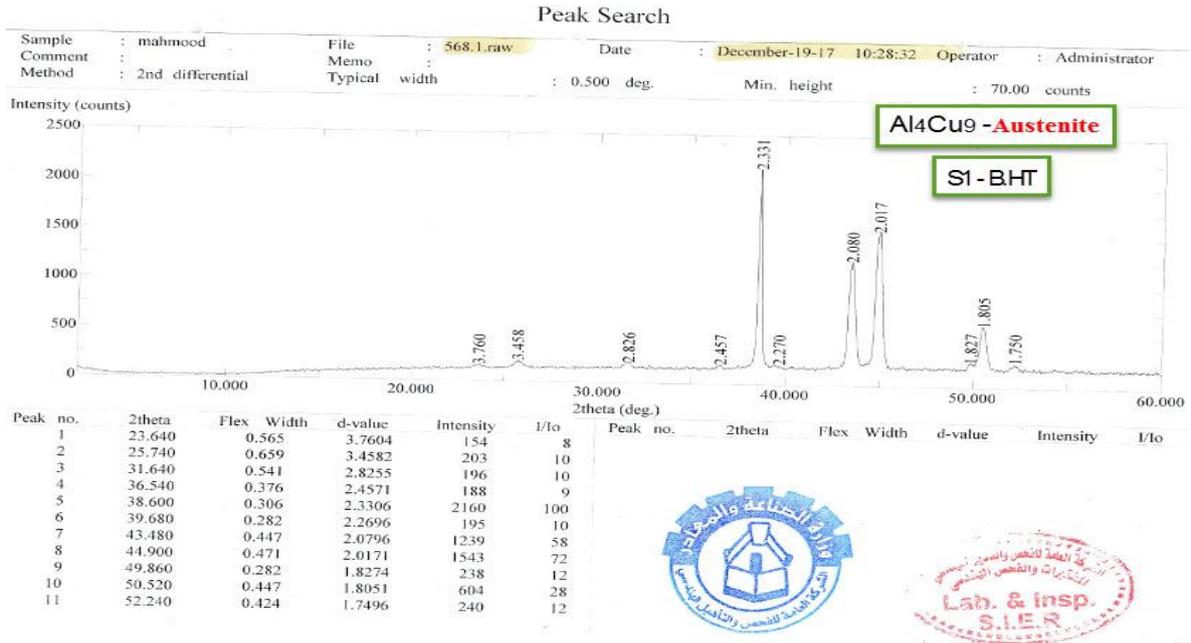
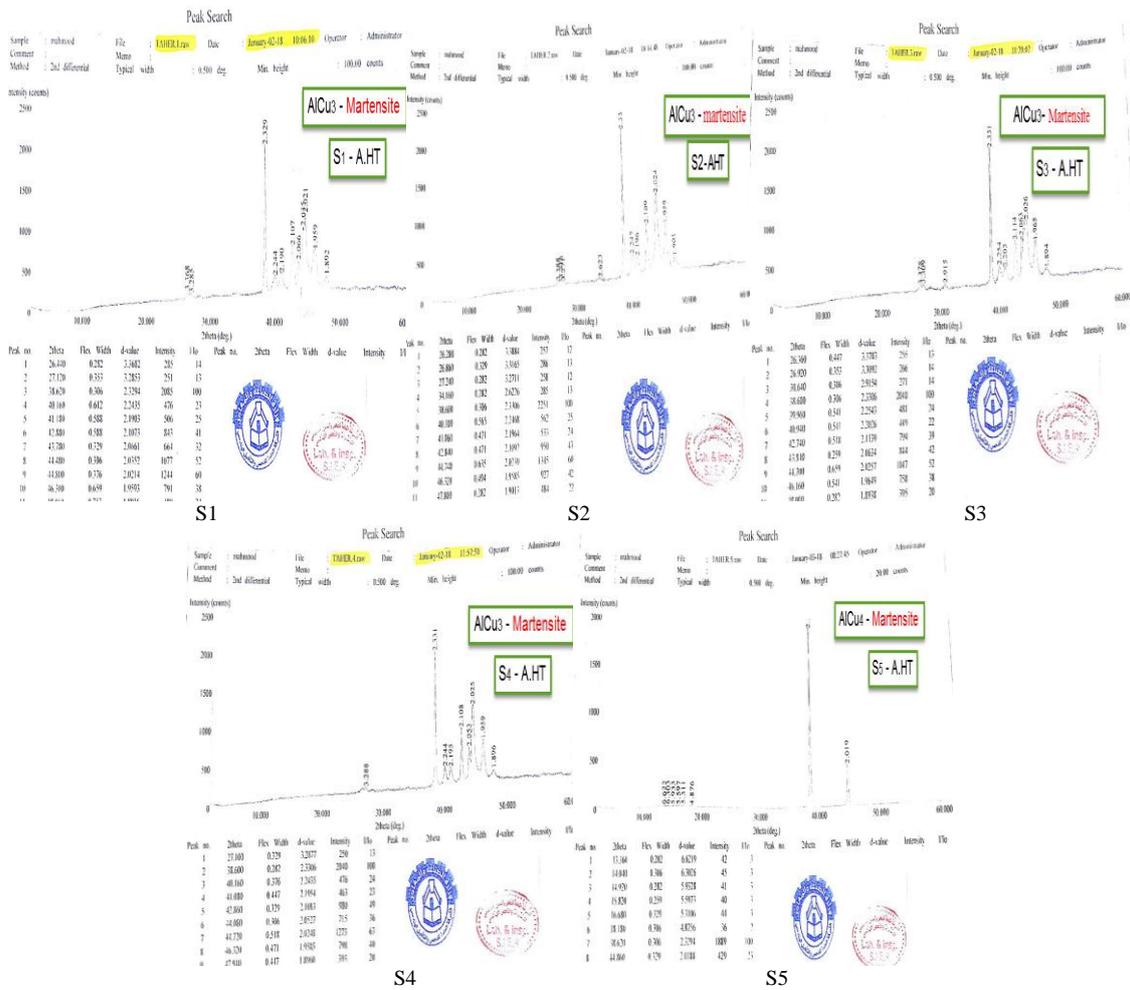


Fig. 14: X-Ray Diffraction test results of each ratio before heat treatment



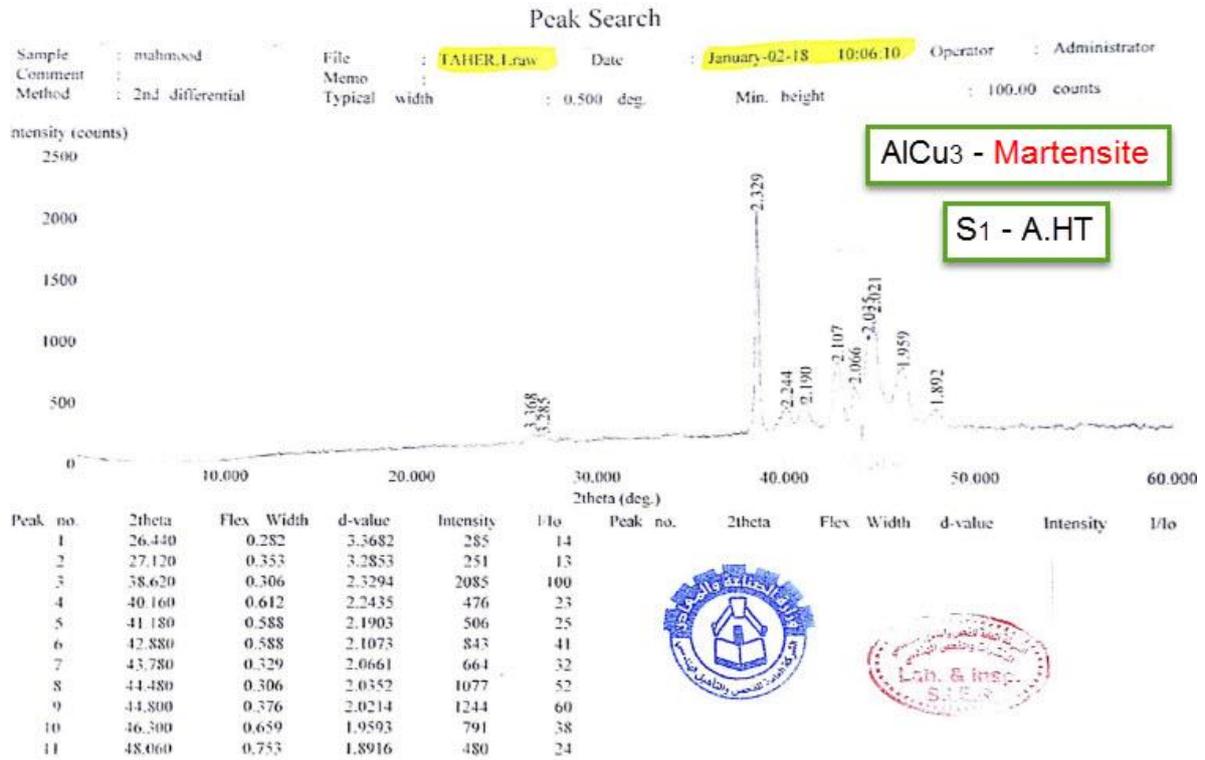


Fig. 15: X-Ray Diffraction test results of each ratio after heat treatment

Table 1: Vickers micro-hardness results

Sample No.	chemical composition	HV ₁	HV ₂	HV ₃	HV(Average)
S ₁	82.8%Cu,13.5%Al, 3.7%Ni	140.9	144.4	107.0	130.77
S ₃	82.4%Cu,13.5%Al, 4.1%Ni	142.9	158.1	146.5	149.17
S ₂	81.8%Cu,13.5%Al, 4.7%Ni	178.7	154.1	132.0	154.93

Table 2: Porosity results

Sample No.	chemical composition wt.%	A (g) in air	B (g) in oil	F (g) in water	Porosity%
S ₁	82.8%Cu,13.5%Al, 3.7%Ni	2.6217	2.6819	1.0811	4.266
S ₃	82.4%Cu,13.5%Al, 4.1%Ni	2.5588	2.6333	1.0557	5.358
S ₂	81.8%Cu,13.5%Al, 4.7%Ni	2.5307	2.6073	1.0488	5.576

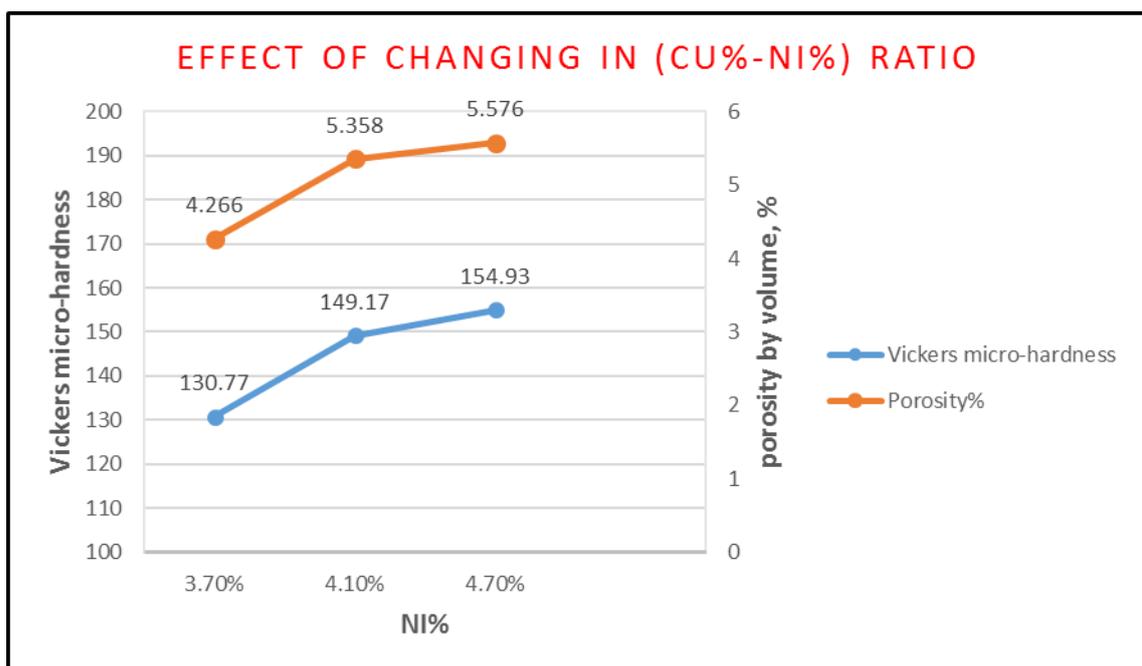


Fig. 16: Graph shows the effect of changing in (Cu%-Ni%) ratio with constant Al% on Vickers micro-hardness and porosity% in (Cu-Al-Ni) smart alloys.

Table 3: Vickers micro-hardness results

Sample No.	chemical composition	HV ₁	HV ₂	HV ₃	HVAverage
S ₄	82.4%Cu,13%Al, 4.6%Ni	130.8	125.1	153.3	136.40
S ₃	82.4%Cu,13.5%Al, 4.1%Ni	142.9	158.1	146.5	149.17
S ₅	82.4%Cu,14%Al, 3.6%Ni	151.4	159.7	156.1	155.73

Table 4: Porosity results

Sample No.	chemical composition wt.%	A (g) in air	B (g) in oil	F (g) in water	Porosity%
S ₄	82.4%Cu,13%Al, 4.6%Ni	2.5923	2.6438	1.0728	3.720
S ₃	82.4%Cu,13.5%Al, 4.1%Ni	2.5588	2.6333	1.0557	5.358
S ₅	82.4%Cu,14%Al, 3.6%Ni	4.1858	4.2983	2.4360	6.853

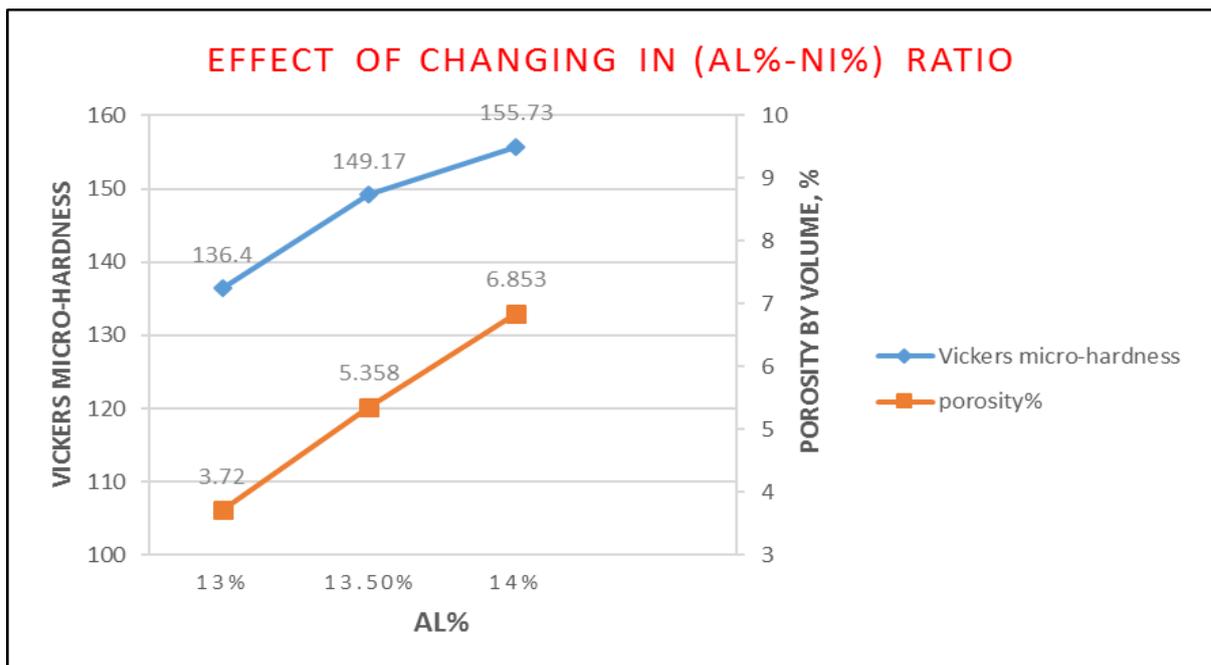


Fig. 17: Graph shows the effect of changing in (Al%-Ni%) ratio with constant Cu% on Vickers micro-hardness and porosity% in (Cu-Al-Ni) smart alloys.

CONCLUSION:

From this experimental work, we concluded that when aluminum & nickel weight percentages are increased, and the copper ratio decreased, this results in increased hardness and porosity properties in smart alloys. But the effects of aluminum concentration on hardness and porosity properties overcomes on the effect of nickel concentration as shown in the tables 1,2,3 &4.

The best smart alloy is S₅ (82.4%Cu, 14%Al, 3.6%Ni), especially for applications such as (high damping composites & self-lubricant applications) because it exhibited the highest hardness (155.73 HV) and highest porosity (6.853% by volume) values among the five samples studied.

It is preferred to choose the weight percentages of aluminum and nickel so that we get smart alloys that possess single martensitic phase (β'_3) because when the aluminum weight percentage increases above 14% that leads to the production of single martensitic phase (γ'_3). This type of martensite is brittle and causes heavy hardness that lead to it lose its ability to recover its original shape and confines to only limited applications at high temperatures as shown in the figure (1), (Recarte V., et al., 2002 & Hautcoeur A., et al., 2015).

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