In recent years, reactive nanolayers (RNLs) have gained notoriety due to their particular heat-releasing characteristics. These materials have interesting potential in ignition, combustion synthesis, and nano-scale heating applications. However, RNLs have been most popularly used as localized heat sources in joining technologies, such as brazing or soldering. The self-propagating nature of the exothermic reaction occurring between the layers, typically Ni and Al, provides a promising and functional heat source. Soldering reactions reported have widely been incomplete, and insufficient to justify the widespread use of Ni/Al RNLs. Therefore, the current study presents preliminary results of in situ nanocompression and nanoindentation analysis of NiAl RNLs (the omission of "/" between Ni and Al here and henceforth indicates polycrystalline NiAl formed via reaction nanolayers).

An obvious effect of the extreme cooling rate of the RNL as a result of the exothermic reaction is residual stress, which in turn would subsequently be relaxed by mechanical distortion. The deformation is macroscopic and clearly visible to the naked eye when a freestanding piece of Ni/Al RNL foil is ignited. When the RNL is confined within a sandwich of layers in a solder joint, its ability to relax stress by mechanical deformation is limited. While Wang et al. has reported RNL cracking in solder joint applications, the study excluded residual stress analysis and provided no explanations of the stress relaxation. Furthermore and perhaps more importantly, the effect of Ni/Al RNL on the adjacent solder layers and beyond was not considered. Prior work has largely focused on understanding the mechanical performance of the entire joint by way of lap shear testing. While successful bonding has been repeatedly demonstrated with RNL in several material systems, microscopic mechanical analysis of RNL produced solder joints has not been studied. The mechanical properties of NiAl formed by self-propagating multilayer reactions reported have widely been incomplete, and insufficient to justify the widespread use of Ni/Al RNLs.

The diffraction pattern as well as the bright field TEM images of the NiAl pillar taken before and after the compression experiment is shown in Figure 1. From the image taken prior to compression in Figure 1(a), it can be seen that the pillar is comprised of two distinct NiAl subgrains, and subsequently, an average grain size of ~100 nm can be inferred. The post-compression image in Figure 1(b) shows a significant increase in the dislocation concentration as well as significant shape change in the top subgrain. There are two events in the associative load-displacement curve presented in Figure 1(c) that are important. The yield point occurs at point (1), where there is a load drop in the curve, and is accompanied by an injection of dislocations into the pillar in the video. Using the video to calculate the contact area, the yield stress for NiAl RNL is ~2.2 GPa, which is slightly higher than values obtained in other polycrystalline NiAl studies. This value is taken cautiously by the authors keeping in mind that, as is the case in all nanopillar compression experiments, FIB milling is known to generate a
The second load drop at point (2) marks the activation of the \(<011>\) slip system, which is indexed using the diffraction pattern. In the video, the crystal appears to be shearing against itself along the slip plane. The observation of this particular slip system is significant. Previous authors have long disputed the subject of ductility in NiAl\(^{13-14}\). In general, slip has only been observed to occur in NiAl on the planes of the \(<001>\) zone, i.e. \([hk0]\)<001>, which provides only three independent slip systems and falls short of the von Mises' plasticity criterion that requires five independent slip systems. In this study, the von Mises' criterion is fulfilled, assuming the common systems of the \(<001>\) zone occur simultaneously with \(<011>\) slip, observed in this experiment.

To try to capture the mechanical data across layers within an RNL solder joint with an arrangement shown in Figure 2(a), a linear nanoindentation array was used. The elastic modulus and hardness values obtained are represented in Figure 3(a). The average hardness and modulus for RNLs here are \(<249>\) and \(<197>\) GPa, respectively. Apart from the much higher modulus and hardness of the RNL, it can be seen that there is a hardening effect on the solder layer in the vicinity of the RNL. At distances shorter than 4 \(\mu m\) from the RNL/solder interface, hardness values of 1.5–3 GPa were measured. Bulk values, in distances beyond 4 \(\mu m\), reduced to below 0.5 GPa. These effects in the solder-altered zone can be attributed to the intriguing microstructure at the solder/NiAl RNL interface, which is shown in the SEM cross-sectional image presented in Figure 2(b). At first glance, the branch-like pattern appears to be solder that has penetrated the RNL. However, previous work has shown that a reaction between NiAl RNL and molten solder does occur, forming hard intermetallic Ni\(_3\)Sn\(_4\) at the interface.\(^{15}\) In some cases, the indentations are not due to Ni\(_3\)Sn\(_4\) and instead come from readings taken directly at the interface, which are then composite values of the NiAl RNL, solder, and the newly formed intermetallic.

Figure 3(b) shows the nanoindentation results of a Ni/Al RNL solder joint aged at 150 °C for 500 h. As expected, not only does the hardening effect still exist, but the depth of the...
The solder-altered zone also increased slightly. The aforementioned thermal aging profile, common in solder bump reliability testing, would cause growth of the intermetallic compound Ni₃Sn₄, which presumably is the reason for the increased matrix-altered zone depth. Also, hardness values in all layers decreased due to grain coarsening processes that accompanied the thermal aging treatment. What was unexpected however, was the substantial decrease in RNL modulus to $\mu = 159$ GPa, a 21.3% difference. While grain growth in effect reduces the density of grain boundaries and subsequently, the resistance to dislocation movement, the stiffness, which is affected by interatomic bonding mechanisms, should be unaffected by this process. Although a Ni/Al intermetallic phase change would cause a change in modulus, this is unlikely considering the high melting temperature of NiAl.

A possible explanation for this behavior is two-fold and may be found by first understanding the residual stresses in the NiAl RNL layer and then analyzing the effect of residual stress on the elastic modulus measurements. The load-displacement curves presented in Figure 4 can be used to determine the residual stress. The utility of sharp indentation data to determine the magnitude of residual stresses and their sign has been previously reported,[16] In the compressive case, the differential force acts counter to the direction of the indentation load and therefore the residual stress would be expected to hinder indentation by increasing the indentation load needed to penetrate the material to a given depth. This difference is quantified by the shift in the load-displacement curve. At fixed depth $h$,

$$P_1 - P_2 = P_1 + \sigma_H f A$$

(1)

where $P$ is load, $\sigma_H$ the compressive hydrostatic, $f$ a geometric term that accounts for the fact that indenter face is slanted, $A$ the contact area, and the subscripts 1 and 2 indicate the virgin and stressed materials, respectively. In other words, the presence of a compressive stress is accompanied by both an upper shift in the load-displacement curve from that of a stress-free material, as well as an increase in slope. Obviously, the phenomenon is the opposite in the case of tensile residual stress, where the effective indentation load becomes larger. In this study, nanoindentation tests performed to a depth of 2000 nm were carried out on NiAl RNL samples that were i) reacted and freestanding, ii) in a reactive foil solder joint as-fabricated, or iii) in a thermal aged reactive foil solder joint (same thermal aging profile as earlier), and resulted in three characteristically different groups of load-displacement curves. The first set of curves with the shallowest slopes corresponds to the freestanding NiAl RNL samples. Even though the dramatic cooling rate of the foil inevitably produces significant residual stresses, the freestanding foil is permitted to release these stresses by mechanical deformation. In this analysis, this group was designated as stress free, virgin material. The second group of curves is made up by the RNL samples in reactive foil solder joints as-fabricated. Unlike the freestanding RNL samples in group 1, the RNLs within the solder joint arrangement presented in Figure 1 are restricted from shape change and consequently residual stress relaxation is inhibited. Although previous work has observed cracking in similar samples, the RNL is indeed a highly stressed layer. Here, the stress relaxation is proven to be incomplete due to not only the apparent lack of curvature in the RNL layer between cracks, but also the noticeable shift in the load-displacement curve. The RNL layers in these samples are compressively stressed, noting the load-displacement...
A curve shift from the group 1 curves as well as the amplified stiffness values, observations that are both supported by previous analysis. After 500 h at 150 °C, group 2 curves of the highly stressed samples receded toward those of the virgin material. This downward shift for the group 3 curves from group 2 is immediately obvious and implies a decrease in the compressive residual stress that was found in the as-fabricated RNL solder joints. The residual stress relaxation of the group 3 joints is incomplete however since its curves are shifted up from those of the virgin material in group 1.

To fully understand the considerable change in modulus, the effect of residual stress on nanoindentation measurements must be accounted for. Previously, Tsui et al. have observed a strong correlation between nanoindentation measured moduli and compressive stress, a trend that is strongly exhibited in this study. The baseline value for modulus acquired from virgin polycrystalline NiAl RNL (group 1) was ~150 GPa. Average modulus values for the RNLS integrated into a solder joint arrangements were ~197 and ~160 GPa for the highly stressed as-fabricated samples and the thermal annealed, partially relaxed samples, respectively. The reason for this difference, Tsui and coworkers established, was due to the fact that contact areas determined by nanoindentation analysis were about 15% smaller than the real contact area in compressively stressed specimens. The modulus is certainly sensitive to the contact area. The effective modulus is calculated from

\[ \frac{1}{E_{\text{eff}}} = \frac{1}{\beta} \frac{S}{2} \sqrt{\frac{h}{A}} \]  

(2)

where \( S (= \frac{dP}{dh}) \) the contact stiffness, \( \beta \) a constant relative to the indenter shape, and \( A \) is contact area. Next, the elastic modulus of the specimen, \( E \), is extracted from the effective modulus using

\[ \frac{1}{E_{\text{eff}}} = \left( \frac{1 - \nu_{\text{sp}}^2}{E_{\text{sp}}} \right) + \left( \frac{1 - \nu_{\text{in}}^2}{E_{\text{in}}} \right) \]  

(3)

where \( E \) and \( \nu \) correspond to modulus and Poisson’s ratio and the subscripts “sp” and “in” stand for specimen and indenter, in that order. When the contact area for RNL nanoindentations is determined by SEM, as shown in Figure 5, the modulus values become significantly closer to the baseline value. Taking the group 2 curves for example, the recalculated modulus using the contact area measured by microscopy becomes ~162 GPa. When compared to the baseline modulus value, taken here as the value obtained from the stress-free group 1 sample measurements, there is only a 4% difference. Whereas, the original value for modulus of 197 GPa for the highly stress NiAl layer in the group 2 samples produced a 19% difference.

In summary, the nanomechanical behavior of NiAl RNLS has been characterized using in situ nanocompression and ex situ nanoindentation. In situ compression was able to provide direct observation of yielding in polycrystalline NiAl, including the activation and operation of \(<011>\) slip. Coupled with previously known slip systems, the occurrence of \(<011>\) slip in NiAl fulfills von Mises’ criterion of ductility. Ex situ nanoindentation was first used to obtain mechanical properties of NiAl RNL and solder layers in a joint arrangement. A hardening effect was observed within the solder layers in proximity to the NiAl RNL, which occurs mostly due to the intermetallic compound Ni3Sn4 that forms at the solder/RNL interface. Nanoindentation results were also used to show that the RNL in RNL solder joints is an extremely compressive stressed layer, but that thermal aging may relieve the stress.

**Experimental**

Solder joints are comprised of a sandwich structure of Ti/Ni/Cu/Au metalized Si bond components, two sheets of Sn63Pb37 solder, and RNL foil, as shown in Figure 2(a). The solder and Ni/Al RNL sheets were 50 and 40–80 μm in thickness, respectively. Ni/Al RNL foil used in this study is provided by Reactive NanoTechnologies (Hunts Valley, MD). The bilayer thickness (combined thickness of one Al and one Ni layer) is 40 nm, however, the thickness of individual Al and Ni layers are controlled such that the atomic ratio is 1:1. The joint area was ~5 × 5 mm². RNLS were ignited in air using an electrical spark generated by approaching one end of the film with electrodes attached to a 9 V battery. To ensure intimate contact between all layers, an applied pressure of ~10 MPa was used. Upon RNL ignition, the solder joint stack was placed on a plexi-glass stand to ensure limited heat transfer away from the joint.

Freestanding, reacted NiAl RNLS were used to prepare nanopillars used for in situ compression testing. Focused ion beam (FEI Strate 235) was used to mill the pillars to aspect ratios near 1:5 with geometries of ~140 nm in diameter, 550 nm in length and a sidewall taper angle of 4–5°. Nanocompression was performed by a flat diamond punch...
on a Hysitron Picoindenter, which itself was inside a JEOL 3010 (300 kV) microscope. Due to the high feedback of using constant displacement mode, decreases in contact stiffness and discontinuous yielding are readily detectable. The compression was operated in displacement-controlled mode with an indenter displacement rate of 10 nm s⁻¹.

Ex situ nanoindentation measurements were conducted at room temperature using a Nanoindenter XP (Nano Instruments Innovation Center, MTS Corporation, Knoxville, TN) equipped with a Berkovich diamond indenter. The continuous stiffness measurement mode was used for all experiments in this study. All indented samples were embedded in epoxy and polished to a 0.05 µm finish.

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