Abstract

Lead-free solder alloys are commonly used in electronic packaging. One concern of the electronics industry is the contribution of creep to the failure of solder-joint interconnects. The activation energy quantifies the necessary energetic conditions for creep and illuminates the mechanism by which creep occurs. The activation energy for a material must be known in order to predict the creep rate in engineering applications. Using nano-indentation, we measure the creep activation energy of SAC305 solder (96.5% Sn, 3% Ag, 0.5% Cu) to be $Q = 64 \pm 22$ kJ/mol over a temperature range of 25–75 °C. The measurement of activation energy requires knowledge of the stress exponent, which we also measure by nano-indentation ($n = 6.82 \pm 1.7$).

Introduction

Rapid changes for electronic packaging have created new requirements for characterization. Nano-indentation was originally designed to be a quick and accurate way to measure the hardness and Young’s modulus of small volumes, yet it has evolved to allow characterization of more complex mechanical properties. Recent developments in nano-indentation have enabled methods for measuring the constitutive properties of creep, including the stress exponent and activation energy.

In his book Fundamentals of Creep and Creep-Rupture in Metals, Frank Garofalo defines creep in this manner: “A specimen undergoing continuous deformation under a constant load or stress is said to creep” [1]. Tensile tests were the first tests used to characterize creep. In 1977, Chu and Li introduced a different approach to estimate the creep. They proposed a creep indentation test using a cylindrical tip with a flat end [2]. Since this time, indentation methods for evaluating creep have been developed by making analogies between indentation testing and tensile testing.

When rendered for nano-indentation, the Dorn constitutive model for creep [3] takes the following form which relates indentation strain rate ($\dot{\varepsilon}$) to hardness ($H$):

$$\dot{\varepsilon} = Be^{-\frac{Q}{RT}}H^n,$$

Equation 1

where $B$ is the base strain rate (determined primarily by microstructure), $Q$ is the activation energy, $R$ is the universal gas constant (8.3145 J/mol/K), $T$ is the absolute temperature, and $n$ is the stress exponent. The most intuitive definition of strain rate is

$$\dot{\varepsilon} = \frac{\dot{h}}{h},$$

Equation 2

where $\dot{h}$ is the displacement rate and $h$ is the displacement. However, in 1999, Lucas and Oliver demonstrated that for force-controlled indentation systems, strain rate is better defined as

$$\dot{\varepsilon} = \frac{\dot{p}}{p},$$

Equation 3

Taking the natural logarithm of both sides of Equation 1 yields

$$ln(\dot{\varepsilon}) = ln(B) - \frac{Q}{RT} + nln(H).$$

Equation 4
Thus, if nano-indentation tests are executed such that temperature is constant and strain rate is varied, then the stress exponent, $n$, can be determined as the slope of $\ln(\dot{\varepsilon})$ with respect to $\ln(H)$. The value for $n$ obtained in this way is the same as would be obtained from a tensile creep test\cite{4}. Recent work in indentation creep has focused on reducing the thermal drift when probing small strain rates\cite{5, 6}.

By performing the experiments indicated by Equation 4, we have measured the stress exponent of our SAC305 solder to be $n = 6.82 \pm 1.7$, where the uncertainty is the standard error of the slope of the best linear fit to the form of Equation 4. The details of our test method are explained in another publication\cite{7}.

Only a few researchers have attempted to use nano-indentation to measure the activation energy, $Q$, because analysis developed by analogy to tensile testing leads to experiments which are extraordinarily difficult. By analogy to tensile testing, Equation 4 is commonly rearranged as

$$\ln(\dot{\varepsilon}) = -\frac{Q}{RT} + \ln(B) + n\ln(H),$$

Equation 5

which implies that if hardness can be held constant while both temperature and strain rate vary, then the activation energy, $Q$, can be calculated directly from the slope of $\ln(\dot{\varepsilon})$ vs. $1/T$.

However, designing a nano-indentation experiment which holds hardness constant while systematically varying temperature is nearly impossible. Lucas and Oliver conducted a series of long-hold nano-indentation experiments on indium, wherein they were able to determine ordered pairs of strain rate and temperature for a particular hardness in order to make use of Equation 5. The creep activation energy they obtained for indium was reasonable (78 kJ/mol), but their procedure could not be applied generally for other materials\cite{4}. Gao et al. used long-hold nano-indentation to measure the activation energy of SAC305 solder. However, the data they analyzed according to Equation 5 did not meet the constant-hardness requirement; this oversight led to erroneously low values for activation energy (3–22 kJ/mol)\cite{8}.

We propose that for nano-indentation, it is far better to rearrange Equation 4 as

$$\ln(H) = -\frac{Q}{nRT} + \frac{1}{T} \ln(\dot{\varepsilon}) + \frac{1}{T} \ln(B),$$

Equation 6

because it is feasible (and quite common) to hold the strain rate constant during a nano-indentation test. For such tests, the second term on the right-hand side of Equation 6 is constant, and so the slope of $\ln(H)$ vs. $(1/T)$ is $Q/(nRT)$; this leads directly to a value for $Q$ if $n$ is known. At a particular strain rate, one simply measures hardness at several discrete temperatures spanning a suitable range. In this application note, we demonstrate this method for determining the activation energy of SAC305 solder (96.5% Sn, 3% Ag, 0.5% Cu) over the temperature range of 25 – 75 °C.
Experimental Procedure

Sample preparation

A Sn-3.0Ag-0.5Cu solder joint was prepared by melting Sn-3.0Ag-0.5Cu between two Cu platens, as shown in Figure 1. The solder paste was produced by Kester, and a heating plate was utilized to execute the reflow suggested by Kester. In order to prepare the joint for nano-indentation, the sample was ground with silicon carbide paper and polished using alumina suspensions (1, 0.3 and 0.05 μm). After polishing, the sample was attached to a sample holder using a polymer repair putty that has a rated temperature of 2000 °F.

Equipment

A Keysight Technologies, Inc. G200 NanoIndenter (XP head, Berkovich indenter) was used for all testing. The Continuous Stiffness Measurement (CSM) option was employed in order to measure the elastic contact stiffness by oscillating the indenter. The sample was heated during indentation testing using Keysight’s Heating Stage option, comprising a heater block, thermocouple, ceramic isolator, argon gas port, and coolant ports. As shown in Figure 2, all of these components were combined in an aluminum stage holder.

Test Method

In this set of tests, the method “G-Series XP CSM Standard Hardness, Modulus, and Tip Cal” was employed with the heating stage in order to measure the hardness and Young’s modulus of SAC305 solder as a function of temperature. Ten indents were performed at each of three different temperatures: 25.5 °C (room temperature), 50 °C, and 75 °C. All 30 indents were executed at a strain rate of 0.05/sec to a maximum displacement of 1200 nm.

Results and Discussion

Table 1 summarizes the properties measured in this work. Figures 3 presents the values of the Young’s modulus (E) of SAC305 solder for three temperatures. At room temperature (25.5 °C), the Young’s modulus was 59.8 GPa which confirms what others have measured by tensile testing. Almit—a manufacturer of solder materials—cites 51 GPa for the Young’s modulus of their SAC305 solder[9]. At higher temperatures, the Young’s modulus decreases as expected due to weakening interatomic forces. Gao et al. measured the Young’s modulus of individual phases of SAC305 solder over a similar temperature range. At 80 °C, they measured the Young’s modulus of both the tin-rich and the eutectic phases to be 35 GPa and 36 GPa, respectively[8].

Table 1. Average properties as a function of temperature for SAC305 solder.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Modulus (GPa)</th>
<th>Hardness (MPa)</th>
<th>N (of 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.5</td>
<td>59.8 ±3.2</td>
<td>275 ±20</td>
<td>8</td>
</tr>
<tr>
<td>50.0</td>
<td>49.5 ±10.1</td>
<td>206 ±73</td>
<td>7</td>
</tr>
<tr>
<td>75.0</td>
<td>43.3 ±4.9</td>
<td>164 ±40</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of soldered sample

Figure 2. Heating Stage option

Figure 3. Modulus of SAC305 at different temperatures.
As expected, hardness decreased significantly with increasing temperature as shown in Figure 4. Figure 5 shows the linear fit to the data in the form of $\ln(H)$ vs. $1/T$. The slope of this line is $M = 1128 \pm 263 \text{ K}$, where the uncertainty is the standard error of the slope. Referencing Equation 6, we calculate the creep activation energy, $Q$, using this slope, $M$, and our previously determined value of $n = 6.82 \pm 1.7$:

$$Q = M n R$$

Equation 7

$$Q = (1127.9 \text{ K})(6.82)(8.3145 \text{ J/mol/K}) = 64 \text{ kJ/mol}$$

By the method of Kline and McClintock\[10\], the relative uncertainty in $Q$ determined in this way can be calculated from the root-sum-square of the two dominant sources:

$$\delta Q/Q = \left[\left(\frac{\delta M}{M}\right)^2 + \left(\frac{\delta n}{n}\right)^2\right]^{1/2}$$

Equation 8

$$\delta Q/Q = \left[\left(\frac{263}{1128}\right)^2 + \left(\frac{1.7}{6.8}\right)^2\right]^{1/2} = 34\%$$

Thus, the uncertainty in the activation energy is 34% of 64 kJ/mol, or about 22 kJ/mol. The uncertainties in the two slopes, $M$ and $n$, contribute about equally to the overall uncertainty.

Our nano-indentation value for creep activation energy of SAC305, $Q = 64 \pm 22 \text{ kJ/mol}$, compares reasonably well with values obtained on similar materials by means of tensile creep experiments. For a solder composition of Sn-3.8Ag-0.7Cu, Chen et al. measured an activation energy of 106 kJ/mol under low-stress conditions (6-10 MPa), and 92.7 kJ/mol under high-stress conditions (12-18 MPa). From these measurements, they speculated that the mechanism for creep gradually shifts, with increasing stress, from that of lattice self diffusion to dislocation-pipe diffusion (which requires more dislocations)\[11\].

The present novelty is in the rearrangement of the Dorn model in the form of Equation 6 in order to make it more suitable for nanoindentation. These measurements did not require the development of a new test method. In fact, these measurements were made with our most popular test method. This method is regularly used to measure the Young’s modulus and hardness of thin films as a continuous function of penetration depth.

**Conclusions**

Analogies to tensile testing have proven so useful in the development of nano-indentation that we hesitate to depart from them. Yet in this work, we applied the Dorn model in a way that is foreign to tensile testing in order to gain experimental advantages for nano-indentation. This new analysis allowed the accurate measurement of creep activation energy by our most commonly used test method. The activation energy we measured for SAC305 solder, 64 ±22 kJ/mol, compared well with tensile-creep measurements of a similar material. Our analysis required prior knowledge of the stress exponent for creep, which we also measured by nano-indentation (6.82 ±1.7).
References


This application note was created by Carlos Morillo, Michael Osterman and Michael Pecht of CALCE (Center for Advanced Life Cycle Engineering) University of Maryland, College Park, MD in collaboration with Keysight Technologies. The content discusses creep activation energy of SAC305 using nano-indentation.