**Engineering**, 2010, 2, 172-178
doi:10.4236/eng.2010.23024 Published Online March 2010 (http://www.SciRP.org/journal/eng/)

# Structure and Properties of Sn-9Zn Lead-Free Solder Alloy with Heat Treatment

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*Received November* 20, 2009; *revised December* 17, 2009; *accepted December* 22, 2009

## Abstract

The Sn-9Zn lead-free solder alloy was prepared by conventional casting technique then cold-rolled into long sheets of 1 mm thickness and 3 mm width. It was annealed at 80, 120 and 160°C for 60 min to investigate the effect of isochronal heat treatment on structure and mechanical properties of the cold rolled Sn-9Zn alloy. The results showed that, the crystallite size and lattice strain have opposite behavior with increasing annealing temperature due to recovery and recrystalization processes associated with the heat treatment process. Vickers micro-hardness number increases continuously from 155 to 180 MPa with increasing annealing temperature. Ultimate tensile strength (UTS) was also calculated. It was found that, it is equal to 61.4 MPa for the non annealed sample and slightly decreases to 60.5 and 58.2 MPa for samples annealed at 80 and 120°C, respectively. While, increases to 65.4 MPa for the sample annealed at 160°C. Also, ductility increases with increasing annealing temperature in opposite manor with the UTS. The new method for Micro-creep behavior as well as the creep rate calculated by this method has been characterized at room temperature.

**Keywords:** Cold Rolling, Annealing, Lead-Free Solder Alloy, Micro-Creep, Micro-Hardness

## 1. Introduction

There are some characteristics which play a major role in the consideration of substitutes for tin-lead solders in electronic soldering, such as a lower melting temperature of solder, adequate strength, the environmental issues related to the toxicity, good electrical/thermal conductivity, low cost, good wetting properties, and availability in sufficient quantities as concerns the base metal. These properties are mostly affected by the methods of preparation of the alloys such as rapid solidification, conventional casting or unidirectional solidification. Furthermore, the working process of the alloys, isochronal, isothermal heat treatments and aging time all of these parameters are mostly affect on the properties of these alloys [1-3]. The present paper concerns with the effect of isochronal heat treatment on structure and properties of Sn-9Zn cold rolling alloy. This alloy is one of the most alloys recommended being alternative to Pb-Sn alloy [4-7]. This recommendation is due to its lower melting point close to that of Sn-Pb (183°C) eutectic alloy and its mechanical properties, e.g. tensile strength is better than that of the Sn-Pb alloy [8]. Moreover, Sn-Zn alloy is advantageous from the economic point of view because Zn is a low cost metal.

## 2. Experimental

The materials in the alloy of composition Sn-9Zn of purities of 99.98% were weighted out and melted in a porcelain crucible using an electrical furnace with calevony as a fluxing agent. The casting was done in a graphite mold at a temperature of 500°C and thermally agitated to perform the homogenization. The resulting alloy was cold rolling into long sheets of about 3 mm in width and 1 mm in thickness. The alloy samples as illustrated in **Table 1** were isochronal heat treated at 80, 120 and 160°C for 60 min to perform the effect of heating temperature on structure and properties of these samples. X-ray diffraction analysis was performed using a 1390 Philips Diffractometer with Cu-K$_\alpha$ radiation ($\lambda$ = 1.54056 A) to determine the phases present. Differential thermal analysis test (DTA) during heating with heating rate of 10°C/min was used to identify the melting reaction of these samples. The polished samples were tested in a Vickers microhardness tester, where a diamond pyramid indenter with square base is used and the Vickers hardness number is given by HV = 0.185 $F/d^2$, where F is the applied load in N and d, is the average diagonal length in mm. Each reading was an average of at least ten separate measurements taken at random places on the surface of the specimens. All of the indentations were at least 0.5 mm away from the edges and from other indentations. Micro-creep measurements [2,9] were carried out on all samples using a fixed load 0.49 N for dwell time up to 300 s. Tensile properties were determined using a conventional testing machine with fixed cross head speed at 10 mm/min.

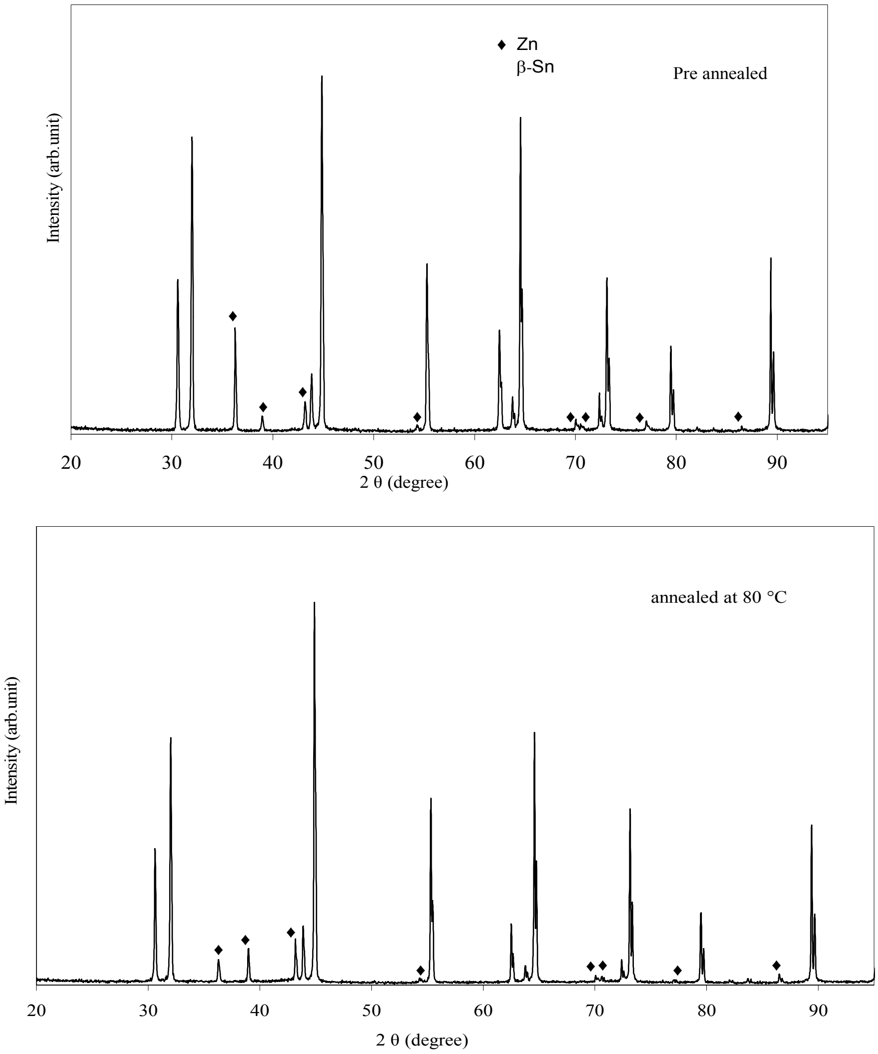
## 3. Results and Discussion

### 3.1. Structure of Sn-Zn Alloy Samples

**Figure 1** shows the profiles of XRD patterns of the Sn-9Zn cold rolled alloy samples before and after isochronal

**Table 1. Chemical analysis of the Sn-9Zn alloy before and after annealing.**

| Sample | Chemical formula | Zn | Pb | Sn | Annealing temperature °C |
|---|---|---|---|---|---|
| Sample 1 | Sn-9Zn | 9.02 | 0.04 | Bal. | Pre-annealed |
| Sample 2 | Sn-9Zn | 9.02 | 0.04 | Bal. | 80 |
| Sample 3 | Sn-9Zn | 9.02 | 0.04 | Bal. | 120 |
| Sample 4 | Sn-9Zn | 9.02 | 0.04 | Bal. | 160 |



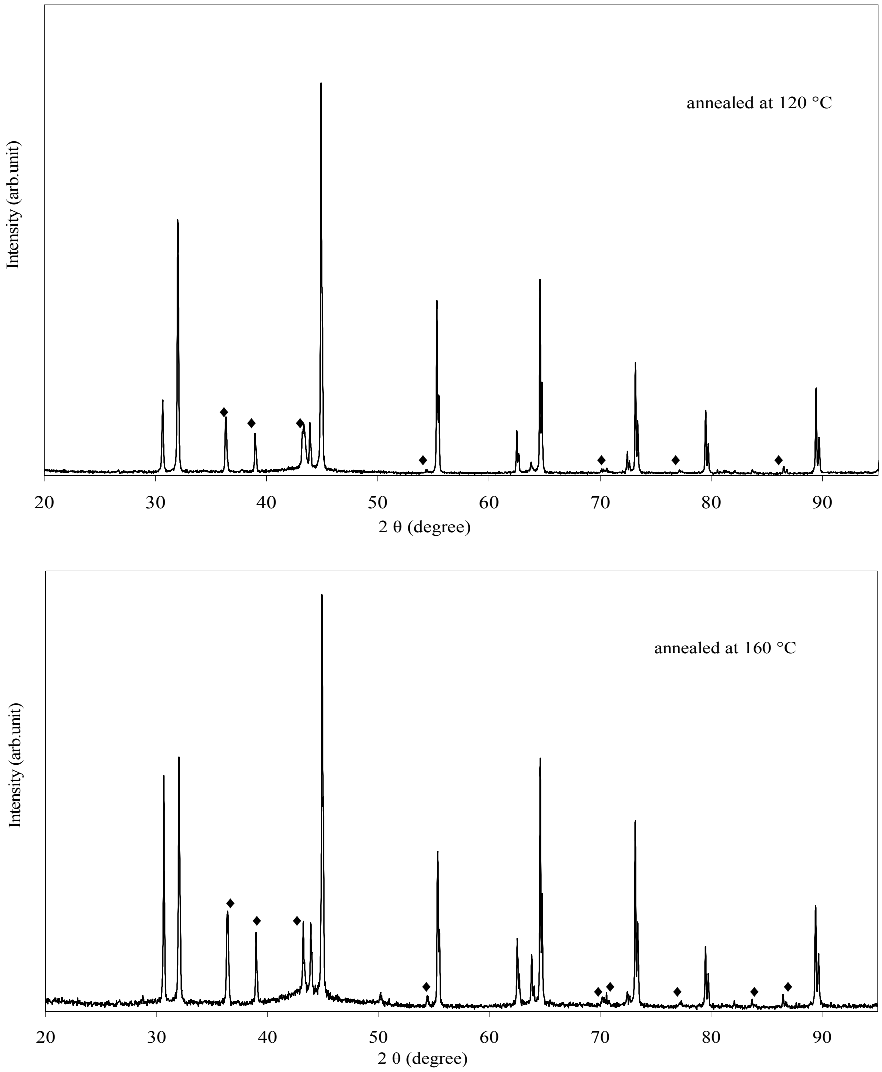


**Figure 1. XRD patterns of Sn-9Zn alloy samples before and after annealing.**

heat treatment at 80, 120, and 160°C for 60 min. Each of the alloy samples exhibit the X-ray diffraction peaks due to β-Sn matrix phase with some precipitations of Zn as a secondary phase. The effect of the isochronal heat treatment is restricted only on the lattice strain and crystallite size [10] of the Sn-matrix phase as illustrated in **Figure 2**. The crystallite size of Sn-matrix is continuously increaseed, while the lattice strain has an opposite behavior with increasing the annealing temperature as shown in **Figure 2**. Actually, cold rolling process may cause an increase in dislocation density then caused the lattice to be strained. Such an array of dislocations gives rise to a substantial strain energy stored in the lattice, so it becomes unstable thermodynamically relative to the undeformed one. Consequently, the deformed alloy will try to return to a state of lower free energy, *i.e.* a more perfect state through the continuous heat treatment process where thermally activated processes such as diffusion, cross slip and climb take place.

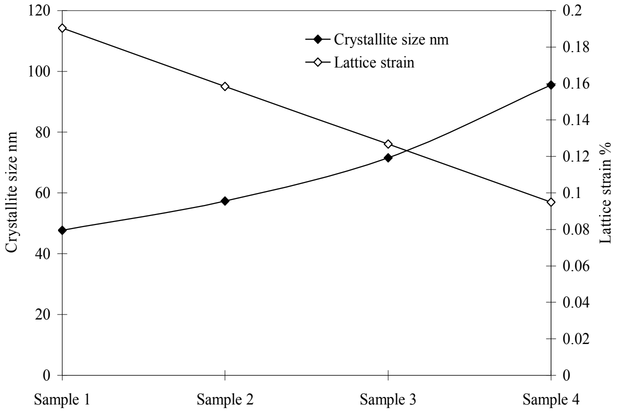


**Figure 2. Crystallite size and lattice strain of Sn-9Zn samples before and after annealing.**

### 3.2. Thermal Properties of Sn-Zn Alloy Samples

**Figure 3** shows the typical DTA profiles of Sn-9Zn alloy samples before and after annealing at 80, 120 and 160ºC for 60 min during heating with heating rate 10°C/min. A large endothermic peak corresponding to the melting reaction was observed for each sample and seems to have the same physical origin. There is no any phase transition occur other than the melting. The melting point of each sample was determined as illustrated in **Table 2**. It shows a slight decrease of the melting point in a narrow range of temperatures (199.9 to 198.7°C). Also, the heat of fusion, $\Delta H$, can be determined by $H = KA/m$, [11] where $K$, is a constant which is defined as a calibration coefficient that depends on the crucible shape and regards as a constant in the DTA system, $m$ is the mass of the sample, and $A$ is the area under the endothermic peak. A slight change of heat of fusion in the range of 82.9 to 87 was observed as illustrated in **Table 2**, which are lower values compared with that of Pb-Sn (104.2) [12]. This means, the Sn-Zn alloy is considered as the most beneficial material for saving energy.

### 3.3. Tensile Measurements

**Figure 4** shows the stress-strain curve of Sn-9Zn alloy samples before and after heat treatment. It shows an increase in the strain as the stress is increased by different amounts. The stress-strain curves can be divided into two regions; the first region which is a linear relation between stress and strain ends at the strain ratio ~ 0.1 of the second region. The second region is slightly curved due to the yielding. Also, it is noticed that the annealed samples have higher values than that of the non-annealed sample. It is also seen from **Figure 4** that, after the peak tensile stresses at 0.1 strains, the alloy samples have a

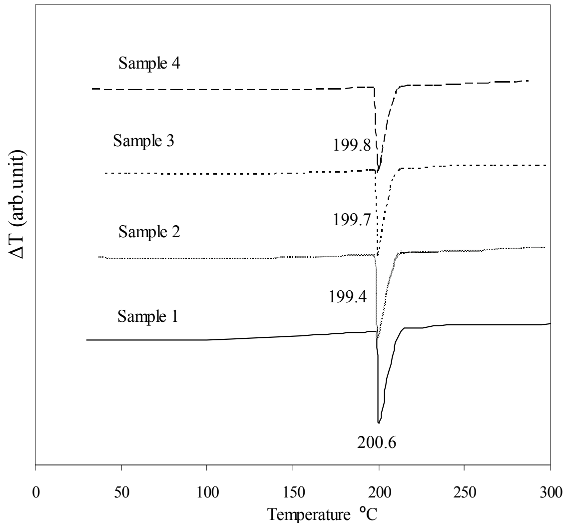


**Figure 3. DTA endothermic peak of Sn-9Zn alloy samples.**

**Table 2. Melting properties of Sn-9Zn samples before and after annealing.**

| Sample | Melting point ˚C | Onset ˚C | Offset ˚C | ΔH ( J/g) |
|---|---|---|---|---|
| Sample 1 | 199.9 | 193.8 | 212.7 | 82.9 |
| Sample 2 | 198.7 | 187.5 | 211 | 84.2 |
| Sample 3 | 198.9 | 188.9 | 211.2 | 87 |
| Sample 4 | 199.1 | 190.1 | 211.8 | 86.6 |

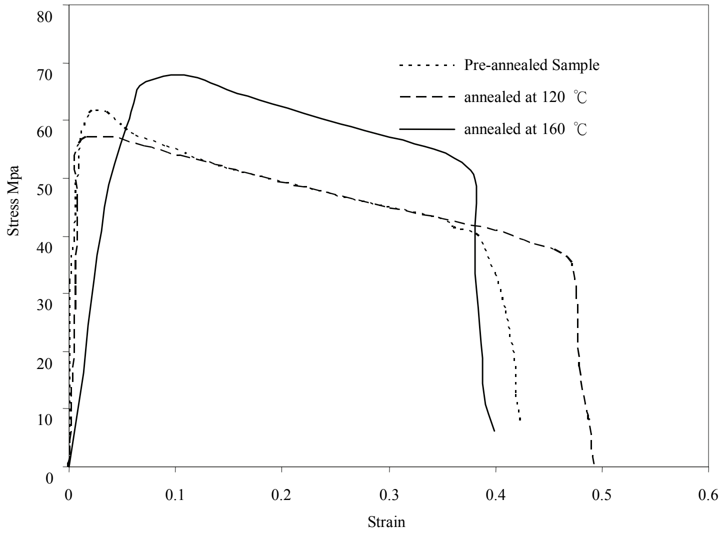


**Figure 4. Stress-strain curve of the Sn-9Zn alloy samples.**

neck. Also, it indicates the deformation up to failure is distributed much more uniformly throughout the alloy volume. The ultimate tensile strength, UTS, which is the maximum engineering stress that a material can withstand in tension, was calculated as illustrated in **Figure 5**. It is equal to 61.4 MPa for sample 1, which slightly decreases to 60.5 and 58.2 MPa for samples 2 and 3, respectively. While, the value increases to its maximum value 65.4 MPa for sample 4.

### 3.4. Micro Hardness Measurement

Micro-hardness measurement is a very sensitive to detect the structural changes of different soft solders. Usually, it is a non-destructive testing and can be the easiest way to determine the mechanical properties of the different phases of the structure. **Figure 6** shows the variation of Vickers hardness number of Sn-9Zn alloy samples before and after heat treatment using loads of 0.098, 0.245 and

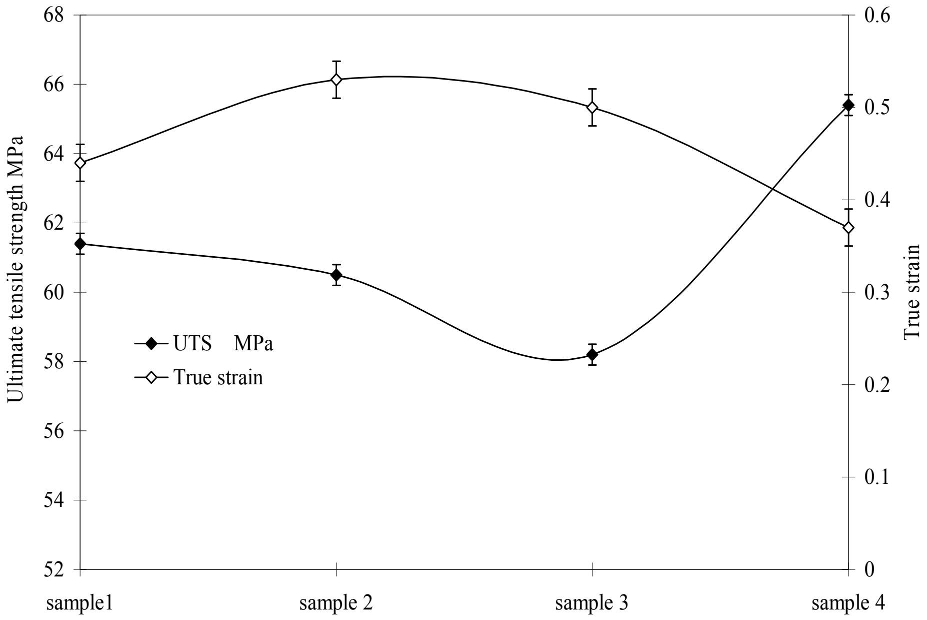


Figure 5. UTS and true strain of Sn-9Zn samples before and after annealing.

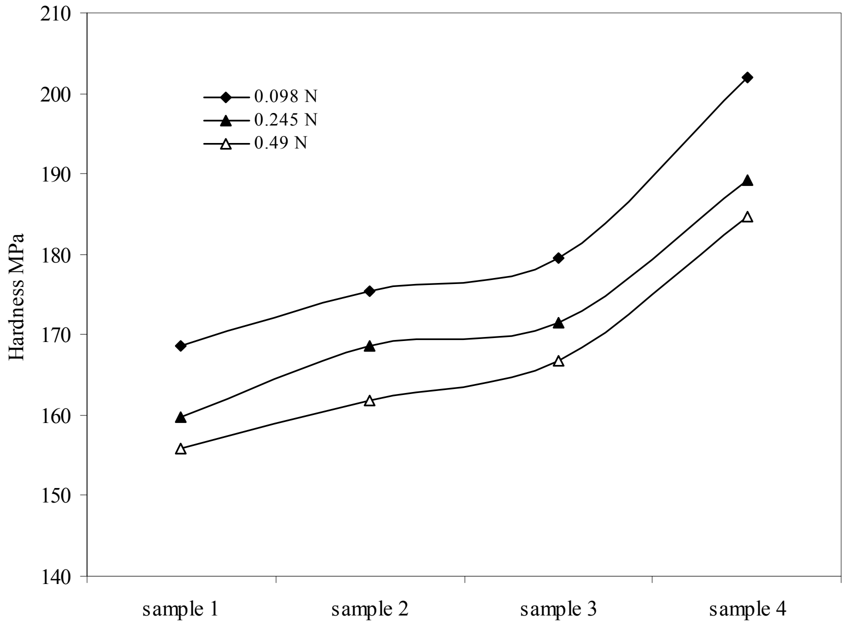


Figure 6. Hardness values of Sn-9Zn samples before and after annealing.

0.49 N for fixed dwell time of 10 s. The hardness increases continuously as the annealing temperature is increased for the three load systems by the same manor. This increase can be attributed to the effect of heat treatment that decreases the lattice strain induced through the cold rolling process. The hardening in metals and alloys induced by forming structure in which dislocation mobility is reduced due to the interaction of dislocations with impurity atoms and the formation of second phase particles. Also, reduction of the lattice strain leads to increase the hardness. Another point is noticed from this figure that the values of HV in all samples are decreased with increasing applied load, which well known as indentation size effect and agree with the results observed elsewhere [13,14].

### 3.5. Micro-Creep Behavior

**Figure 7** shows the variation of local strain with indentation time through the interval 0 to 300 s. All of the alloy samples have two stages namely as primary and secondary creep. The first stage starts from the beginning to 120 s, followed by the second stage up to 300 s. This

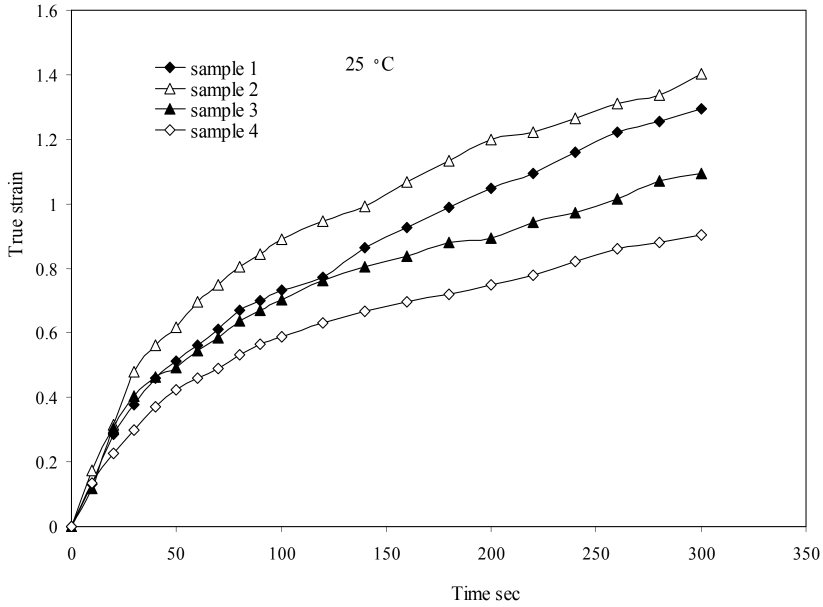


**Figure 7. Micro-creep curve of Sn-9Zn samples before and after annealing.**

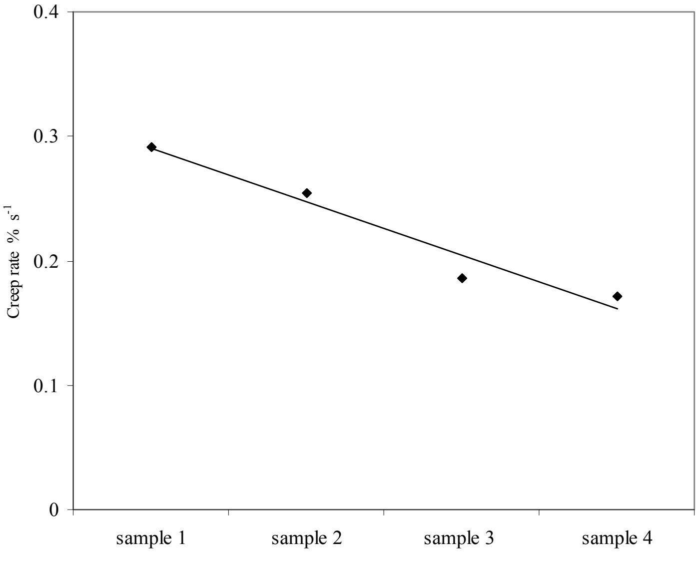


**Figure 8. Creep rate of Sn-9Zn alloy samples.**

stage called the steady state region in which the strain increases linearly with indentation time. The third stage of creep is not noticed here since it is impossible because this method is a compressed method. From the steady state region, the creep rate of the alloy samples can be calculated and the results are illustrated in **Figure 8**. It shows a continues decrease of creep rate with increasing annealing temperature which indicates that, the annealed samples have higher creep resistance due to the decrease of the lattice strain as illustrated from the X-ray diffraction analysis.

## 4. Conclusions

The present paper aimed to study the effect of annealing temperature *i.e.* 80, 120 and 160°C for 60 min on structure and mechanical properties of Sn-9Zn alloy prepared by conventional casting technique then subjected to cold-rolling process. The results showed that:

1) The crystallite size of Sn-matrix phase was increased continuously with increasing annealing temperature, while the lattice strain induced through the cold rolling process was decreased.

2) Vickers hardness number of this alloy increased continuously with increasing annealing temperature. Also, the hardness values were decreased with increasing applied load, which agree with other previous works.

3) The micro-creep behavior of this alloy was also described, which differ than that obtained by tensile methods by the third stage of creep. So, the micro-creep method is not destructive method and useful for small samples of alloys.

4) The creep rate calculated by this method was decreased continuously with increasing annealing temperature.

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