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# PREPARTATION OF THICK NI/AL REACTIVE MULTILAYER FILMS AND PROSPECTIVE USE FOR SELF-POWERED BRAZING OF TI-6AL-4V

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## ABSTRACT
In this study we demonstrate a new method for depositing thick reactive multilayer films (RMFs) (thickness > 14 μm) by using Ti interlayer integration and substrate preheating during fabrication. These two adjustments are designed to alleviate internal planar stresses that cause delamination between deposited layers and peeling off the substrate. Decreasing the distance between Ti interlayers helps to eliminate delamination between deposited layers. Through high speed camera measurements, the reaction propagation speed of an RMF sample with preheating is 42% slower than the same RMF that was not preheated, indicating a slower heat release rate. The preliminary experiments on brazing Ti-6Al-4V coated with BAlSi-4 brazing material revealed dendritic structure branching out from the RMF surface into the brazing material. The dendrite structures most likely form because of rapid melting and solidification of the brazing material. However, this rapid melting and solidification cycle does not appear to occur uniformly across the BAlSi-4RMF interface which is linked to its low bonding strength. When the Ti-6Al-4V substrate is heated to 150 °C prior to ignition, the strength increases to 0.47 MPa when the total RMF thickness is 84 μm and 15 MPa of pressure is applied.

## INTRODUCTION
Self-powered brazing is a novel, innovative joining process in which the heat required for joining comes completely from the heat produced by an exothermic reaction in the brazing materials. This technique was designed for extreme conditions where external power sources such as welding arcs, plasma torches, etc. are cumbersome or not technically feasible. For example, the Sealing, Seaming, Sterilization, and Separation (S4) process is a NASA technology for full preservation of samples collected from space missions and for ensuring the safe handling of samples and planetary protection when returned to Earth for analysis [1]. In addition, in-space repair is useful for a wider range of exploration mission capabilities as well as personnel survival in human operated missions. Brazing is one of the most effective methods of joining structures and it would support both S4 and repair procedures, however, brazing generally requires high input energy. The power levels required to braze using induction would limit exploration missions to such bodies as ocean worlds in the solar system, including Europa, Enceladus, Ganymede, Callisto, Ceres, and Pluto, which are increasingly a potential target of proposed exploration. An innovative solution that removes the power requirement for brazing is self-powered brazing using reactive multilayer films (RMFs). RMFs are composed of alternating nanolayers of two different materials and produce rapid bursts of heat through a homogeneous, self-propagating and exothermic reaction initiated by a laser pulse, electric heating or mechanical strike. The process of RMF soldering/brazing has been demonstrated in air, vacuum, and underwater for joining dissimilar metals, ceramics and semiconductors [2, 3]. RMFs have been extensively studied for soldering applications. However, various limiting factors prevent RMFs from being used for brazing applications (> 450 °C) including limited

 

energy supply, delamination, heat sinking, and low film ductility. For this study, we will discuss preparation of Ni/Al RMFs join Ti-6Al-4V (Ti64) using BAlSi-4 as the brazing filler metal and Ni/Al RMFs as the heat source and demonstrate the potential of this new technique. Ti64 was chosen as the base material in order to act as a thermal barrier to mitigate heat sinking of the RMF reaction heat and meets the lightweight consideration for in-space manufacturing.Ni/Al RMFs were chosen because of their metallurgical compatibility with the Al-based BAlSi-4 and high reaction stability during fabrication (i.e. limited chance for premature ignition).

Nomenclature

Ti64 – Ti-6Al-4V alloy

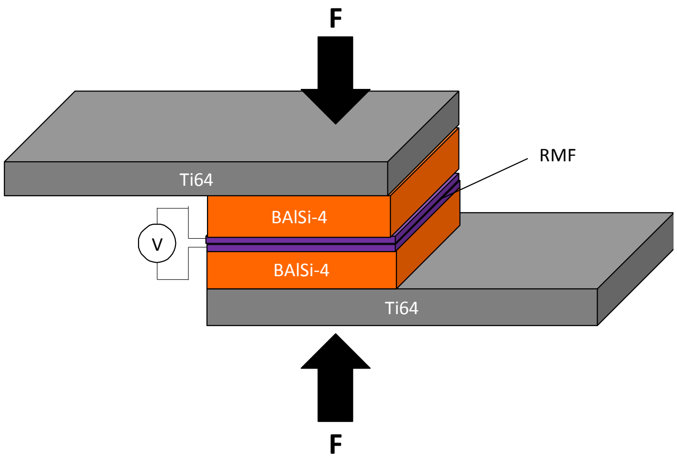


Fig. 1: Schematic of the brazing configuration

RMF – reactive multilayer film
SEM – scanning electron microscope
XRD – x-ray diffraction
DSC – differential scanning calorimetry

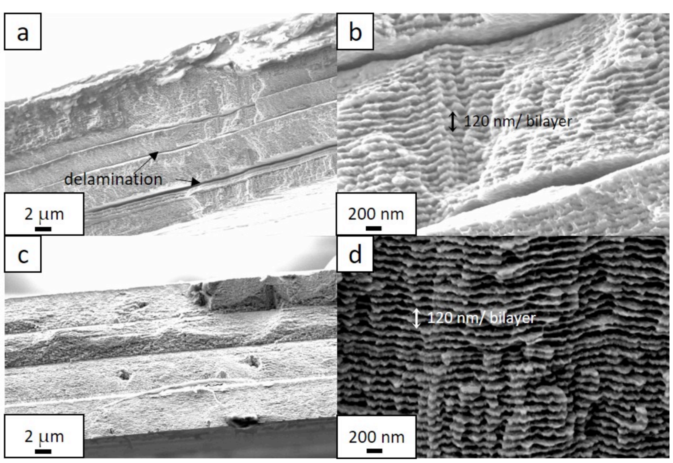


Fig. 2: (a-b) 21 µm RMFs 30 nm with Ti layers on every 7 µm shown at low magnification and high magnification (c-d) 20 µm RMFs 30 nm with Ti layers on every 5 µm shown at low magnification and high magnification

EDS – Energy Dispersive Spectroscopy

## METHODS

Ti64 chips were coated with BAlSi-4 by melting a BAlSi-4 strip (liquidus temperature = 582 °C) directly on Ti64 using a plasma welding torch. The BAlSi-4-coated Ti64 (hereon simply referred to as BAlSi-4) was polished with diamond paste up to a mirror finish. Ni/Al RMFs were deposited using electron beam physical vapor (e-beam) deposition. Each layer is 60 nm thick and it was deposited at a rate of 0.65 nm/s. A 60 nm-thick Ti layer was added as the bottom layer to help the film adhere to the substrate and 30 nm Ti interlayers were added intermittently to offset the internal stresses in as-deposited RMFs that cause the film to peel off the substrate or delaminate during deposition [4]. Ti was also chosen because of its compatibility with the Ni/Al reaction [5]. The substrates were preheated to 100 °C in addition to including Ti interlayers to help relieve internal stresses during deposition. Ni was used as the final layer to prevent oxidation. The deposition parameters are controlled by the software Inficon XTC/2. The total RMF thickness achieved is up to 21 µm. RMFs were peeled off

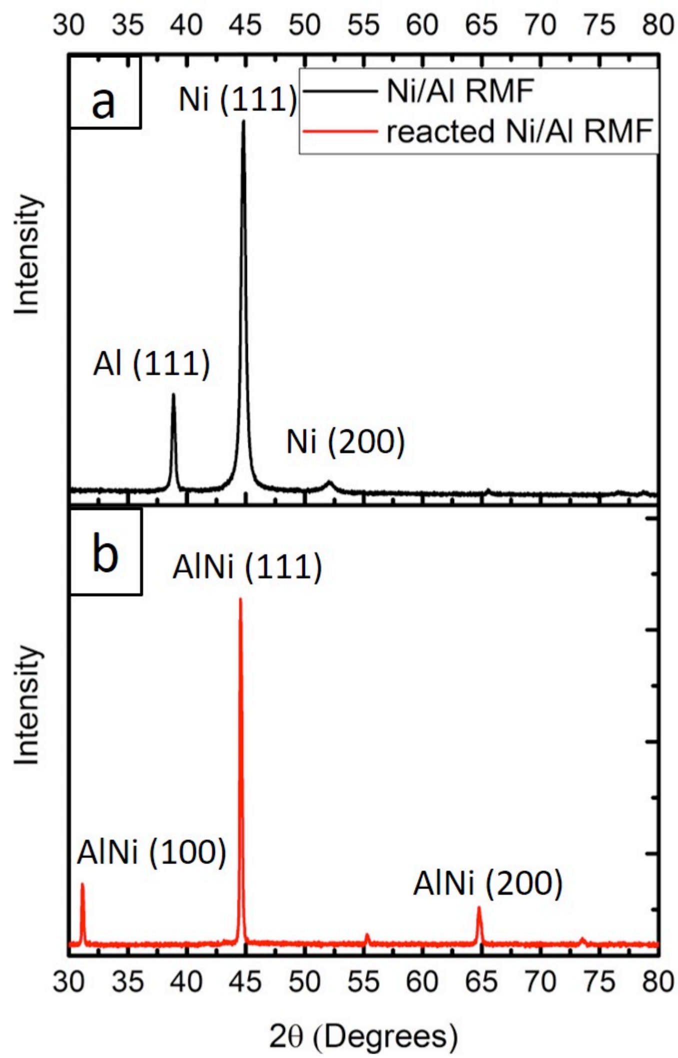


Fig. 3: XRD pattern of the Ni/Al RMF (a) before reaction (b) after reaction

polyimide sheets for SEM and XRD analysis. For brazing, the BAlSi-4 are arranged in the configuration shown in Fig. 1 with applied pressure and ignited using electrical heating via a 12 V power source. Extra RMFs were peeled off and added between the BAlSi-4 layers in addition to the as-deposited amount to vary the thickness.

Scanning Electron Microscopy images were collected using a Zeiss Auriga Scanning Electron Microscope (SEM). X-ray diffraction measurements were conducted using a Panalytical Empyrean X-ray Diffractometer, and Energy Dispersive X-ray Spectroscopy (EDX) measurements were performed using a Zeiss MA15 EVO SEM equipped with a Bruker xFlash 6|30 detector. A PowerView HS-650 highspeed camera was used to determine the reaction propagation speed of Ni/Al films. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q2000 Differential Scanning Calorimeter.

## RESULTS AND DISCUSSION

### *Fabrication*

The RMFs as deposited have a confirmed bilayer thickness of 120 nm. The Ni (light color) and Al (dark color) are equal in thickness, which makes the Ni/Al atomic ratio ~1.5:1. As previously mentioned, Ti layers were inserted into the film to aid in deposition of films >14 μm. If Ti layers are not inserted frequently enough, delamination can highly likely to occur throughout the film. This can be seen in a 21 μm Ni/Al film

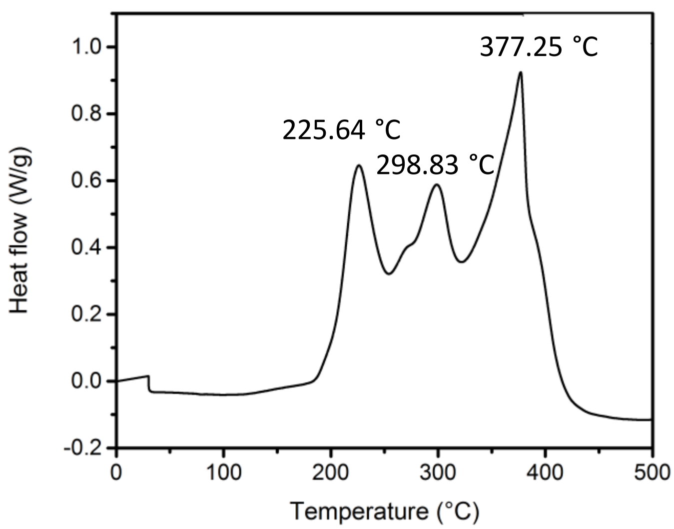


Fig. 4: DSC profile of Ni/Al RMFs without Ti interlayers

with Ti layers inserted every 7 μm (Ni/Al-7; Fig. 2a-b) compared to a 20 μm Ni/Al film with Ti layers inserted every 5 μm (Ni/Al-5; Fig. 2c-d). Even though the delamination does not appear to be catastrophic, it does show the subtle effects of using additional Ti layers as a way of alleviating internal planar stresses in Ni/Al RMFs.

The XRD pattern shows distinct peaks of Ni and Al prior to reaction (Fig. 3a). After reaction, an AlNi intermetallic compound is formed (Fig. 3b). There is a clear narrowing of the XRD peaks after reaction, implying that the crystallite size has increased.

### *Reaction characteristics*

By integrating the area under the three DSC peaks, we determined that the total heat of reaction of Ni/Al RMFs is 1097 J/g (Fig. 4). The energy output of RMFs is primarily

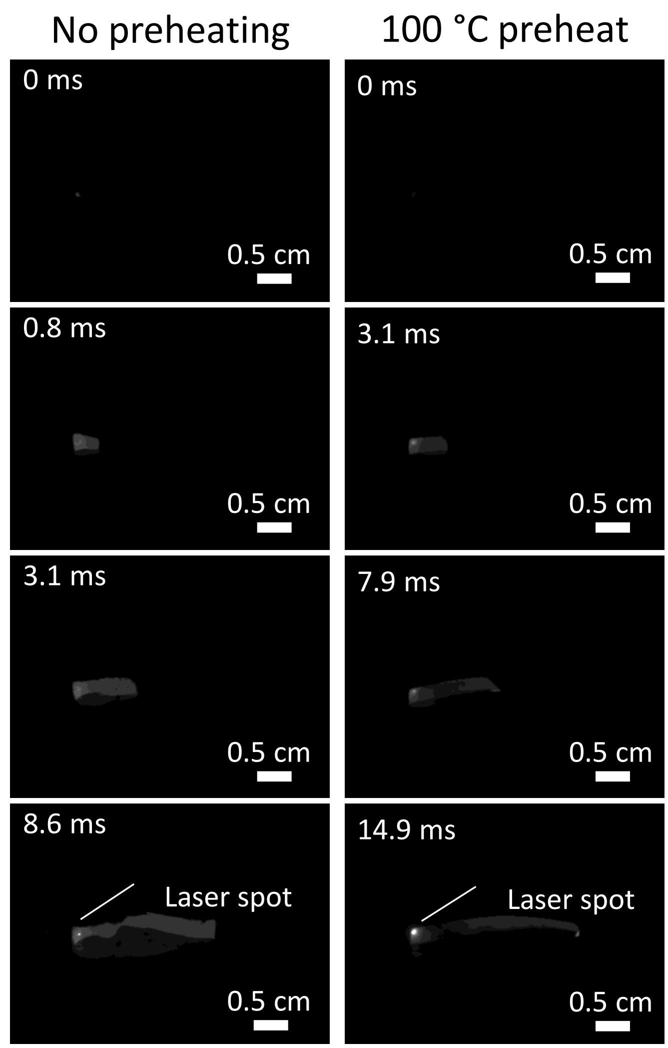


Fig. 5: High speed camera images used to determine the propagation speed of Ni/Al RMFs with a preheated substrate (right) and without preheating (left)

determined by a multitude of factors including reactants, premixed layer thickness, and bilayer thickness. The DSC peaks at 225.64 °C and 298.83 °C are caused by the formation of metastable solid solutions before the final transformation to the AlNi intermetallic compound at 337.25 °C. The heat of reaction was taken without the Ti interlayers.

The reaction propagation speeds of Ni/Al RMFs were measured at room temperature compared to determine the effects of preheating on the RMF reaction kinetics. The reaction propagation speed is also analogous to the heat release rate [6]. Both RMFs in Fig. 5 were Ni/Al-5 samples . Without preheating the reaction propagation speed is 2.31 m/s. the reaction speed 1.34 m /s and it is 40% lower than the film fabricated without preheating. Based on the theoretical model of self-propagating reactions, the reduced speed can be caused by three factor: (1) decrease in thermal diffusivity, (2) increase in activation energy for mass diffusion and (3) increase in the length scale of diffusion [7]. The thermal diffusivity and activation energy are fixed thermodynamic quantities at a given temperature. Therefore, the increase in diffusion length scale is the most probable culprit. The diffusion length scale is theoretically ¼ of the bilayer thickness (i.e. ½ of the monolayer thickness when the thickness of each layer is equal). However, in a real case there is a premixed layer between each alternating layer, which forms during deposition. This premixed layer increases as temperature increases. Increase in the premixed layer thickness most likely occurs when the RMF is deposited on a heated substrate.

Greater premixed layer thickness is also problematic for the total heat of reaction because the premixed volume does not participate in the reaction, but instead absorbs some of the heat when the full reaction occurs [8]. Note that reaction heat and reaction propagation speed (i.e. heat release rate) do not automatically have a positive correlation because it is possible to increase the total reaction heat while decreasing the heat release rate. They do however share common parameters such

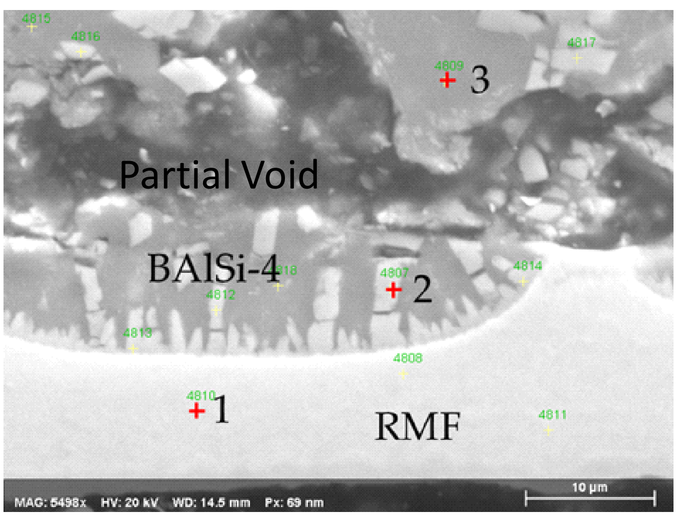

Fig. 6: Brazing interface between BAlSi-4 and the Ni/Al RMF

as diffusion length scale and activation energy that decrease the reaction heat or heat release rate by increasing same parameter. If reaction propagation speed is indeed lower because of an increase in the premixing layer thickness, then that could also mean that the reaction heat is also decreased by using the preheating procedure in exchange for making thick film deposition more robust.

### *Prospective brazing application*

Brazing is a difficult process using Ni/Al RMFs due to the short brazing time. The short brazing time limits the time usually needed to develop a healthy diffusion zone. To braze BAlSi-4, applied pressure is needed to ensure intimate contact with the RMF [9]. The Ni/Al-7 RMFs (total thickness = 105 μm) were then ignited by electrical heat with a 12 V battery while applying 5 MPa pressure. As shown in Fig. 6, at the interface between the RMF and the BAlSi-4 there are some dendrites branching out from the RMF surface. EDS point analysis was performed on points of interest and the results show that these dendrites (point 2) are Al-rich according to an EDS point scan on the area (Table 1). The formation of these dendritic structures is most likely caused excess Ni from the

Table 1: Phase summary of the EDS point analysis shown in Fig. 6

| Region | Ni | Al | Si | Identified Phases |
|---|---|---|---|---|
| 1 | 69.3 | 30.8 | 0 | $AlNi+Al_3Ni_5$ |
| 2 | 17.1 | 74.7 | 8.2 | $Al_3Ni$ |
| 3 | N.D. | 98 | N.D. | (Al) |

RMF diffusing into the molten brazing material and rapidly solidifying on the interface The melting and solidification is evidence of the possibility of RMF-powered brazing. However, these dendritic structures are not present across the entire RMF-BAlSi-4 interface. While clear dendrites cannot be seen when the total RMF thickness is 84 μm, the RMF-BAlSi-4 interface does contain regions where the $Al_3Ni$ phases are present. The formation of dendritic structures appears to have a positive effect on the brazing performance as the appearance of these structures correlates with higher bonding strength.

When the substrate is preheated to 150 °C before ignition (total RMF thickness = 84 μm; applied pressure = 15 MPa), the bonding strength reached 0.47 MPa. Without sufficient preheating, joining does not occur because the diffusion between the brazing material and RMF is insufficient. At least 150 °C is needed for successful joining. At 175 °C, the bonding strength is 0.25 MPa, indicating that 150 °C is an optimum preheating temperature. It is interesting to note that failure occurs at the interface between the RMF and the braze material. Typically, the RMF thickness used in similar soldering experiments is thicker than 100 μm and the applied pressure is >15 MPa [10, 11]. Therefore, it is expected that the bonding will be strengthened by further increase of the thickness or pressure.

## CONCLUSIONS AND OUTLOOK

Currently, Ni/Al RMFs can be deposited with thicknesses up to 21 μm more easily through a combination of Ti interlayer integration and preheating the substrate during RMF deposition. Adding more Ti interlayers decreases the amount of delamination in the film. However, using the preheating method comes at the cost of slower reaction propagation speed, which is analogous to slower heat release. If the heat release is too slow, heat can dissipate into the adjacent material, making it more difficult to braze higher temperature materials with lower film thicknesses. The preliminary brazing data demonstrates potential of RMFs for brazing applications. The dendritic structures on the RMF-BAlSi-4 interface are a result of melting and solidification of the brazing mater during the reaction. However, the lack of strength is partially attributed to a lack of uniform melting across the BAlSi-4 surface. Further development of RMFs needs a good balance of total heat release, heat release rate, and film thickness need to be determined.

## ACKNOWLEDGMENTS

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## ANNEX A

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