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Reactive Nanocomposites for Controllable Adhesive Debonding

by Michael Minnicino and James M. Sands

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14. ABSTRACT

The ability to selectively attach and remove items from the surfaces of vehicles, aircraft, and other platforms without damaging the structures is a research interest of the military. An approach to achieving selective attachment, which includes adhesive bonding with on-demand debonding, has been demonstrated as a viable concept. However, the practical use of this approach is unrealized. The U.S. Army Research Laboratory (ARL) demonstrated that a bonded bimetallic stratified nanocomposite structure can completely and quickly separate two adhesively coupled surfaces using a small electrical or thermal initiation. The key benefits of the ARL concept are rapid decoupling but also very high bond strengths that can be selected via traditional commercial adhesives. The novelty of an inserted coupling media, the stratified nanocomposite, offers infinite tunability and control of coupling strength. In this report, the critical elements of the approach are demonstrated using bimetallic layers composed of nickel and aluminum fabricated using a vapor deposition process. Unlike other debonding approaches, this method allows for fast, remote, and on-command separation of structurally bonded materials.

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reactive, nanocomposite, debond

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Contents

List of Figures

1. Background

As far back as 2001, EIC Laboratories, Inc. (Norwood, MA) has been advertising the ElectRelease[*] adhesive concept that allows debonding to be performed through application of a small electrical current (*1*). The challenges associated with early ElectRelease products included limited strength, especially in tensile and shear performance, by comparing aerospace-grade adhesives. As many applications are specified to high-performance adhesive requirements, ElectRelease products failed to meet most fielding requirements of interest to the military. The most demanding U.S. Army requirements were that the debonding event occur quickly (few microseconds), the debonding event be robust and reliable (100% debond), and that the debond technology does not reduce the load-carrying capability of the structure prior to activating the debond event (high initial strength and environmental durability). Commercial systems were unable to meet these design requirements. Therefore, Army researchers began developing alternative approaches to debonding technology. One approach involved creating a debonding capability that was independent of the adhesive type, thus allowing any commercial adhesive to be applied to the bonding requirement, but allowing on-demand separation of surfaces. In this pursuit, Army engineers developed a suite of debonding technologies over the past few years to bridge the gap between commercial and military applications (*2–4*). The Army debonding technologies include shape memory alloy (SMA)-based approach, a chemical foaming agent (CFA) approach, and a reactive nanocomposite (RNC) approach.

SMA debonding works by integrating SMA material at the adhesive interface during initial bonding and then activating the SMA material transformation by applying a stress load on the adhesive interface. This resulted in a high strain field at the adhesive/substrate interface that weakened the bond so that it had little residual strength (*2*). The approach proved quite effective for low toughness resin systems such as paste epoxy adhesives. However, strength retention for toughened adhesives found in most commercial adhesives remained quite high and resulted in damage to soft substrates such as composite skins over honeycomb core.

The CFA method applies the principles of foam manufacturing to an adhesive system. The foaming agent is designed to “erupt” using a designed stimulus condition (*5*). A thermal trigger is used to activate the debond process. Therefore, to debond, the temperature of the bond line is raised above the designed “activation” temperature. Blowing the foam induces through-thickness degradation of the adhesive that reduces the mechanical load-carrying performance of the adhesive to extremely small loads. The foaming adhesive approach has some limitations in unfilled adhesive applications, as adding the foaming agent can alter baseline adhesive performance. Further, the foaming agent is thermally sensitive and therefore limits service temperatures of formulated adhesives using this technology.

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[*] ElectRelease is a trademark of EIC Laboratories, Inc.

The RNC approach is unique in that it requires creating an additional interface to insert the reactive composite into the bond line (*3, 4*). However, once designed, the RNC is far more stable than a foaming adhesive, although it can also be activated thermally. The activation process causes a physical change within the nanocomposite interfaces to mechanically decouple the nanocomposite from the adhesive. The interlayer is based on technology often found in brazing applications (*6*). Therefore, the nanolayer applies heat to the interface while simultaneously converting physical and chemical bonds. The decision to further develop the RNC approach was based on three criteria: (1) the flexibility of the design, which allows the incorporation of numerous adhesive materials; (2) adaptability to many surface bonding applications, which allows use of many commercial adhesives; and (3) the rapid conversion via multiple initiation methods, which allows contact and noncontact debond initiations. It is also noted that the RNC provides the quickest debond found in published literature.

2. Nanocomposite Debond Technology

The nanolayered bimetallic systems were first developed for joining applications (*6*). The reactive nanolayered bimetallics are typically produced by sputter deposition of alternating 10- to 100-nm-thick bilayers of metallic or intermetallic materials onto optically polished surfaces such as silicon, glass, or cleaved mica (*6*). The nanolayered bimetallic, or nanocomposite, system is depicted in figure 1. In joining applications, the stratified nanolayered bimetallic structure is cleaved from a polished deposition surface to produce a freestanding, reactive structure that is suitable for insertion between components to be reactively joined. This freestanding material is commonly referred to as a nanofoil. Similarly, the nanolayered bimetallic debond approach was first demonstrated using the stratified nanofoil structure sandwiched in the bond line, as depicted in figure 2a (*3*). The nanolayered bimetallic debond approach was expanded in the development of reactive coatings applied directly onto metallic/nonmetallic substrates of interest by direct-current magnetron sputtering. This configuration is shown in figure 2b. The commercially available, free-standing nanofoil and the U.S. Army Research Laboratory (ARL) directly deposited nanocoating show good adhesion and have been demonstrated as practical embodiments of the nanocomposite debond technology. However, both of these approaches have their advantages and disadvantages.

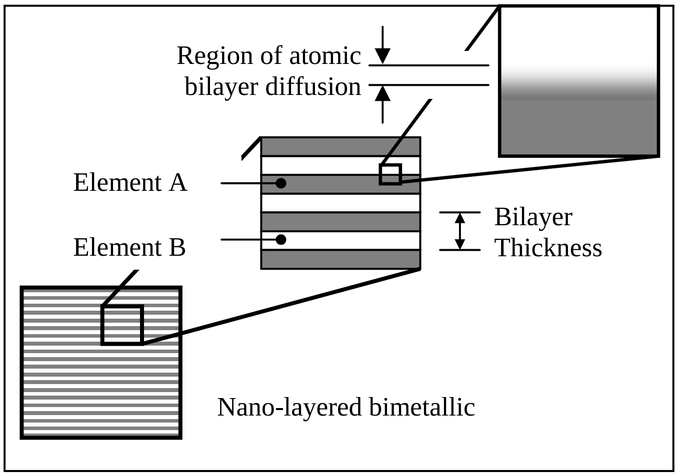

Figure 1. Nanocomposite illustration showing composition, bilayer thickness, and bilayer diffusion.

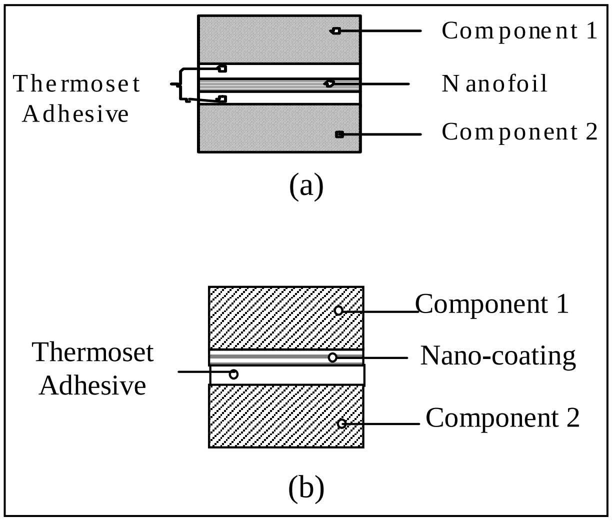

Figure 2. Debonding approach where (a) freestanding nanocomposite (nanofoil) is sandwiched between the adhesive layers of the bond line and (b) the nanocomposite is directly deposited on component 1.

Besides bond strength, the nanofoil arrangement has integration issues that need to be addressed. One design issue is that the nanofoil has to be sufficiently thick for placement. Our research found that thin nanofoils (~25 µm thick) often fractured either during placement of the nanofoil into the bond line or during adhesive cure due to the small pressure applied to achieve strong bonds. Nanofoil fracture potentially causes multiple reaction wave fronts or prevents the propagation of a reaction wave front. These situations are illustrated in figure 3. In this figure, looking down onto the outer surface of the nanofoil, the nanofoil is partially cracked. The reaction wave front propagates around the crack. In figure 3b and c, the nanofoil has completely fractured into two separate pieces. The reaction wave front can "arc" across the crack and continue, as depicted in figure 3b, or become "arrested" at the crack, as seen in figure 3c. As figure 3 suggests, the controlling difference between figure 3b and c seems to be the size of the separation between the two nanofoil pieces, which agrees with experimental observations.

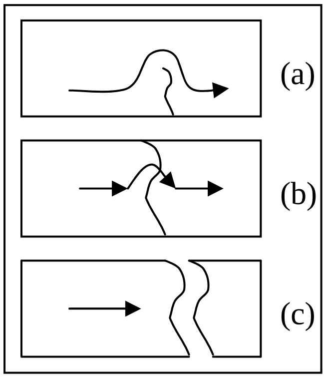

Figure 3. Thin nanofilm fracture and possible reaction wave front paths.

Controlling adhesive flash in paste and film adhesives is difficult for nanofoils and nanocoatings; however, it is a larger problem for nanofoils. With paste adhesives, the pressure is applied uniformly, and excess resin in the bond line is forced out of the interfacial area to the thickness offered by bond line control agents. During this flow, the nanofoil is floating on the resin bed, and alignment issues result. Excess resin outside of the film surface area can bridge the sample surfaces together, providing additional bond strengths that limit easy separation after the reaction of the foil. However, this difficulty is often minor. Although the pieces are not fully debonded, the residual strength is significantly reduced. Sensitivity of the foil occasionally resulted in premature ignition of these foils during the process of removing the excess flash. A typical example of adhesive flash on a substrate of a lap-shear joint is shown in figure 4. This figure shows how the adhesive flow allows bridging between the substrates, as evidenced by thickened edges. The excess adhesive bonds to the edge surfaces of the lap joint.

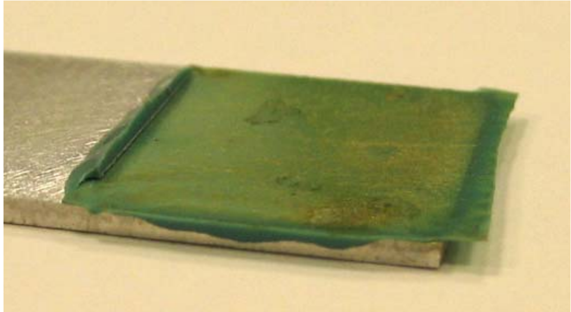

Figure 4. Example of adhesive flash (after debond).

The direct deposition nanocoating approach is beneficial because it reduces the number of interfaces (adhesive layers), which increases performance, reduces bond line thickness, and greatly simplifies component fabrication. Additionally, the nanocoating can be significantly thinner and remain workable because the substrate provides the stiffness. Another benefit is that the coating can be designed larger than the adhesive contact area and therefore nullifies any negative performance effects, i.e., residual strength resulting from adhesive flash. Unlike the nanofoil approach, the nanocoating approach has the disadvantage of needing the substrates at the time of deposition and having deposition equipment capable of depositing uniformly over a bond area which can be quite large and may have significant curvature.

The bilayer constituents and thicknesses can be chosen on the basis of their reaction temperatures and their propagation rates (typically, 1–10 m/s), where the propagation rate is typically inversely proportional to the bilayer thickness. Nanocomposite reaction stability appears linked to the sharpness of bilayer interfaces on the nanometer scale and the total number of bilayers (*7, 8*). "Stable" infers that the nanocomposite reaction wave front self-propagates until the medium is completely consumed. "Unstable" refers to the reaction wave front self-extinguishing. Typical bilayer systems are aluminum/nickel (Al/Ni) or aluminum/titanium (Al/Ti), with the total bilayer thickness in the 0.1- to 0.3-µm range. The reaction propagation of an Al/Ni nanofoil system is shown in figure 5.

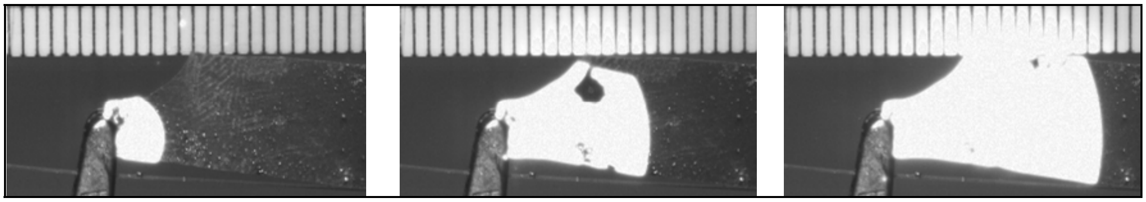

Figure 5. Individual frames from high-speed digital camera (frame rate = 10,000 frames/s) showing reaction propagation. The scale on the top edge of the picture frames is used as a geometric reference to calculate propagation velocity (*4*).

ARL has investigated stoichiometric variation and bilayer diffusion and their effect on propagation velocity and initiation sensitivity (*8*). Figure 6 is an energy spectrum of 2-MeV He ions elastically backscattered via Rutherford Backscattering Spectrometry (RBS) from a four-period bilayer stack of Ni/Al nanocomposite. The periodic variation in yield is directly due to the two-element composition of the nanocomposite and can be converted into their relative thicknesses and interfacial diffusion, which governs exothermic rates and initiation sensitivities (*9*).

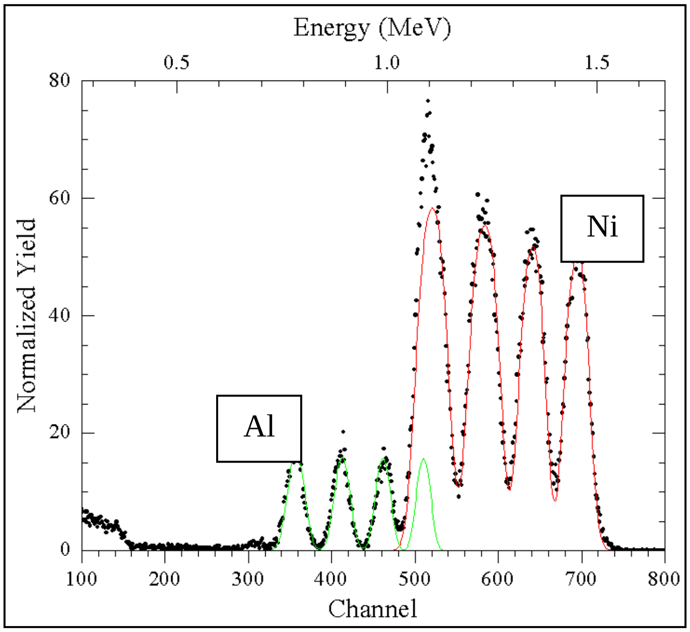

Figure 6. RBS spectrum of ARL four-period array of sputtered Ni (85 nm)/Al (45 nm) nanocomposite stack.

Blickley et al. (*8*) showed that the initiation energy increased as the stoichiometric ratio was varied from its balanced ratio of 1:1. The initiation energy was seen to increase significantly when annealed at 105 °F. These results are shown in figure 7. The experimental upper bound was 200 mJ, and nanocomposite systems listed with this initiation energy did not initiate/react. The propagation velocity was also shown to decrease with nonbalanced stoichiometric ratio and heat treatment. These results are shown in figure 8. The reason for the increase in initiation energy and decrease in propagation velocity was the increase in the size of the region of atomic bilayer diffusion with nonstoichiometric systems and annealed systems. The region of atomic bilayer diffusion acts as a barrier that impedes mixing the two nanocomposite constituents during reaction, thereby making the reaction more difficult to initiate and propagate (*8*).

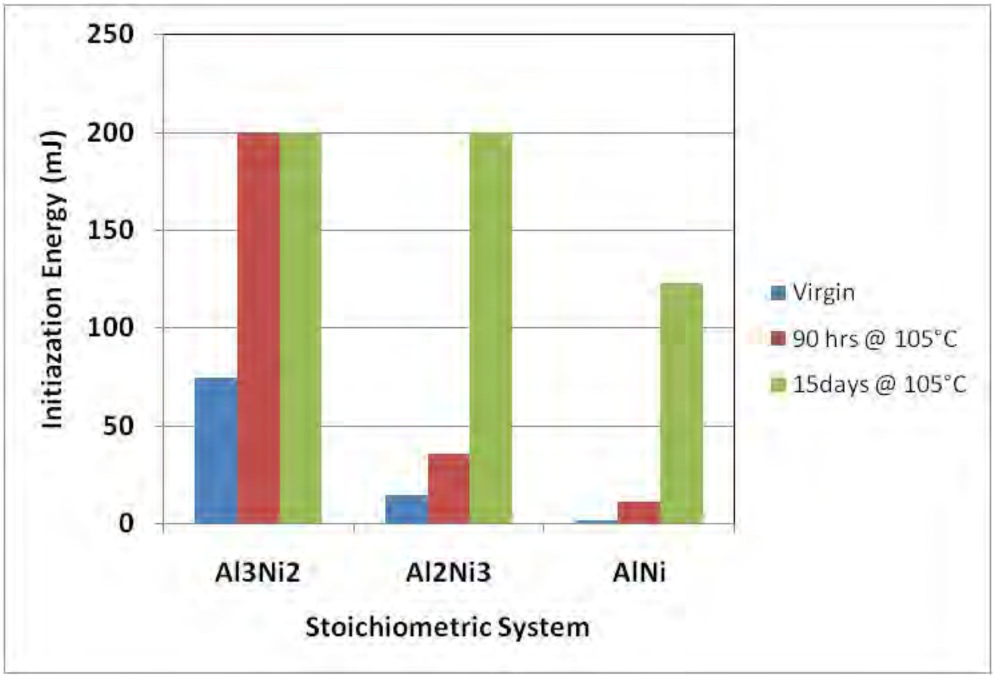

Figure 7. Initiation energy of various low-temperature annealed reactive nanocomposite systems. Systems recorded as 200-mJ initiation energy did not react or reaction was not stable (*8*).

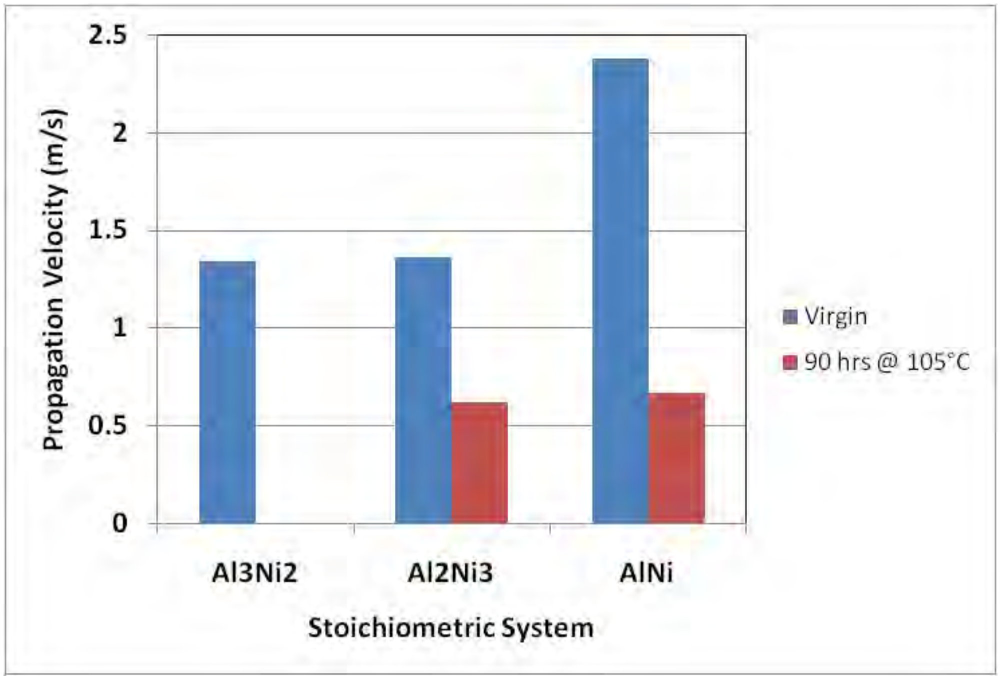

Figure 8. Propagation velocity of virgin and low-temperature annealed nanocomposite systems (*8*).

3. Summary

The research presented demonstrates the importance of applying engineering design principles to improve commercial products for military applications. The existing technology in reactive nanofoil development was investigated and used to demonstrate the feasibility of rapid separation of bonded structures. The presented study demonstrates the feasibility of manufacturing the nanofoils and nanocoatings and principles for applying this technology to provide separation of bonded structures. The characteristics of the nanocoatings and the value of nanocoating capability for military specific applications are reviewed.

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