



## **Friction Stir Reaction processing to Develop Sphene in Aluminum**

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Table of Contents

Abstract.....	3
Introduction.....	3
Background.....	4
Broader Impact.....	6
Experimental Procedure	
Materials.....	7
Powder Preparation.....	8
Friction Stir Welding.....	13
Weld Temperatures.....	14
Analysis.....	15
Results & Discussion	
Optical Microscopy/Macrographs.....	16
Scanning Electron Microscopy.....	16
X-Ray diffraction.....	19
Conclusion.....	21
Future Work.....	21
Acknowledgments.....	21
References.....	22

## **Abstract**

Friction stir reaction processing was used to determine if a chemical reaction would occur between three compounds to produce sphene in aluminum substrate. Combinations of CaO, CaCO<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> powders were combined and stirred in Al plates. The resulting welds were polished and analyzed using scanning electron microscopy and x-ray diffraction.

X-ray diffraction did not pick up any evidence of the powders stirred into the weld. SEM showed that the particles were distributed throughout the weld; however the individual particles are too fine to resolve using SEM. TEM would be a more suitable technique for this experiment.

## **Introduction**

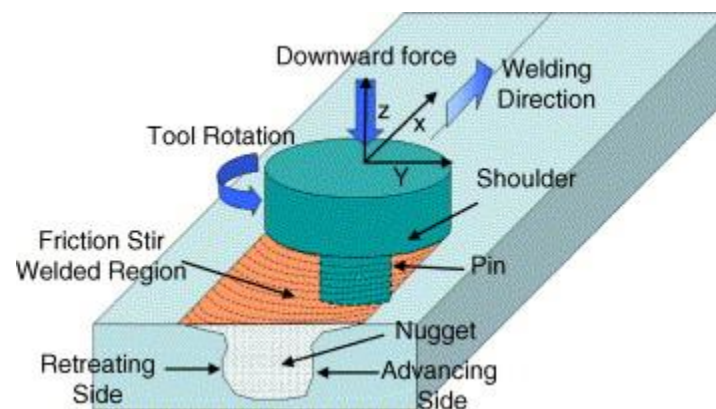
Friction stir welding (FSW) was developed in 1991 as a way to join aluminum alloys as a solid-state function [2]. Since then, FSW has been developed to be used in numerous applications. It has environmental and metallographic advantages over other welding techniques [8]. Friction stir processing (FSP) uses the principles of FSW to modify microstructure [2] and friction stir reaction processing (FSRP) is used to stir particles into the metal and induce a reaction.

The purpose of this experiment is to enhance the optical properties of aluminum by using FSRP to develop sphene on the surface of aluminum. The experiment involved mixing three powders, calcium oxide (CaO), Calcium Carbonate (CaCO<sub>3</sub>), Silica (SiO<sub>2</sub>) and titania (TiO<sub>2</sub>). After mixing, these powders were processed by FSP. The welds were examined under the scanning electron microscope (SEM) and by x-ray diffraction (XRD) to determine the compounds that

formed during the reaction. The scope of this report does not include mechanical properties of the resulting weld.

## Background

FSW uses friction from a non-consumable rotating pin tool submerged in between two pieces of material to heat up the metal and induce a flow. The material flows together which creates the weld. Since the material is not heated past the melting point, FSW is considered a solid-state joining technique [8]. Figure 1 is a diagram demonstrating how the pin tool moves through the plate, joining them together.



**Figure 1** Schematic drawing of friction stir welding [2]

The plastic deformation that occurs during FSW produces a fine microstructure that has better mechanical properties than the parent material. FSW does not use gas or flux and uses less energy than conventional welding which makes it environmentally friendly. Another advantage

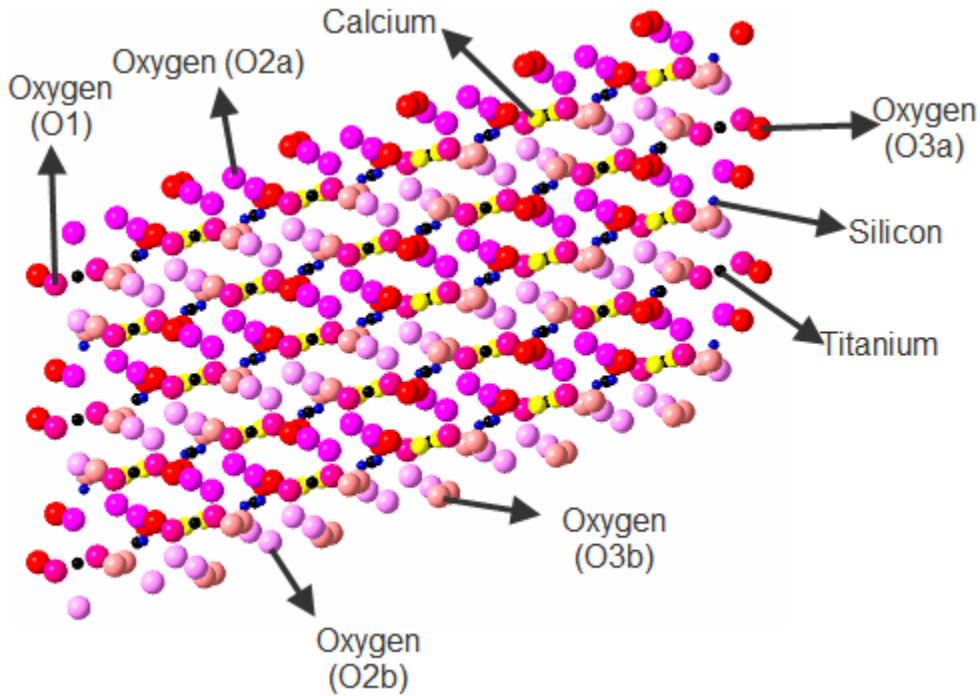
is that heat is not involved which creates a safer and more comfortable work space for the operator. [8]

The goal of FSP is to use the technology from FSW to alter the properties of the material. Principles of FSW used in FSP include: The low amount of heat generated, plastic flow of material, resulting fine grain size, reduction of flaws in cast metal, mechanical mixing of layers and redistribution of grain boundaries [2]. FSP can be used to enhance the mechanical properties of metals.

Aluminum is a highly reactive metal, which suggests that any metal oxide will react with Al to create  $\text{Al}_2\text{O}_3$  [6]. Other compounds may form along with the aluminum oxide, as long as stable compounds are formed [6]. FSRP is based off of this idea. This report examines the use of FSRP to develop sphene on aluminum alloys from a mix of three powders. FSRP has successfully been used to fabricate SiC composites onto the surface of aluminum alloys [9] and to produce  $\text{Al}_3\text{Ti}$  [5].

Sphene ( $\text{CaTiO}(\text{SiO}_4)$ ) is a mineral most commonly found as an accessory mineral in granite located in Russia [1]. The pleochroic properties of sphene cause the mineral to appear gray, brown, yellow, green or black depending on which angle it is viewed from [1]. Pleochroism is caused by the double refraction of light, this occurs because the crystal structure of the mineral causes light to bend and follow various paths which absorb different colors [3].

Sphene has a monoclinic crystal structure with a space group  $p21/a$  [3]. The structure of sphene is shown in figure 2 at an orientation of  $[1\ 1\ 0]$ . This orientation is interesting because of the gaps in the structure caused by the helix formed by the oxygen and calcium atoms.



*Figure 2 Sphene crystal structure  $[u\ v\ w]=[1\ 1\ 0]$ . [4]*

### **Broader Impact**

The direct application for developing sphene on aluminum is to change the spectral response of aluminum. If this FSRP is successful, it has the potential to change the absorption and emissivity to provide for thermal coatings on aluminum [4]. There is also a potential for architectural applications. Buildings could be coated with sphene, and the decorative possibilities are endless.

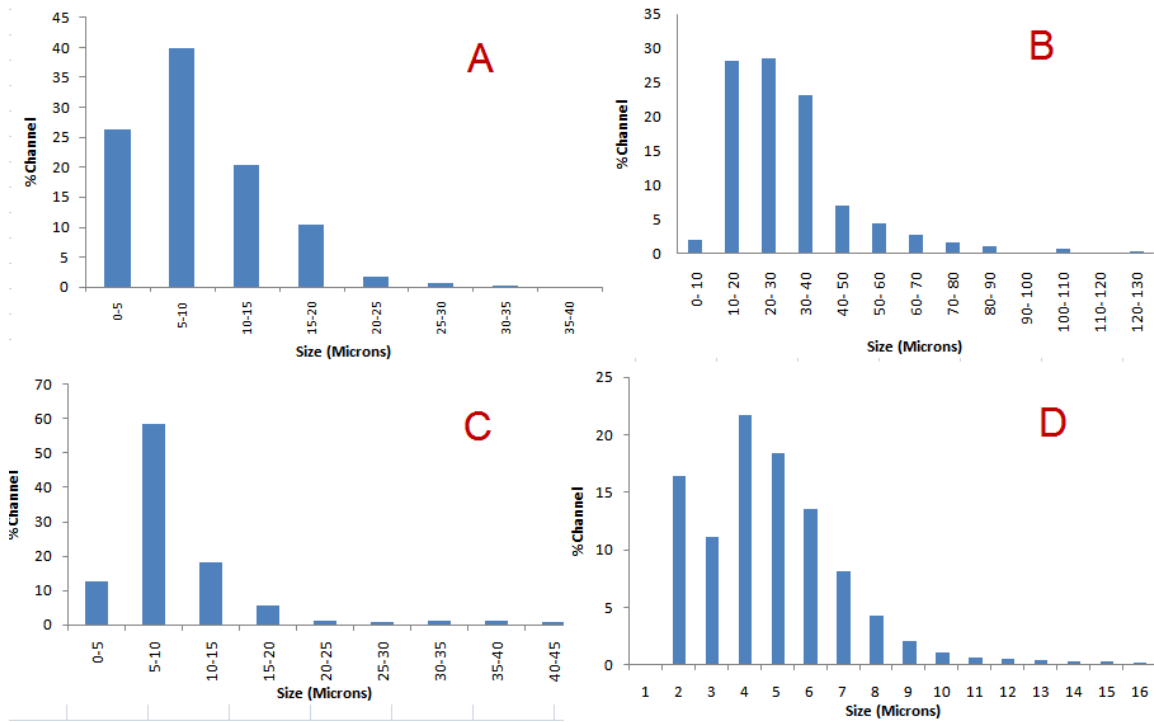
This experiment could also have an artistic impact on the general community. Sphene is a rare mineral, and it is used in jewelry and occasionally in paint pigment [1]. The pleochroic properties of the mineral provide many opportunities for applications in the artistic realm. If the gem can be reproduced synthetically, jewelers could use it more widely. The decorative aspect of the gem could be used more widely than it is in use now.

## **Experimental procedure**

### **Materials**

The powders used were gathered from various labs on the school's campus. TiO<sub>2</sub> 99.9% purity nanopowder from American Elements, CaO 98% purity nanopowder from American Elements, CaCO<sub>3</sub> nanopowder from the school chemistry store and fumed SiO<sub>2</sub> 98% purity were used. Nanometer sized particles are preferred because of their small size; a reaction is more likely to occur. Particle size analysis was performed on all powders prior to mixing, and after mixing using a Microtrac S 3000. These powders were mixed and packed into a 1/8 inch square aluminum 3003 tube 6 inches long. The ends of the tube were sealed using aluminum tape and then sandwiched between aluminum 1100 plates.

XRD analysis was performed on the starting powders, and it should be noted that the CaO powder had CaCO<sub>3</sub> and Portlandite (Ca(OH)<sub>2</sub>) in it. This discovery was made after the powder was already in use. The powder was over two years old and it is possible that it went through some sort of decomposition, or absorbed moisture from the air.



**Figure 3** Powder particle size analysis, prior to mixing powders  
A: CaCO<sub>3</sub> B: SiO<sub>2</sub> C: TiO<sub>2</sub> D: CaO

Figure 3 contains the results from particle size analysis of each individual powder before they were mixed. According to these charts, the particles range in size from 5-30 microns. These powders are supposed to be on the nanometer size scale, which means the particles agglomerated during the size analysis. The analysis was repeated 3 times using ultrasonic dispersion, yielding the same results. More accurate particle size discussion is located in the results section of this report.

### Powder Preparation

ThermoCalc analysis using the tab function and the Poly3 function was performed to determine the best powder mix ratios. Table 1 shows the reaction combinations tested through ThermoCalc. This computer program searches databases and phase diagrams to determine if a reaction is



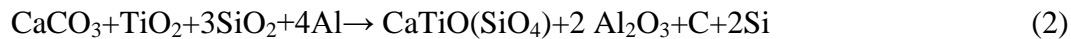
thermodynamically possible. The results give Gibbs Free Energy ( $\Delta G$ ) in the unit of joules. The more negative  $\Delta G$  is, the more favorable it is that the reaction will occur.

**Table 1 Possible Reaction Combinations**

Reaction	$\Delta G$ (J)
$3\text{CaO}+2\text{Al} \rightarrow 3\text{Ca}+\text{Al}_2\text{O}_3$	228600
$3\text{CaCO}_3+2\text{Al} \rightarrow 3\text{Ca}+3\text{CO}_2+\text{Al}_2\text{O}_3$	-647900
$3\text{SiO}_2+4\text{Al} \rightarrow 3\text{Si}+2\text{Al}_2\text{O}_3$	363900
$3\text{TiO}_2+4\text{Al} \rightarrow 3\text{Ti}+2\text{Al}_2\text{O}_3$	-454500
$\text{CaO}+\text{TiO}_2+\text{SiO}_2 \rightarrow \text{CaTiO}(\text{SiO}_4)$	-112400
$2\text{CaO}+\text{TiO}_2+2\text{SiO}_2+2\text{Al} \rightarrow \text{Al}_2\text{O}_3+\text{CaTiO}(\text{SiO}_4)+\text{CaSi}$	454000
$4\text{Al}+3\text{SiO}_2+\text{TiO}_2+\text{CaCO}_3 \rightarrow \text{C}+\text{CaTiO}(\text{SiO}_4)+2\text{Si}+2\text{Al}_2\text{O}_3$	-977313
$2\text{CaO}+\text{TiO}_2+2\text{SiO}_2+2\text{Al} \rightarrow \text{Al}_2\text{O}_3+\text{CaTiO}(\text{SiO}_4)+\text{CaSi}$	-356491

*\*All calculations performed at 577° C and 1 atmospheric pressure*

Based on the analysis, two powder mixes were produced, the difference between the mixes is that one used CaO and the other used CaCO<sub>3</sub> to provide calcium to the mixture. The powders were mixed based on reaction equations 1 and 2.



Stoichiometry was performed to determine the amounts of powder to mix together. The amounts used are listed in table 2.

**Table 2: Amounts of Powder mixed**

Mix 1		Mix 2	
Compound	Amount (g)	Compound	Amount (g)
CaCO <sub>3</sub>	37.52	CaO	14.24
TiO <sub>2</sub>	9.98	TiO <sub>2</sub>	9.98
SiO <sub>2</sub>	22.52	SiO <sub>2</sub>	15.02

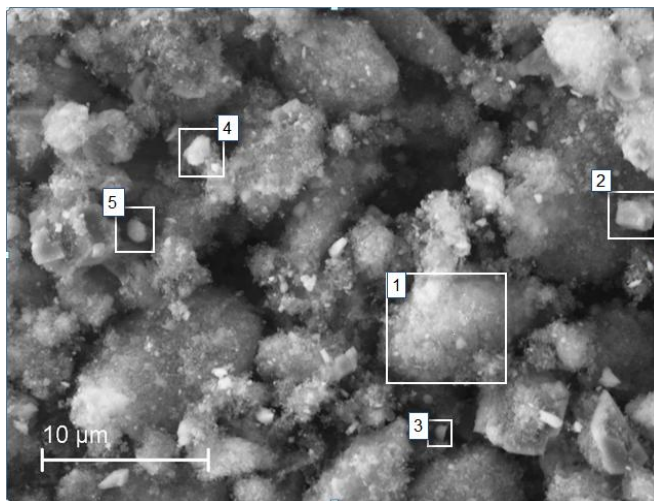
The powder was first mixed in a beaker with 290 ml of methanol. Then the mixture was transferred into a wide mouth polypropylene bottle with ceramic balls. The powders were ball milled for approximately 15 hours. This was done to ensure uniform mixing throughout the powders.

Two methods were used for drying the powder. The first method used an Erlenmeyer flask with a hole in the side. A hose connected to a vacuum pump was put in the hole; a funnel was set on top of the flask through a rubber stopper. Filter paper was put into the funnel and the powder solution was poured into the filter paper. This set up is shown in figure 4. After the methanol was filtered out, the remaining powder was put under an infrared lamp to dry out. This method of powder separation proved to be slow and tedious. Also, some powder was pulled through the filter paper proving the method to be ineffective. Partially through separation of the CaO mixture a different separation method was used.

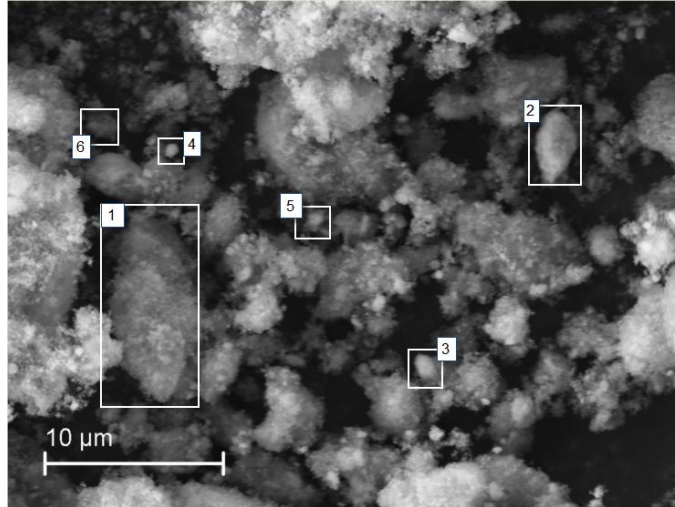


**Figure 4** Powder separation set up method 1

For the second method, the solution was poured into a Pyrex dish. A furnace was heated to 100 degrees Fahrenheit and the methanol evaporated out. This took approximately 3 hours for the full amount of the  $\text{CaCO}_3$  mixture to dry. The powder left from the evaporation was crushed using a mortar and pestle, then forced through mesh. First 106 micron mesh, and then 46 micron mesh. The final powder mixture was analyzed using SEM analysis.



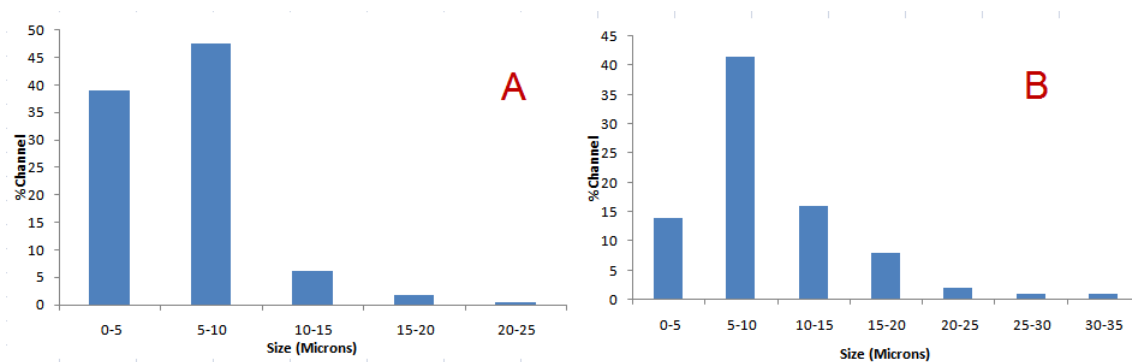
**Figure 5** SEM micrograph  $\text{CaCO}_3$  raw powder mixture generated at 1 kV, 7,000X 1)  $\text{SiO}_2$  particles 2&3)  $\text{CaCO}_3$  particles 4&5)  $\text{TiO}_2$  Particles



**Figure 6** SEM micrograph CaO raw powder mixture generated at 1 kV, 7,000X 1&2) SiO<sub>2</sub> particles 3&4) TiO<sub>2</sub> particles 5&6) CaO particles

Figure 5 and Figure 6 show images of the raw powder. These two powder mixes look very similar. The silicon particles are very fine, but agglomerated into clumps, while Ca and Ti particles are larger and can be distinguished individually and are scattered amongst the silicon agglomerates. It is possible that the Ca and Ti particles that appear to be individual are actually clumps of these particles but it is difficult to tell from this photo. These images show that the powders have been mixed well.

Particle size analysis was also performed on the mixed powder.

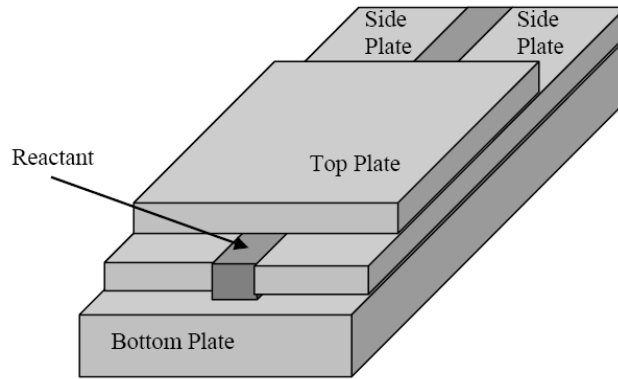


**Figure 7** particle size analysis on mixed powder A) CaCO<sub>3</sub> powder mix B) CaO powder mix

Figure 7 contains results from the particle size analysis performed on the final powder mixes. This analysis shows that average particle size for the mixed powders is 5-10 microns. As before, these particles may have agglomerated for the analysis so it may not be accurate, even though ultrasonic dispersion techniques were used.

### **Friction Stir Welding**

Experimental set up for the welds is shown in figure 8. The side, bottom and top plates were made of aluminum 1100 and the reactant powders in the middle are packed into a 3011 aluminum square tube.



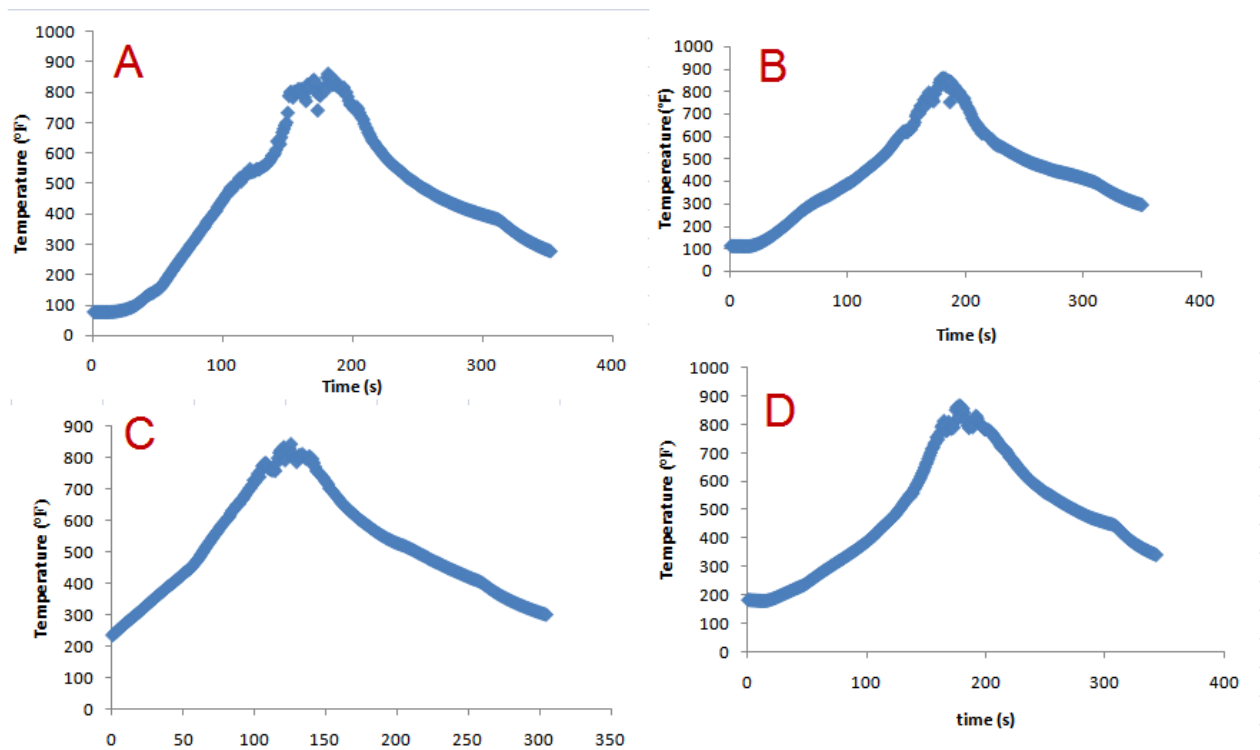
*Figure 8 Aluminum plates with reactant embedded for FSRP [6]*

Welds were performed at 1400 revolutions per minute (rpm) travelling at 1 inch per minute. These parameters were chosen based off previous welds and were expected to generate high heat. An image of the pin tool is included in figure 9; this image shows the size of the pin tool. Three passes were done, each offset by from the previous pass. Thermocouples were embedded along the weld to determine if enough heat was produced to induce a reaction. After processing, the samples were cut in the transverse and longitude direction and polished using standard procedure.



*Figure 9 image of the pin tool used for welding*

### Welding Temperature



*Figure 10 Temperature readings from thermocouples placed in the weld A) CaO 1<sup>st</sup> pass B)CaO 2<sup>nd</sup> Pass C) CaCO<sub>3</sub> 1<sup>st</sup> Pass D )CaCO<sub>3</sub> 2<sup>nd</sup> pass*

Temperature was tracked during the welding process by using thermocouples. Figure 10 includes charts representing the thermocouple data. The data from the third pass was improperly recorded and could not be recovered, for this reason only data from the first two passes is presented.

Figure 10 shows that the maximum temperature reached was approximately 850 degrees Fahrenheit. This temperature is lower than the 980 degrees Fahrenheit that was initially predicted using the ThermoCalc program.

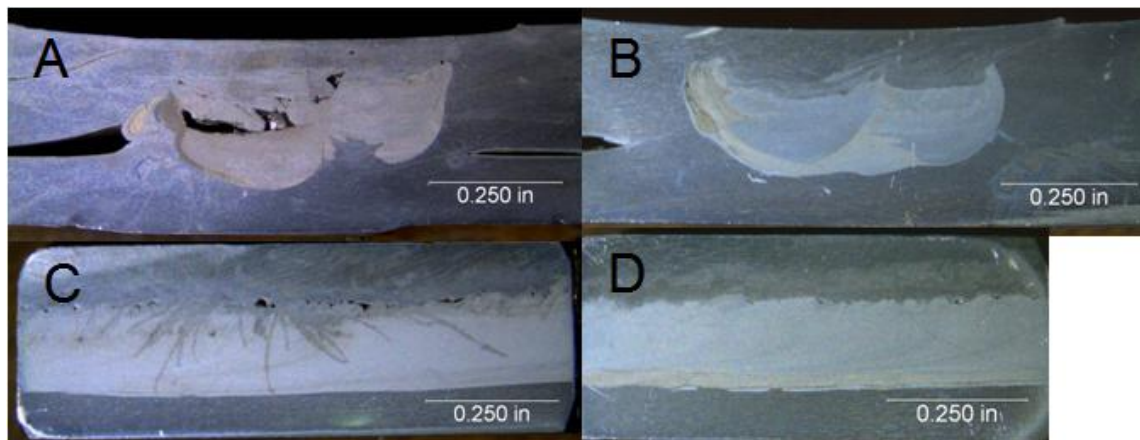
A ThermoCalc analysis was conducted again to determine if the reaction would still be possible at the actual temperature achieved which was 850° Fahrenheit.  $\Delta G$  for the CaO reaction was -363902 and  $\Delta G$  for the  $\text{CaCO}_3$  reaction was -994752. The negative  $\Delta G$  values indicate that the reaction is still possible, however according to table 1 it is more favorable to occur at a higher temperature.

### **Analysis**

The welded and polished samples were analyzed using optical microscopy, Scanning Electron Microscopy and x-ray diffraction. Optical microscopy was done using an Olympus microscope. XRD was performed using a Rigaku Altima Plus X-Ray diffractometer (XRD). Copper K alpha radiation and a graphite micrometer were used for the XRD.

## Results & Discussion

### Optical Microscopy/Macrographs



**Figure 11** Macrographs of cut, polished and lightly etched welds. The lighter shade of gray highlights the nugget zone where powders are stirred in. A: CaO transverse section B: CaCO<sub>3</sub> transverse section C: CaO longitude section D: CaCO<sub>3</sub> longitude section

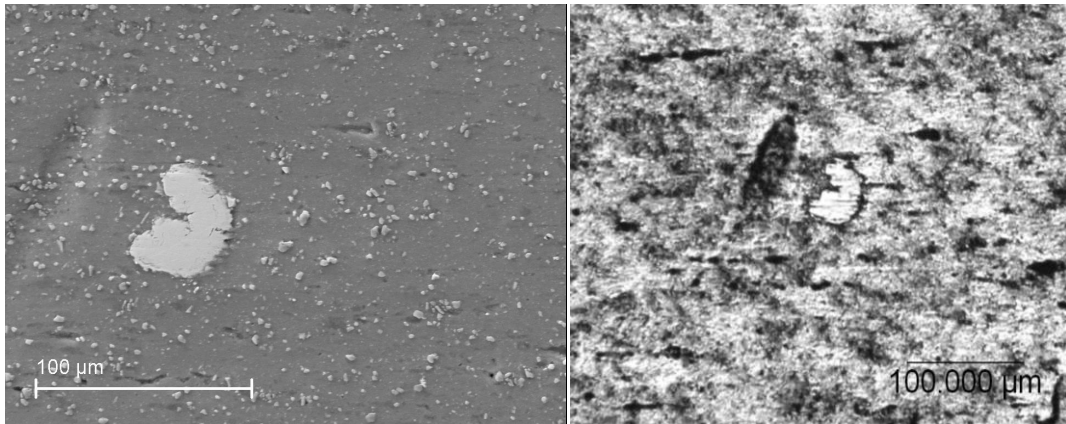
Figure 11 shows the welds after they were cut, polished and lightly etched with a dilute kellers etchant. These photos show the nugget section in a different shade gray than the parent material. Picture D shows layers produced by the weld tool. Picture A shows that the CaO sample has a large hole running through it, this was caused by operator error. It is likely that a large quantity of powder is stuck in the hole.

### Scanning Electron Microscopy

SEM analysis revealed that particles originally of interest viewed under the optical microscope, were actually a combination of contamination and impurities from the parent metal. Figure 12 shows an SEM image and an optical microscope image of the same particle. The large light color particle turned out to be Ni and Cr. This indicates stainless steel, and the only place stainless steel would have come from is the mesh used to crush the powder. This image also shows

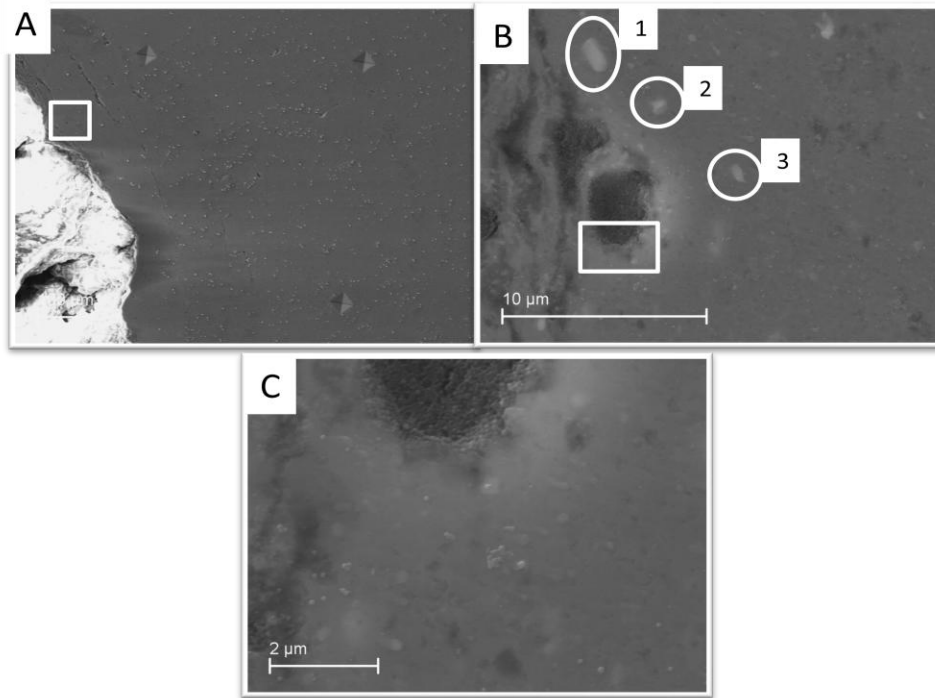


smaller particles around the large particle and these were composed of mostly Si and C. The size of these particles suggests that this is not the Si from the powder that was stirred in, and instead may have been picked up from the silicon carbide polishing wheels or was alloyed into the parent Al material.



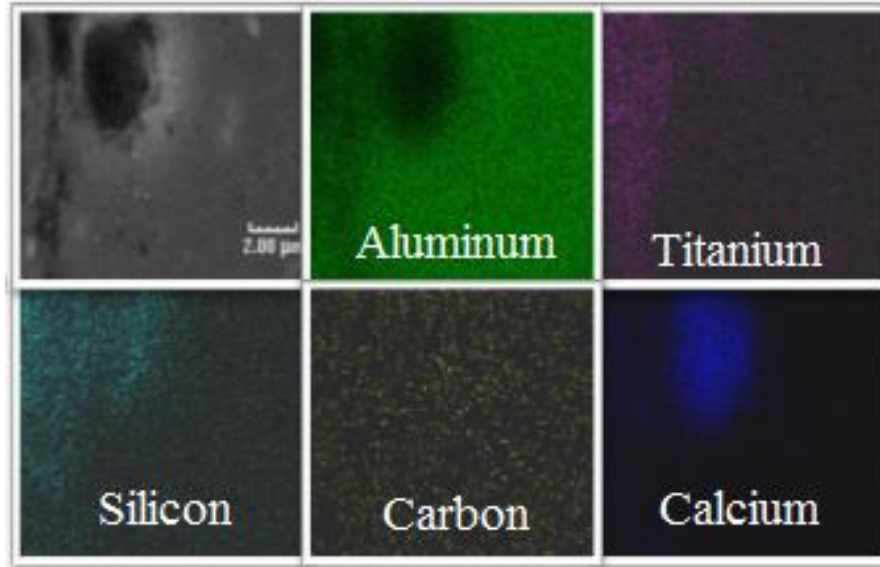
**Figure 12** *Optical and SEM Images of CaO longitude section Left: SEM image at 1000X. Right: optical microscopy image at 800X. This shows Ni Cr contamination, and Si particles that are most likely impurities from the Al parent material.*

Figure 13 shows SEM images taken of the  $\text{CaCO}_3$  transverse section. The image on the left has part of a hole where the powder did not get stirred, but next to this section is an area where powder certainly got stirred. The image on the right is a zoomed in area indicated on the image on the left. The particles number 1-3 were all determined to be composed of Fe. Again these are not particles of interest and most likely came from the parent metal. Both Al 1100 and Al 3011 have a small amount of Fe alloyed into them. The third image on the bottom of the figure is zoomed into 30,000X and is the area labeled 4 on the second image. All of the very fine particles in this image are the powder particles that were stirred in. These particles are on the nanoscale and very difficult to resolve using the SEM. EDS analysis has shown that these particles are the stirred in powders, however the equipment is not accurate enough to pinpoint on particle from another, enough to give labels.



**Figure 13** SEM images of the  $\text{CaCO}_3$  transverse section. A) 80X image taken from the nugget zone. The light zone on the left is the powder unstirred. B) Area zoomed in indicated by the white square on image A, magnification of 11,000X. Particles number 1-3 are iron particles. C) Area zoomed in, the area is indicated by the white square in figure B, magnification of 30,000X. This shows very fine particles, which are the stirred in particles of interest.

Figure 14 is an x-ray map highlighting the elements from the powders that were stirred into the aluminum. These images show how very fine the particles are and that there is a large quantity distributed throughout the Al. It also shows that the powder is fairly well distributed. Each element highlights in a different color. Ca seems to have accumulated heavier in one spot, other than that the powders seem to have dispersed well into the stir zone. This image demonstrates that the stirred in powders are very fine, and SEM is not an appropriate technique to use for resolving the particles.

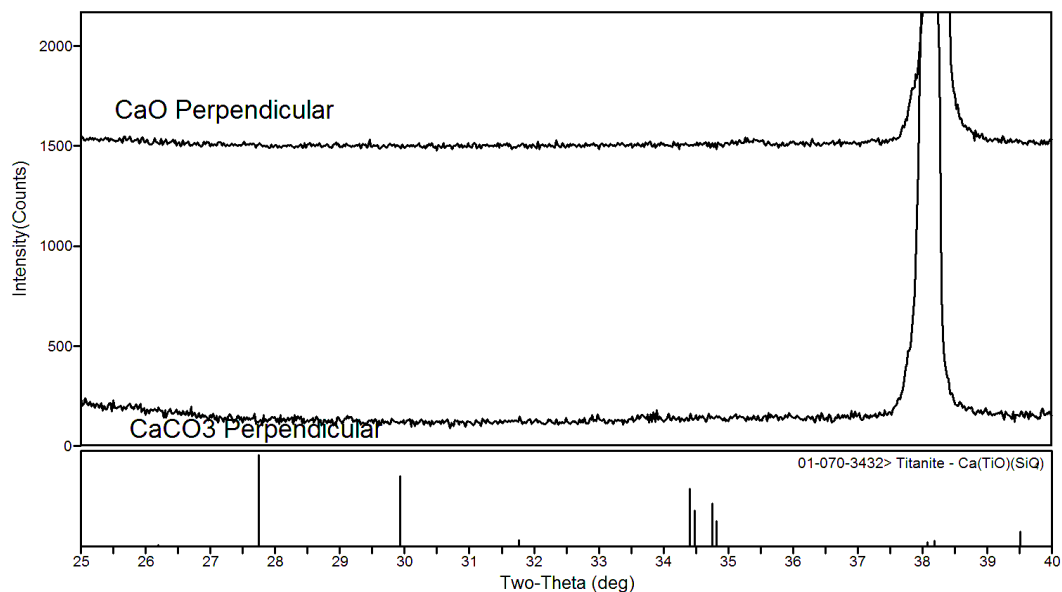


*Figure 14 SEM x-ray analysis to highlight powder particles next to the stir zone*

### **X-Ray Diffraction**

X-ray diffraction was conducted to determine if any compounds formed. First a general scan was performed on the transverse cut for each of the welds. The x-ray beam was focused onto the nugget of the weld, where reaction compounds should be present. A speed of 2 degrees per minute from angles 15 to 80 was used. The scans show only aluminum to be present, there is no evidence that any powder was stirred in according to these results.

The scan was performed again, with the speed slowed down to 0.5 degrees per minute starting at angle 15 and ending at angle 40. This angle range is where the sphene peaks are located, so a slower scan run over these angles would most likely show something of interest. The scan results are in figure 15.



**Figure 15** X-ray diffraction results show no indication of sphene peaks.

Figure 15 is an overlay of the slow scan. The top scan is from the CaO sample, the middle scan is from the CaCO<sub>3</sub> scan and the lines displayed along the bottom indicate where sphene peaks should be located. The large peak observed is from aluminum and again, there is no indication of any other substance in the powder.

It is possible however unlikely that the reaction caused the powders to have an amorphous structure, which would not be detected by XRD. A more likely explanation of why the stirred powders are not showing up is because they are nano sized crystalline structures. The original powder used had particles on the nano scale, and particles of this small size will not be detected by XRD. It is also possible that there is not enough particles in the aluminum to meet the detection limit requirements for XRD.

## **Conclusions**

Optical microscopy images show that there are particles present, but it is impossible to know what they are. SEM analysis shows that many of the particles are contamination, either impurities from the Al parent metal, or contamination gathered from some other way. Nickel particles on the micron scale were found, which is most likely from the mesh used to crush the powder. Micron sized Si particles were found which are most likely alloyed into the original Al. Upon zooming in closer, it could be seen that the stirred in particles are much finer, on the nanometer size scale, and hard to resolve using the SEM. XRD did not yield any usable results. It is possible that sphene is present, however undetectable using the characterization techniques available in the short amount of time for experimentation.

## **Future Work**

This experiment could be carried on by using Transmission Electron Microscopy (TEM) to resolve fine particles and determine if compounds formed. Also, the procedure could be repeated with different weld parameters to generate more heat.

## **Acknowledgements**

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