Loading rate effects on the fracture of Ni/Au nano-coated acrylic particles

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Abstract. Mechanical failure of monodisperse Ni/Au coated acrylic particles has been investigated by individual compression tests using nanoindentation-based technique equipped with a flat diamond punch. We have found that both fracture property and morphology of particles depend on the compression loading rate. The breaking strain of the metal coating decreases with increasing loading rate, while the breaking stress increases. Two obvious fracture patterns with cracking in meridian or latitude direction are identified according to the loading rate, and attributed respectively to tension- or bending-dominated deformation of the coating. The findings reported here give a significant guiding to the manufacture design of metal coated polymer particles for Anisotropic Conductive Adhesive (ACA) packaging.

Keywords: nanocomposites, nanoindentation, loading rate, mechanical properties, fracture and fatigue

1. Introduction

Metal coated polymer particles have been increasingly used in new electronic packaging technologies, for example, Anisotropic Conductive Adhesive (ACA) [1]. As a substitute for compact metal particles, the use of such composite particles in ACA possesses a number of advantages in terms of reducing the package size, increasing the reliability of the interconnections, and developing the environmentally friendly process by replacing formerly used tin-lead solders [2]. In ACA, the electrical conductivity is established by the contact between particles and electrodes on chips/substrates. A sufficient contact area is preferred to achieve a low resistance connection; thus a large deformation of particles is required although an excess deformation of particles may cause a significant impact to the electrical property. How the metal coated polymer particles behave under such large deformation is a key issue for the ACA performance. This consideration has motivated us to study the fracture property of the metal coated polymer particles undergoing large deformation.

The metal coated polymer particle used in ACA typically consists of a monodisperse micron-sized polymer core ranged from 3 to 10 μm for improving contact compliance, a nanoscale Ni inner layer for developing electrical conductivity and yielding adhesion to the polymer core, and a nanoscale Au outer layer for protecting inner layer from the oxidation and hence enhancing contact reliability and efficiency [3, 4]. Most of studies in this field exist related to the preparation and the plating process of metal coated polymer particles [5–7]. The literature concerning mechanical properties of nanostructured composite particles is relatively sparse. However, mechanical characterization of single micron-sized particles has to cope with the challenges of

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small volume, spherical geometry, composite structure and large deformation. A nanoindentation-based flat punch method has been developed to measure mechanical properties of single micron-sized polymer particles by the authors [8–11]. In a previous study, we have identified a three-stage deformation process of single Ni/Au coated acrylic particles under compression [12]. Subject to a compression stress, the Ni/Au coated acrylic particles shows failure including the rupture of the metal coating at a critical deformation and the collapse of the polymer core at a considerably larger deformation. Due to the viscoelasticity of the polymer core, the deformation behaviour of particles is rate dependent [13–15]. Moreover, the adhesion between the metal coating and the polymer core is influenced by the loading rate because of the substantial difference between the deformation resistance of metal and polymer to the external stress. Therefore the rate sensitivity of the particle behaviour is critical for the use of particles in ACA. The aim of this study is to reveal fracture properties and failure mechanisms of single Ni/Au coated acrylic particles at different loading rates.

2. Experimental setup

The particles used in this study contained an acrylic polymer core (Concore™, Conpart AS, NO) sized 3.8 μm in diameter and a Ni/Au bilayer coating of around 80 nm thickness. The chemical composition of the polymer core was 40% acrylic strongly crosslinked with 60% diacrylic. The glass transition temperature of the core was around 40°C and hence the core was in an amorphous type at room temperature. The coefficient of variance (C.V.) of the core size distribution was less than 2% where C.V. was defined as the ratio of the standard deviation to the mean. The Ni/Au coating with the Ni inner layer of about 50 nm thick and the Au outer layer of about 30 nm was deposited on the acrylic particle surface through an electroless plating process. The dispersion process previously established for polymer particles was used to obtain isolated particles [9]. Based on a nanoindentation device (TriboIndenter®, Hysitron Inc., MN, USA), the compression test was performed by using a diamond flat punch of 100 μm in diameter rather than a sharp tip commonly used for nanohardness measurement [16, 17]. The standard load-control mode was employed, in

which the normal load followed a predefined load function. Three loading rates 0.02, 0.2 and 2 mN·s^{-1} were applied to compress single particles to the same peak load 10 mN. The contact load-displacement relationships were directly obtained. For each set of experimental conditions, flat punch test was replicated on different single particles in order to check the repeatability of the results. It has previously been shown that the polymer particles from the same manufacturing batch display remarkably consistent behaviour [8, 9]. This indicates a homogeneous material microstructure and a uniform particle size, as well as highly reproducible test setup. After 12 days of the mechanical test, the surface morphology of the compressed particles was observed by using a field emission scanning electron microscope (SEM) (Zeiss Ultra 55 LE FeSEM, Germany).

3. Results and discussion

The representative stress-strain relationships of particles at three sampling loading rates are plotted in Figure 1. From the current experiment the real contact area between the particle and diamond flat punch (or silicon chip) was unknown hence the true stress-strain relationship of particles could not be derived. Instead, the nominal compression stress σ_C and strain ε_C of the particles were calculated by normalizing the contact load to the maximum cross-section area of undeformed particles and the displacement to the initial diameter of particles [18], as shown in Equations (1) and (2):

$$\sigma_C = \frac{P}{\pi R^2} \tag{1}$$

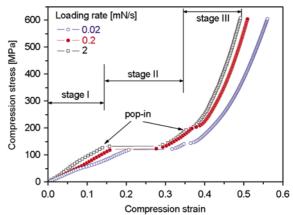**Figure 1.** Representative compression stress-strain curves of Ni/Au coated acrylic particles at three loading rates

$$\varepsilon_C = \frac{D}{2R} \qquad (2)$$

where P was the applied load, D was the contact displacement and R was the radius of undeformed particles, respectively. The particle displays a strong rate dependence that the faster the compression is, the stiffer the particle behaves. According to the effect of the metal coating, the deformation process of the particle can be clearly divided into three stages [12]. At the initiation of the compression, shown as stage I, the contact stress monotonously increases with strain. The metal coating has a strengthening effect on the Ni/Au coated acrylic particles in comparison with the deformation of the uncoated counterpart. Thereafter, the pop-in appears and the coating effect is significantly reduced in stage II. It has been clarified that the pop-in represents cracking and delamination of the Ni/Au coating from the acrylic core [12]. Finally the coating effect disappears completely and the coated particle behaves the same as the uncoated counterpart in stage III.

The corresponding SEM images of compressed particles are shown in Figure 2. The images were taken from top view, namely in the direction of the compression. Unlike the compact metal, it can be observed that the metal coating is constituted by tiny particles adhering and clustering on the surface of the acrylic core. All images show the severe cracking of the Ni/Au coating and its delamination from the acrylic core, and furthermore cracking and delamination are aggravated with the increase of loading rate. The arrows in the images point out the cracking initiating location and propagating direction. For the particles compressed at two higher loading rates, shown in Figure 2b and 2c, a flattened surface area is clearly observed, while it is not apparent in Figure 2a which represents the slowest compression. The flattened area indicates the expected contact area during the compression and the residual deformation after unloading. The thickness of the fragmented section measured by SEM is in a range of 70 to 100 nm, which is in agreement with the coating characteristics after plating. It implies that the delamination happens at the metal–polymer interface where there is a weaker adhesion than the Ni–Au interface. However, there are significant differences on the fracture pattern between the particle shown in Figure 2a and those in Figure 2b
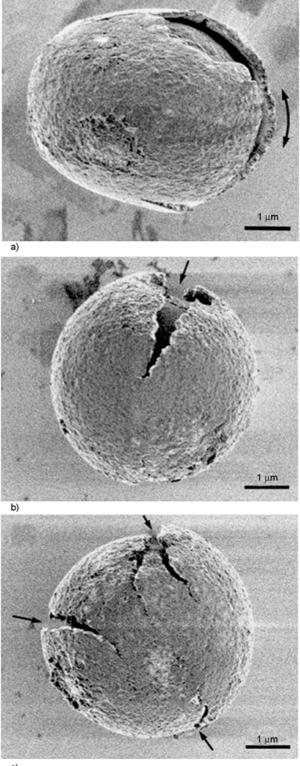

Figure 2. The corresponding SEM images of particles after compression at loading rate (a) 0.02 mN·s^{-1}, (b) 0.2 mN·s^{-1} and (c) 2 mN·s^{-1}. The images are taken from top view (in the direction of compression). Electron high tension (EHT) = 0.5 kV; working distance (W_D) = 2 mm.

and 2c. The cracking of the Ni/Au coating propagates at different directions, depending on loading rates. While the coating is disrupted in meridian direction at loading rates 0.2 and 2 mN·s⁻¹, cracking grows in the latitude direction under the compression with loading rate 0.02 mN·s⁻¹, if considering the compression on two geographic poles. Moreover, the metal coating is expanded in different directions due to the varied cracking paths. As a result, the particles exhibit different projected shapes after compression: elliptic at the smallest loading rate and round at two higher loading rates. Further tests prove that the current observation of two fracture patterns at the corresponding loading rate are repeatable and are the intrinsic response of the Ni/Au coated acrylic particles.

Figure 1 clearly shows that the fracture properties of particles are influenced by the loading rate. The effect of varying loading rates on the fracture properties, such as breaking stress and breaking strain of the Ni/Au coating, is summarized in Figure 3. The breaking strain and the breaking stress were read directly from the corresponding values at the starting point of the first pop-in on the stress-strain curve. While the breaking stress increases with the loading rate, the breaking strain decreases. These results further prove rate dependent behaviour of these particles.

The mechanical behaviour of Ni/Au coated acrylic particles is connected to both composite materials and spherical geometry. The responses of metal and polymer to the external stress are constitutively different. The metal coating of composite particles consists of coagulated nanoparticles to form a heterogeneous shell and it is not as strong as the compact metals with a continuous phase. The dependence of particle behaviour to the loading rate is mainly contributed by the polymer core due to its viscoelastic nature. It has been demonstrated that the highly crosslinked polymer particles under compression experience a viscoelastic deformation which is highly rate dependent. However, the observation of two distinct fracture patterns of particles suggests that the metal coating possesses different deformation mechanisms when varying the loading rate.

The compression of the Ni/Au coated acrylic particle is schematically illustrated in Figure 4, in which f_1, f_2 and f_3 are the resultant forces on the metal coating and M represents the bending moment, respectively. During the flat punch test, the coating suffers concomitant bending and tension resulting from both the external stress applied on the particle and the internal pressure of the core. The observed cracking propagation in different directions indicates that the dominating factor at varied loading rates is alternating between bending (M) and coating tension (f_3). When the loading rate is up to 0.2 and 2 mN·s⁻¹, the propagation of the coating cracking in meridian direction, as shown in Figure 2b and 2c, implies there is a relatively high tension in latitude direction and thus f_3 dominates the coating fracture. At the loading rate of 0.02 mN·s⁻¹, the coating opening in latitude direction, as shown in Figure 2a, suggests that the bending moment M controls the coating deformation. The exact analysis of coating fracture pattern relies on the viscoelastic properties of the polymer, the mismatch of the properties between the coating and polymer as well as the rate-dependent fracture toughness.

Besides, the adhesion quality between the metal coating and the polymer core might influence the particle response to the external stress. The good
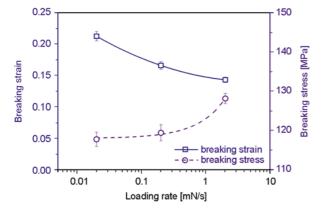

Figure 3. Plots of particle fracture properties versus loading rate. The lines in the figures are guides for the eye
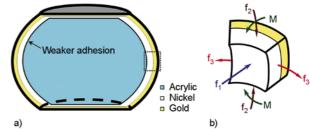

Figure 4. The schematic plots of (a) the vertical section of a compressed particle in compound view and (b) stress illustration of a coating element. The Ni/Au coating is considered as one material and the interactional effect between Ni and Au layers is neglected.

adhesion of the Ni/Au coating bonded to the acrylic core may retard local strain concentrations in the coating and hence increases the apparent consistency of the coating with the core. Due to the absence of the experimental results for the adhesion strength, the effect of the adhesion quality has not been quantified in this study. The assumption that the mechanical contact between the particles and flat punch/substrate is frictionless has been made.

It is worth noting that a theoretical or analytical model to describe large deformation and failure behaviour of metal coated polymer particles is still missing. The reported studies in the literature used finite element modeling to analyze the response of coated spheres and focused on elastic contact and yielding inception [19, 20]. These studies give indication of stresses distribution at the coating/core interface, which improve the understanding of particle deformation. But they only consider the small strain behaviour of coated spheres with the assumption of elastic and elastic-plastic material properties, the continuous phase of the coating and the perfect-bonding of the coating to the spherical substrate. In contrast, in this work the breaking strain of the metal coating is over 15% and even large deformation up to 60% is achieved on the particles. The viscoelastic nature of the core material and the granular microstructure of the metal coating greatly complicate the analysis. The electroless plating prepares heterogeneous bilayer coating on the polymer core with weak bonding. The lack of material constants, such as interfacial adhesion property, elastic modulus and Poisson's ratio of the metal coating, moreover limits the use of these models. Therefore the existing models are not applicable to the current study and further development of physically based model is necessary to verify the deformation mechanism of the metal coated polymer particles at different loading rate.

4. Conclusions

In conclusion, we have conducted the nanoindentation-based flat punch experiments on the Ni/Au coated acrylic particle to investigate the loading rate effect on particle fracture properties under large deformation. The compression stress-strain relationship of single micron-sized particles has shown significant rate dependence which states that the faster compression leads to the stiffer behaviour,

associated with the viscoelasticity of the polymer core. The fracture parameters of the metal coating are also sensitive to the loading rate: whereas the breaking stress increases, the breaking strain and the fracture energy decreases as the loading rate increases. Two fracture patterns of particles due to different loading rate have been identified that the cracking of the metal coating propagates in the latitude direction under the slowest compression but in the meridian direction at two higher loading rates. This reveals that the metal coating experiences a bending-dominated deformation at the smallest loading rate while a tension-dominated deformation at two larger sampling loading rates.

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