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Effect of Sn Addition on Transformation Temperature and Thermal Properties for Cu-Al-Si Shape Memory Alloy

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Abstract. Sn was added to Cu-14%Al-4.5%Ni shape memory alloy in three Percentages (0.5,1,3)%to study the effect of the addition on microstructure, Transformation temperature, thermal properties and activation energy. SEM-EDS, XRD tests were performed on the specimens; DSC Measurement was performed on the alloys. A computer model was built via MATLAB to calculate the thermal properties by means of graphical integration for the DSC data. Results showed an increase in the transformation temperature and Equilibrium temperature outside the domain, also an increase in hysteresis and spread with the increase of Sn Percentage, also results shown an increase in thermal properties (enthalpy and entropy and free energy), results showed also a decrease in activation energy more than the base alloy the 3% Sn Addition gave the best results in both transformation temperature and activation energy.

1. Introduction
From the beginning of this century Shape Memory alloys were included within smart materials, there is an increase in demand for it applications including the nonmedical field[1]Since Cu-alloys are good alternative for Ni- Ti Alloys for industrial application (MEMS, Actuators ,Valves, Damping applications) because of the low cost, easy manufacture and high temperature range [2] but this alloy has a problem in brittleness , low shape recovery strain ,To overcome these problems, two methods have been identified by the researcher thusfar , the addition of the alloying elements or heat/ aging treatment to control grain size which has an effect on the mechanical properties. recent studies showed that to add the fourth element to the alloy can effect the Mechanical properties & shape memory Properties, the works of Saud etal[3,4]by adding a cretin amount about (1% of Ti, Mn, Co, Zr ,Be ,Nb and B) to Cu-Al –Ni Showed an improvement in both mechanical & shape memory properties, Abbass etal [5-6] added Ge, and Te to Cu-14%Al- 4.5%Ni resulted in an improvement in mechanical properties ,and a shifting in Transformation Temperatures for the SMA ,Sari[7] added 2.5% Mn to Cu-14%al- 4.5Ni SMA result showed an increase in mechanical properties and in shape memory Properties. AbudlRaheem etal[8] added Fe to Cu-14%Al-4.5Ni which led to an improvement in both corrosion and Wear Resistance .This alloy is commercially wanted for High temperature applications for the high range compared with Ni-Ti and with by adding elements to precipitate in matrix to stabilize the β phase and forming new Phases so that the alloy can be considered as High Temperature Shape memory alloys HTSMA with a range can reach up to (300 °C) and above for a better and more economical. . This Paper aims to study the effect of Sn Addition on Cu-14%Al-4.5%Ni Shape memory Alloys with three different percentages (0.5% ,1%and 3%) and study its effect on Microstructure ,Thermal Properties, Activation energy and Transformation Temperature by building a computer mode of the governing equation via MATLAB.
2. Experimental Work

2.1 Materials and procedures
A Pure Cu(99.99%) wires, Al(99.99% purity) Foils & Ni(99.99%) powder were melt in vacuum induction furnace under argon atmosphere at 1200 °C and then the melt was poured into a cylindrical alloy steel die (1.4 cm in diameter), then it was re-melted and Sn was added and stirred in three percentages (0.5%, 1.0%, 3.0%) at 1100°C, Homogenization was carried out at 900 °C for 30 min and then quenched in Iced brine solution, wire cut into specimens are cut into a 0.5 cm height for SEM, DSC and XRD, and chemical compositions as cast and homogenized as shown in Table 1.

| Alloy    | Sn%  | Al%  | Ni%  | Cu%  |
|----------|------|------|------|------|
| Base SMA | ---  | 14   | 4.5  | Rem  |
| S1       | 0.5  | 14   | 4.5  | Rem  |
| S2       | 1    | 14   | 4.5  | Rem  |
| S3       | 3    | 14   | 4.5  | Rem  |

2.2 XDR and Microstructure
XRD was performed by using Shmidzoo 3000 XRD-EDX instrument, Cu Target Cu(α) λ=1.45 A°. Also for microstructure examination the specimens were ground and polished and etched in solution which consists of (FeCl3.6H2O+HCl+Methanol) and then examination was performed using for 4 min and then microstructure by Kruss optical microscopy & Tescan easy probe SEM – with attached Oxford EDS Unit

2.3 DSC Test
DSC preformed in SATRAN LabSYS 300 with range (25 °C - 250 °C) in both directions exothermic and endothermic result were exported to Microsoft excel To Calculate The equilibrium temperature from equation (1), Hysteresis from equation (2) and Spread From equation (3) [1].

\[ T^o = \frac{1}{2} (M_s + A_f) \]  
\[ H = A_s - M_f \]  
\[ S = A_s - A_f \]

2.4 Computer Role
The results were into MATLAB so that to calculate the Enthalpy (ΔH) by way of Area Under the curve, Then a Mathematical Model was made to calculate the Entropy (ΔS) the Free energy(ΔG) as shown in equations (4) and (5) respectively[9]

\[ \Delta S = \frac{\Delta H}{T^o} \]  
\[ \Delta G = \Delta H - T^o \Delta S \]

And afterwards calculating the Activation energy by the model suggested by Ozawa[10]

\[ E = -\frac{R}{b} \left[ \frac{d(\log \varphi)}{1/T_m} \right] \]

Where b is a constant (0.4567) R =8.314 universal gas constant T_m Maximum DSC Peak temperature °C. Figure 1 shows the flow chart of the computer model.
3. Results and Discussion

3.1 XRD Results
XRD results shown in figure (2, 3, 4 and 5) for base alloy respectively. Figure (2) shows the XRD Analysis for the base alloy SMA (Cu-14%Al-4.5%Ni) it was observed that the formation of phases indicates the form both Martensitic β’ and γ’ phase while in Figure (3) the XRD analysis of base alloy SMA(Cu-14%Al-4.5%Ni-0.5%Sn) it was found that pure Sn particles with mentioned phases the same case also shown in figures (4) and figure (4) respectively.
3.2. Microstructure

The obtained microstructure results shown in Figure (6,7) the SEM for the base alloy in which the Martensitic Phase $\beta'$ is found intensively as in figures (9,10) in fine needle shape also the $\gamma'$ closed stacked with the $\beta'$ phase is the major phase and the $\gamma'$ just as Kim et al found [11]. same thing goes for S alloys group just as Kim et.al did after Zr addition [11]. in these figures the perceptions of Sn Particles are randomly distributed as Abbass etal concluded with adding Te to microstructure of SMA [6], the Sn particles were randomly distributed on the matrix of the martensite structure grain the in figure 9 and with increase of the Sn percentage in figure(8) and figure(9) the $\beta$ Phase is restrained be the distribution of the Sn grains , in particular the smaller size martinsite in manner similar to Saud et.al[4] concluded in the use of B particles also it also restrained the martensite phases.EDS results shown in figure 10 and figure 11 confirmed the chemical composition for the alloys.
Figure 6. Microstructure for Base SMA

Figure 7. Microstructure for S1 Alloy

Figure 8. Microstructure for S2 Alloy

Figure 9. Microstructure for S3 Alloy
3.3 DSC Results
Figures 11, 12, 13 and 14 show the thermograms of the base and modified alloys while Table 2 shows the shape memory properties of Cu-Al-Ni and the $A_s$, $A_f$, $M_s$, $M_f$ transformation temperature and the equilibrium temperature and Maximum Temperature and hysteresis and spread for the alloys results shows increase in temperature range beyond 200°C beyond the domain (100-170)°C and increase in hysteresis loop as shown in Table 2 an increase of spread for alloys S1 and S2 and as we observe in Figure 13 the DSC results of SME DSC test of alloys. It was observed that test range exceeded the known domain (100-170°C). This is due to the effect of Sn addition which increased the Martensite temperature limit. These results are confirmed by Saud et al.[4] and Abbass et al.[5-6]. They concluded that the addition of the Fourth element in SMA alloy controls the SME properties [4] there are multi peaks in figure 13 as Sari[7] noted that the multi peaks are attributed with the interface transformation the two peaks confirm the two Phases $\beta^+$ + $\gamma^+$ martensite transfer to $\beta$ while the on the other $\beta$ transfer to $\beta^-$ in which it is stabilized $\beta$ as shown in figure 5.

Table 2. DSC Results for Alloys

| Alloy | $A_s$ °C | $A_f$ °C | $M_s$ °C | $M_f$ °C | $T$ °C | H | S | $T_{max}$ °C |
|-------|---------|---------|---------|---------|-------|---|---|-------------|
| Base  | 129     | 165     | 133     | 100     | 149   | 29| 36| 150         |
| S1    | 150     | 183     | 122     | 92      | 153   | 58| 33| 160         |
| S2    | 143     | 198     | 137     | 91      | 168   | 52| 55| 156         |
| S3    | 206     | 225     | 128     | 88      | 177   | 118| 19| 151         |
Figure 11. DSC Thermogram for Base SMA

Figure 12. DSC Thermogram for S1 Alloy

Figure 13. DSC Thermogram for S2 Alloy
3.4 Mathematical Model

The results were exported into MATLAB a mathematical model was built from the equations 3-6 to calculate the enthalpy ($\Delta H$), entropy ($\Delta S$) and free energy ($\Delta G$) for the base alloys with the addition of Sn after calculating ($\Delta H$) by means of area under the curve and applying equation 4-5 to calculate the entropy and free energy as shown in figure 15 and figure 16, then by applying Ozawa equation to calculate the activation energy results are shown in table 3 and table 4. Result showed an increase in enthalpy and entropy and free energy in the exothermic direction with increase of Sn percentage and a decrease in the endothermic direction this is a result to the addition of Sn. in the results of the activation Sn Addition showed a decrease in activation energy that the thermo-mechanical transformation is less required while with the increase of maximum temperature and equilibrium temperature, Sn is a low melting temperature so with this characterisation the energy is more with Sn Increase of percentage. The transformation of the SMAs is related to the energy which the materials retain in their structure. So this energy consists of chemical energy and reversible mechanical energy and $T^*$ is the temperature at which the chemical energies of austenite and martensite phases are equal [12]

![DSC Thermogram for S3 Alloy](image)

**Figure 14. DSC Thermogram for S3 Alloy**

| Alloy | $\Delta H_{M-A}$ /J$\cdot$g$^{-1}$ | $\Delta H_{A-M}$ /J$\cdot$g$^{-1}$ | $\Delta S_{M-A}$ /J$\cdot$g$^{-1}$·c$^{-1}$ | $\Delta S_{A-M}$ /J$\cdot$g$^{-1}$·c$^{-1}$ | $\Delta G_{M-A}$ /J | $\Delta G_{A-M}$ /J |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------|----------------|
| Base  | 19                              | -254                           | 0.12                            | -1.7                            | 1.12           | -0.7          |
| S1    | 787                             | -391.2                         | 4.44                            | -22.1                           | 1.12           | -0.3          |
| S2    | 326.3                           | -976.1                         | 19.42                           | -58.1                           | 0.44           | 0.2           |
| S3    | 411.4                           | -758.5                         | 26.8                            | -4.95                           | 13.6           | 1.15          |

**Table 3. Results of Mathematical Model for Thermal Properties of base Shape Memory Alloy**
Table 4. Activation energy for the base and SMA Alloys with Sn

| Alloy | $T_{max}$°C | $E_a$(J) |
|-------|-------------|---------|
| Base  | 150         | -22.5661|
| S1    | 160         | -24.0705|
| S2    | 156         | -23.4688|
| S3    | 151         | -22.7166|

Figure 15. Computer solution for Base SMA

Figure 16. Computer solution for Base S3 Alloy
4. Conclusions
1. Sn Addition resulted in an increase in transformation temperature As, Af, Ms and Mf outside the domain of Cu-14%Al-4.5% Ni Shape memory alloys.
2. There is a rise in equilibrium temperature $T^\circ$ and maximum temperature $T_{\text{max}}$ for Cu-14%Al-4.5%Ni Shape memory alloys due to Sn Addition.
3. Particles were randomly distributed in the matrix as shown in SEM Images.
4. The Microstructure Images obtained from SEM showed the Martensite phase in both shapes (The Needle Head ($\beta$') and the stack pile ($\gamma$'))
5. There is a rise in the enthalpy $\Delta H$, Entropy $\Delta S$ and the free energy $\Delta G$ in the Endothermic direction while enthalpy $\Delta H$, Entropy $\Delta S$ and the free energy $\Delta G$ in the Exothermic direction due to Sn Addition.
6. The activation energy reduced with the increase of maximum temperature of SMA due to Sn Addition.

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