Reaction Synthesis of TiAl-TiB_2 Metal Matrix Composites

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Abstract

The objective of this study was to define and develop measurable processing parameters to guide the synthesis, design and characterization of reaction-synthesized TiAl-TiB_2 composites. Measurements of energy release during the high temperature self propagating reaction between Ti, Al, and B were used to determine the effects of environment (air or helium), atomic percent Al, and volume percent TiB_2 on the reactivity of the sample. Experimental results were compared to theoretical models developed using published thermodynamic data in order to inspect the adiabatic nature of the reaction. The compositions tested were those of Ti-50Al + 30, 40 and 50 volume percent TiB_2, Ti-43Al + 30, 40 and 50 volume percent TiB_2, and Ti-35Al + 30, 40 and 50 volume percent TiB_2. Experimental results showed that compositions tested in a helium atmosphere provided inconsistent results in both ignition temperature and heat of reaction that were counterintuitive to trends predicted by the theoretical models. Experimental results of compositions tested in an air atmosphere provided better consistency in ignition temperature, along with considerably higher heats of reaction which were much closer to predicted values. These results qualitatively followed the trends produced by the theoretical models.

Keywords: Intermetallic matrix composites, self-propagating high temperature synthesis, titanium diboride, titanium aluminde

1. Introduction

The properties of particulate reinforced metal matrix composites rely heavily on the nature of the interface between the reinforcement and matrix materials, as well as the size, geometry, and volume fraction of the reinforcing phase. Traditional processing methods such as casting, powder metallurgy, and mechanical alloying have several drawbacks that encourage the use of non-conventional processing techniques. In traditional processing schemes, the reinforcing phase is added directly to the molten or powder material, leading to surface contamination and poor wettability between matrix and reinforcing phases. This weak particle matrix interface ultimately leads to poor mechanical properties.[1] These problems have been combated through the development of alternative processing schemes such as combustion synthesis, also known as self-propagating high-temperature synthesis (SHS).

1.1 Combustion Synthesis (SHS)

Combustion synthesis involves heating a green compact of elemental or pre-alloyed powder material to an "ignition" temperature that initiates a highly exothermic reaction that can reach temperatures in excess of 2700 K. Subsequently, the heat evolved provides the thermal energy needed to react the remaining elemental powder. The reaction proceed as a self-propagating reaction front, hence the term self-propagating high temperature synthesis.[1,2] In the case of intermetallic matrix composites (IMMC), combustion synthesis is known as an in situ procedure in which the reinforcement phase is synthesized in situ by the self propagating reaction.[1] SHS offers several practical and theoretical advantages over conventional processing because of the thermodynamically stable matrix/reinforcement interfaces that form during the process.[2] However, despite this obvious advantage, SHS still has drawbacks that must be addressed in order to fully utilize the potential of the reaction. In particular, in many cases of combustion synthesis, the reaction between individual components is hard to control due to the highly exothermic nature of the process as well as rapid reaction rates.[1] This study will begin to address the issue by correlating reactant products to synthesis parameters which will allow reaction design regardless of speed or exothermicity.

1.2 Factors Affecting Combustion Synthesis and Composite Microstructure

As mentioned, the size, shape and distribution of reinforcing phases within a composite microstructure significantly influence its mechanical properties. When IMMC's are produced using combustion synthesis, the above factors are typically related to the reaction parameters such as the amount of heat evolved during the reaction as well as the highest temperature achieved. Several studies have identified key variables, including heating method/rate, particle size, elemental ratios, porosity, and environment, that affect the heat of reaction, the maximum temperature reached, and ultimately the mechanical properties of the composite.[1-5] Kampe and Martin et al. have studied the TiB_2/TiAl system, where both the reinforcing and matrix phases contribute to the exothermicity of the reaction. Their study examined the effects of alloy composition, (volume percent of TiB_2), on the resulting microstructure and adiabatic temperature (highest temperature reached during reaction). However they did not examine fully the correlation between reaction parameters and the resulting microstructure and mechanical properties. Kampe and Martin explored the effects of volume percent of TiB_2 on the theoretical adiabatic temperature and heats of reaction. They concluded that the diameter of the TiB_2 particulates increased with the nominal formulated percentage. From analysis of the predicted adiabatic temperature, they suggest that the larger TiB_2 particles resulted from the higher temperatures associated with the formation of higher volume fractions of the exothermic TiB_2 during synthesis.[2]

1.3 Research Objectives

Based on the previous research of Kampe and Martin, this project sought to define and develop measurable processing parameters which can serve to guide the synthesis, design and characterization of reaction-synthesized TiAl-TiB_2. Specifically, measurements of energy release during synthesis reactions will provide an independent means to characterize the influence of atomic percent Al in the matrix, volume percent of TiB_2 reinforcement, and environment on the reactivity and the microstructural characteristics of the final product. The specific matrix compositions tested were those of Ti-34Al, Ti-43Al, and Ti-50Al with volume percent of TiB_2 at 30, 40 and 50 volume percent. The reaction was studied in both helium and air.

1.4 Theoretical Heat of Reaction and Adiabatic Temperature

A theoretical model was developed to determine the expected heats of reaction and adiabatic temperatures as a function of atomic percent Al and volume percent TiB_2, using published thermodynamic data and incorporating all phase transitions for both reactants and products. The adiabatic temperature is

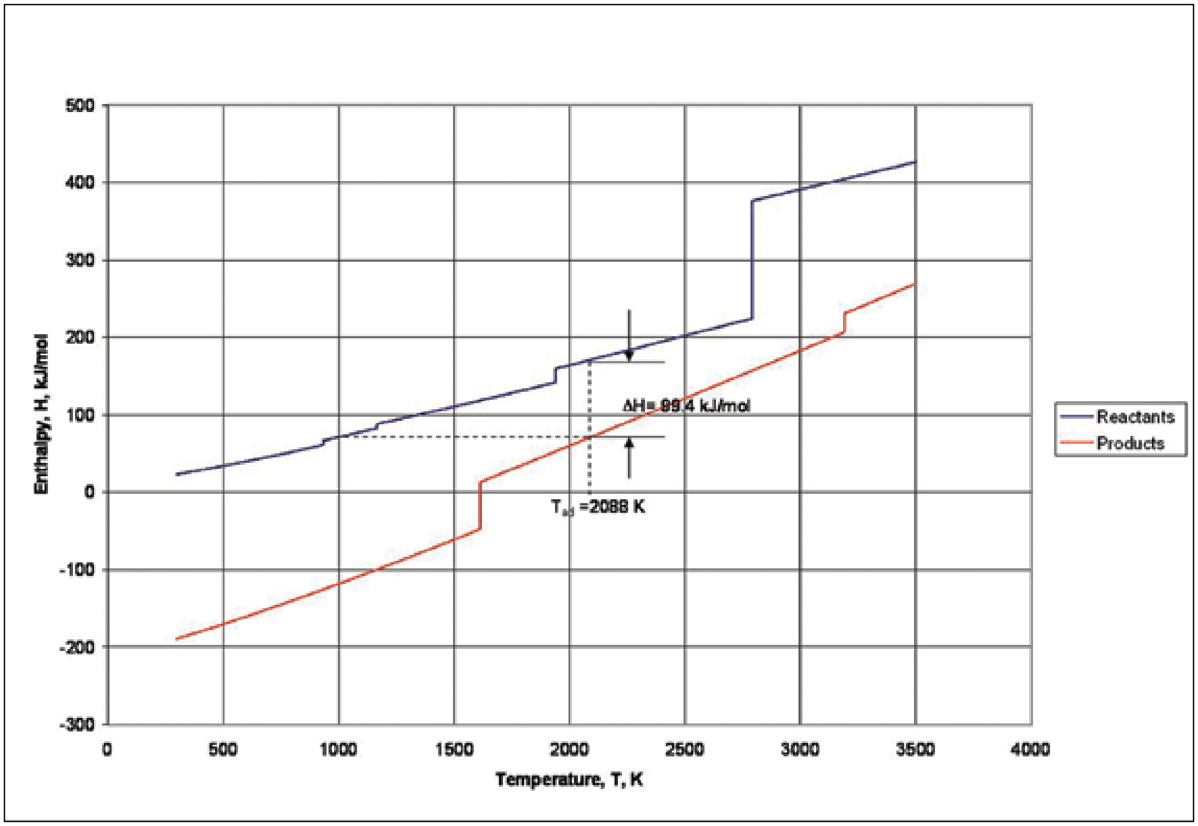


Figure 1. Theoretical enthalpy vs. temperature for Ti-34Al + 20 volume percent TiB_2

defined as the difference in the heat of products and heat of reactants measured an ignition temperature. In the case of the Ti-Al-B system, it is assumed to be 1000 K, or approximately the melting point of aluminum. It is thus assumed that the all the heat generated by the reaction acts to increase the temperature of the remaining unreacted material. The heat of reaction is taken as the difference in reactant and product enthalpies at the adiabatic temperature. Figure 1 graphically depicts the definitions of both reaction enthalpy and adiabatic temperature.

Table 1. Constituent amounts for each sample composition

Composition	TiB2 in Vol. %	Ti (g)	Al (g)	B(g)
Ti-50 Al	30	6.5680	2.3526	1.0794
Ti-50 Al	40	6.6201	1.9723	1.4076
Ti-50 Al	50	6.6699	1.6084	1.7218
Ti-43Al	30	6.9746	1.9699	1.0555
Ti-43Al	40	6.9610	1.6575	1.3815
Ti-43Al	50	6.9482	1.3562	1.6957
Ti-34Al	30	7.4667	1.5066	1.0268
Ti-34Al	40	7.3774	1.2730	1.3496
Ti-34Al	50	7.2904	1.0461	1.6635

2. Procedure

2.1 Powder Constituent Calculations

The elemental constituent powders needed for each composition were titanium, aluminum and boron. The titanium powder used was >325 mesh, the aluminum powder was >100 mesh and the boron was >100 mesh. The amount of each varies based on the target matrix and reinforcement volumes. Three target compositions of α2-phase Ti_3Al and γ-phase TiAl were chosen. Each of the three compositions was chosen based on the modeled thermodynamic transitions and attempted to represent the full α2+ γ phase of the Ti-Al phase diagram. Of these three matrix variations the volume fraction of reinforcement loading was varied between 30 and 50 volume percent. The reinforcement phase is TiB_2.

A previous iteration of a Matlab program was utilized to aid in quickly determining the matrix and reinforcement weight percents and volume percents. The amounts listed in Table 1 are based on a 10 gram batch of sample.

2.2 Sample Preparation

To optimize the thermal analysis measurement, each composition was cold compacted before testing. The sample was pressed to 20 Ksi with a 0.5 inch diameter compaction die. The optimum differential scanning calorimetry (DSC) sample weight was 10 mg.

2.3 Thermal Analysis

Crucibles made of alumina were used with the Netszch Simultaneous Thermal Analysis system. Each sample was placed into an alumina crucible, covered and loaded into the Netszch DSC. Tests were run in both helium and air. The helium

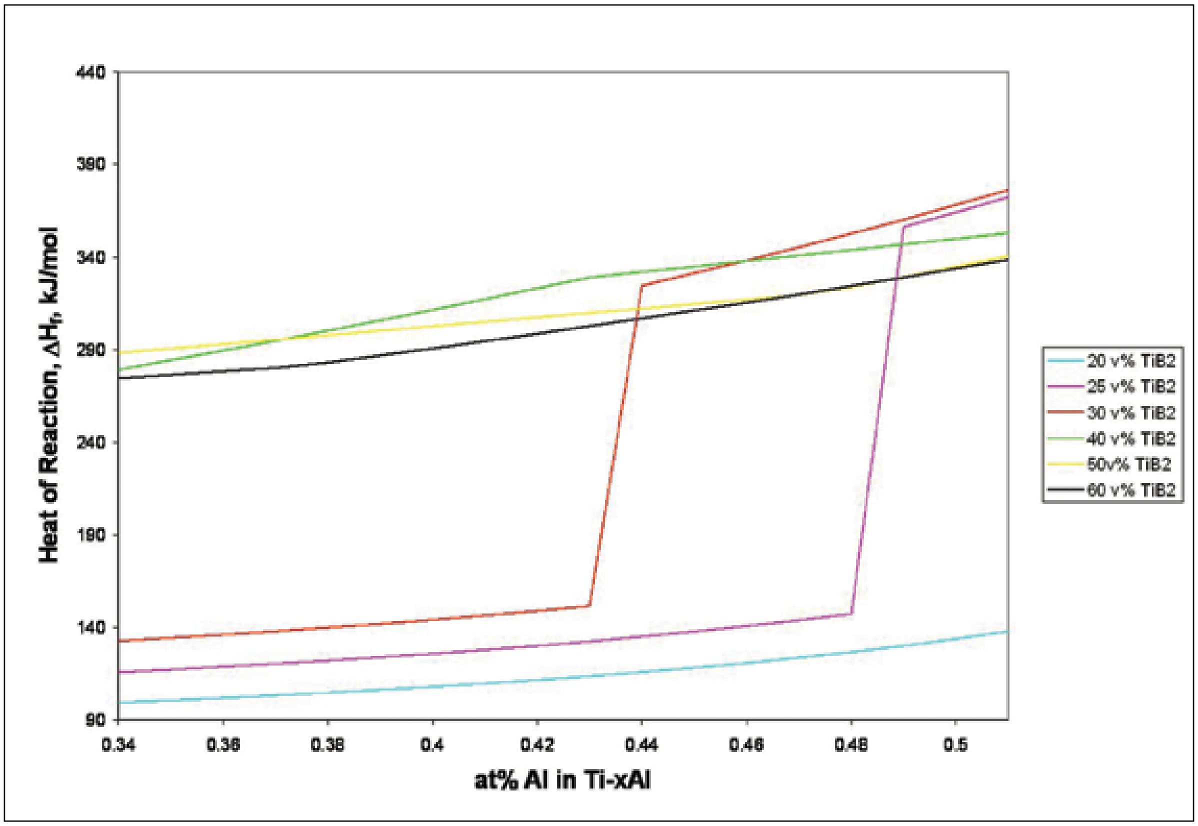


Figure 2. Theoretical heat of reaction vs. atomic percent Al

temperature profile starts at 40 ºC and ramps to 1050 ºC at 40 ºC/min. However, the tests run in oxygen/nitrogen mixture need to be heated to 1200 ºC at 40 ºC/min.

3. Results and Discussion

The DSC results showed that the compositions tested in the helium atmosphere produced large variations in heat of reaction and ignition temperature, as well as values of heat of reaction that were an order of magnitude smaller than those predicted by theoretical models. Those compositions tested in the air atmosphere produced results that were much more repeatable heats of reaction and ignition temperature, as well as values of heat of reaction that were on the same order of magnitude as those predicted by the theoretical models.

3.1. Theoretical Model Results

The results from the theoretical models were used to determine the compositions to be tested experimentally based on variations in predicted reaction characteristics. Theoretically, as shown in Figure 2, the heat of reaction varies significantly with atomic percent Al and volume percent TiB_2.

As shown in Figure 2, the amount of heat evolved increases with increasing amounts of both Al in the matrix and volume percent of TiB_2 in the composite. Also, there is a large jump in the heats evolved for all atomic percentages of Al. This large jump occurs because the reaction reaches the vaporization temperature of Al. The 50 atomic percent of Al demonstrates this large jump in heat evolved much sooner than the 34 and 43 atomic percentages of Al. This shows that, theoretically, increasing the atomic percent of Al increase the reactivity of the system.

As with the heat of reaction, the adiabatic temperature also increases with increasing amounts of Al in the matrix and volume percent of TiB_2 in the composite, as shown in Figure 3. Both the 34 and 43 atomic percentages of Al show a plateau region in adiabatic temperature. In this region, T_{ad} equals the melting temperature of TiB_2, or 3193 K

3.2 Differential Scanning Calorimetry Results

3.2.1 Helium Atmosphere

The DSC results in the helium atmosphere demonstrated a significant amount of scatter in both heat of reaction and ignition temperature for all samples tested, as exemplified by the three DSC traces of the Ti-34Al +30 volume percent TiB_2 composition in Figure 4. In this trace, endothermic reactions appear as upward peaks, while exothermic reactions appear as downward peaks.

Figure 4 presents DSC traces that demonstrate representative variation in ignition temperature and heat of reaction. The first endothermic peaks represent that of the melting of aluminum. These peaks were found to be very consistent in heat of fusion and melting temperature for all compositions tested, indicating

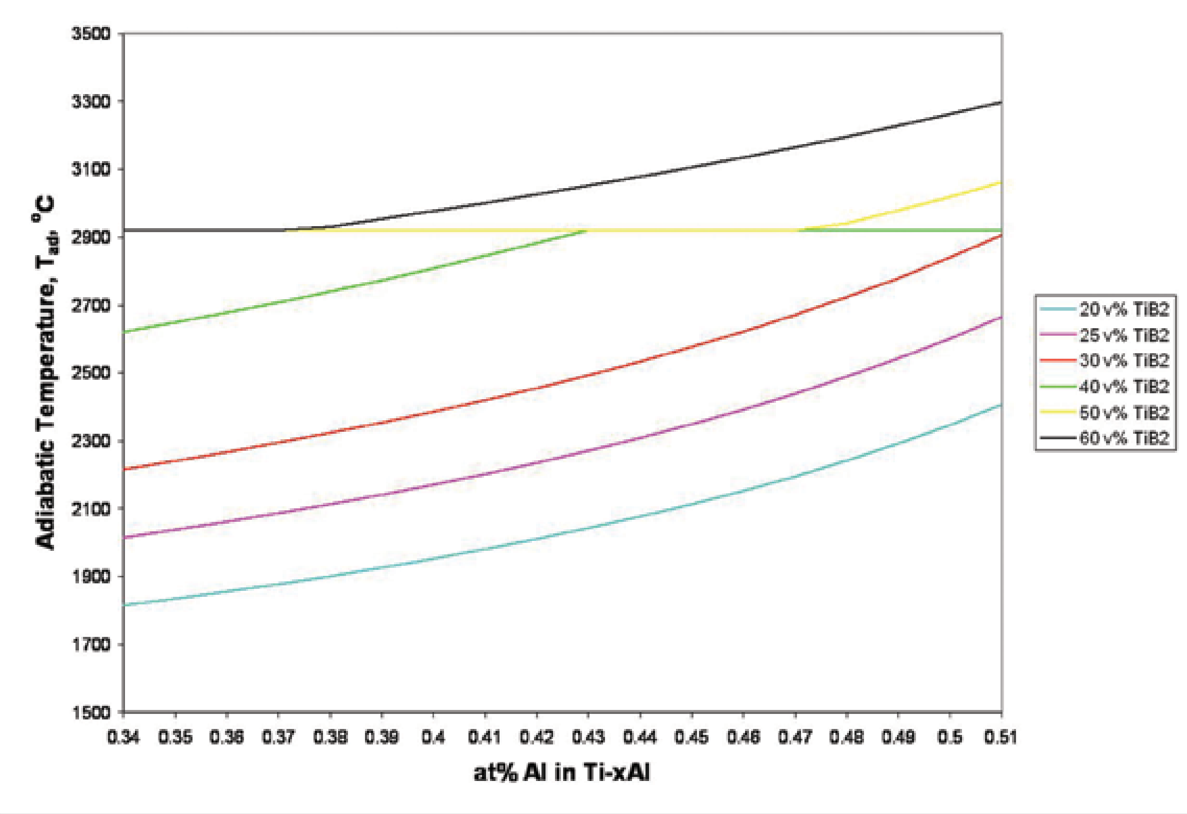
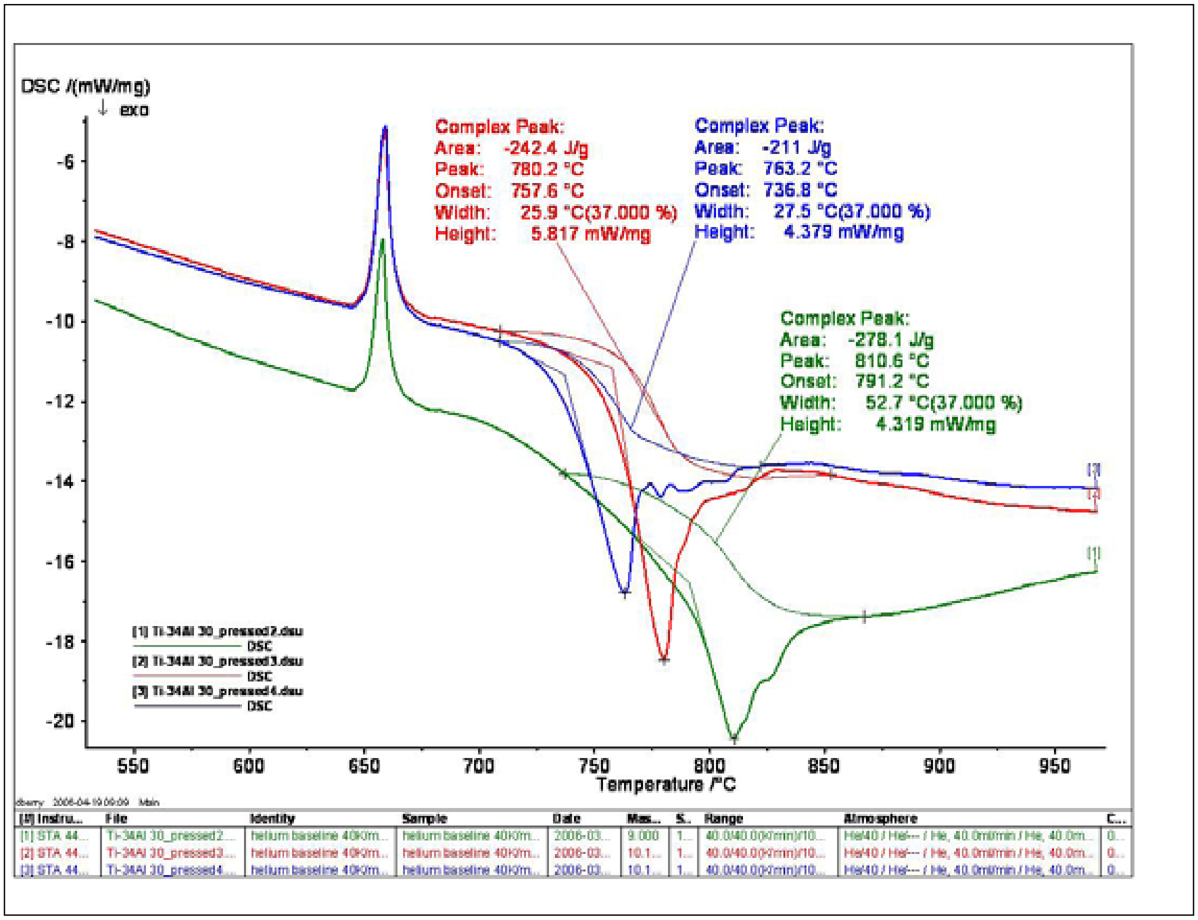


Figure 3. Theoretical adiabatic temperature vs. atomic percent Al



[#] Instru...	File	Identity	Sample	Date	Mas...	S..	Range	Atmosphere	C...
[1] STA 44...	Ti-34Al 30_pressed2...	helium baseline 40K/m...	helium baseline 40K/m...	2006-03...	9.000	1...	40.0/40.0(K/min)/10...	He/40 / He/--- / He, 40.0ml/min / He, 40.0m...	0...
[2] STA 44...	Ti-34Al 30_pressed3...	helium baseline 40K/m...	helium baseline 40K/m...	2006-03...	10.1...	1...	40.0/40.0(K/min)/10...	He/40 / He/--- / He, 40.0ml/min / He, 40.0m...	0...
[3] STA 44...	Ti-34Al 30_pressed4...	helium baseline 40K/m...	helium baseline 40K/m...	2006-03...	10.1...	1...	40.0/40.0(K/min)/10...	He/40 / He/--- / He, 40.0ml/min / He, 40.0m...	0...

Figure 4. DSC trace of Ti-34Al + 30 volume percent TiB_2

that the variations in the amount of aluminum did not affect when or how much of, the aluminum melted. The exothermic peaks in Figure 4, however, showed large variation in both ignition temperature and heat of reaction. Two of the peaks also demonstrated oscillations near the end of the exotherm. These could possibly indicate several small reactions occurring after the initial heat evolution. The DSC results for all compositions tested in helium are presented in Table 2.

Table 2. DSC results in Helium

Atomic % Al	Volume % TiB_2	run 1 (J/g)	run 2 (J/g)	run 3 (J/g)	run 4 (J/g)	Avg. heat J/g	Standard Deviation in % of Avg.
50	30	227.3	310.9	312.7		283.63	17.20
50	40	112.1	270.6	186.0		189.57	41.84
50	50	64.8	173.1	207.0	132.8	144.43	42.33
43	30	289.2	231.9	310.2		277.10	14.63
43	40	114.3	197.8	260.2		190.77	38.37
43	50	313.83	124.4	129.3		189.18	57.08
34	30	278.1	242.2	211.0		243.77	13.78
34	40	151.8	131.0	149.1	112.6	136.13	13.37
34	50	91.58	102.3	1063.3		419.06	133.14

The data presented in Table 2 again shows the large variation in heats of reaction for all the compositions. These variations may result from density and composition variations within each sample material. Also, many of the average heats of reaction, with their standard deviations, overlap one another, thus making it impossible to determine the effects of varying compositional ratios on the reactivity of the material.

The resulting test of Ti-34Al + 50 volume percent TiB_2 shown in Figure 5 (green line), demonstrated a large increase in the exothermicity of that reaction. Also, two large exotherms were noted as opposed to small oscillatory reactions near the end of the exotherm.

3.2.2 Air Atmosphere

Compositions of Ti-34Al + 30 and 50 volume percent TiB_2, as well as Ti-50Al + 30 and 50 volume percent TiB_2 were tested in an air atmosphere consisting of 80%

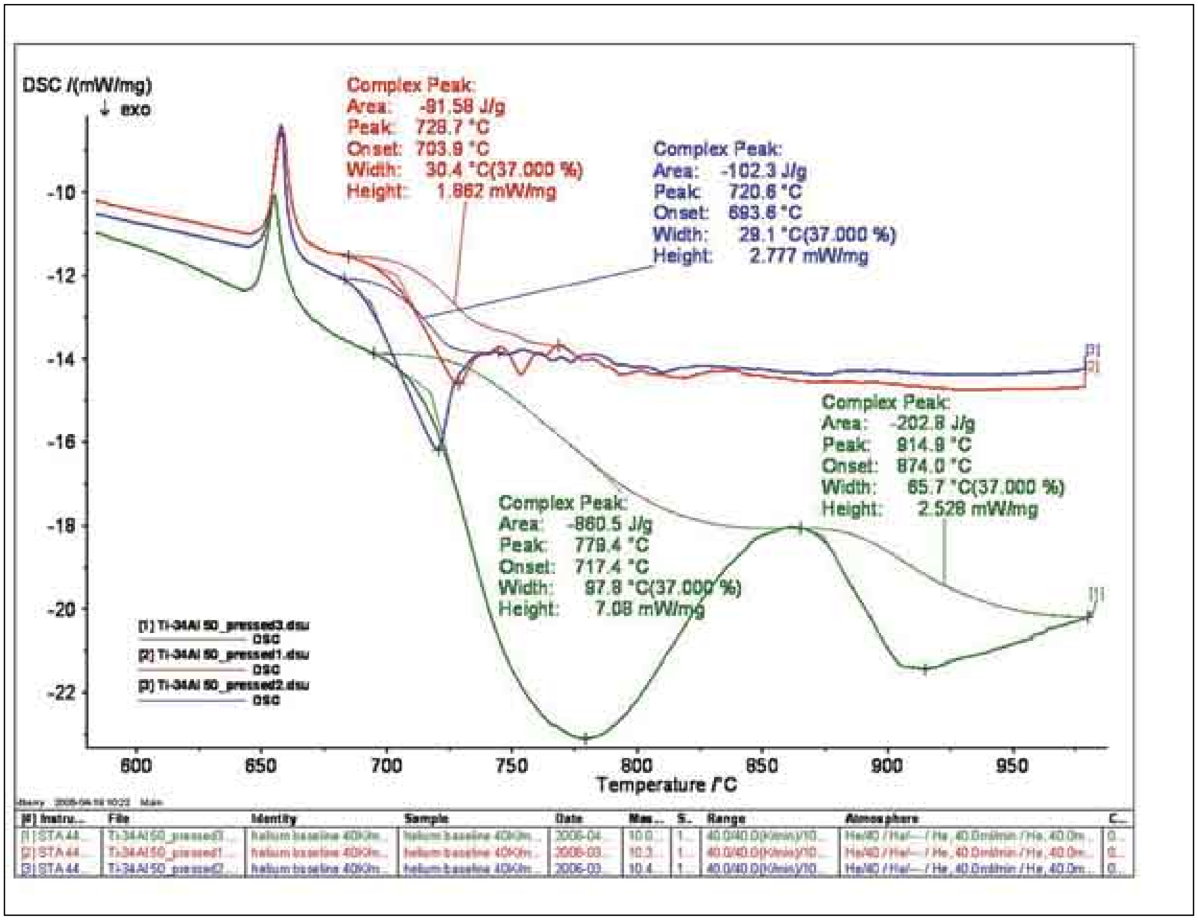


Figure 5. DSC trace of Ti-34Al + 50 volume percent TiB_2

nitrogen and 20% oxygen. The results of the DSC tests in air proved much more repeatable, and also demonstrated reaction exotherms that more closely resemble those expected from the theoretical models. For example, Figure 6 presents the DSC trace of Ti-34Al + 30 volume percent TiB_2

This graph illustrates a desirable and repeatable correlation between two samples of identical composition. The aluminum melting endotherm is still consistent in quantity and onset yet the reaction has three distinct exothermic reactions instead of the one large exotherm shown in tests with a helium atmosphere. Table 3 summarizes the results of the DSC tests in air atmosphere and tabulates the heats from all three reactions as indicated in Figure 6.

The average heat of reaction for each matrix composition and loading scenario in air are much greater than heats for similar compositions tested in helium. The standard deviation for these samples when compared to the average heat evolved is a much smaller ratio than shown for data in the helium atmosphere. The standard deviation for the Ti-50Al+50 volume percent TiB_2 in helium is 42.33% of the average heat compared to a value of 4.33% for the same composition tested in air.

Each of the samples tested in the air atmosphere revealed three reaction isotherms and an absence of oscillations. The placement of the isotherms for air samples changed with an increasing atomic percent of aluminum. An example DSC trace of a matrix composition with 50 at% Al is shown in Figure 7.

The arrangement of the reaction has shifted to the left (down in temperature) as the atomic percent of aluminum in the matrix increases. Three reactions still occur and the respective heats are tabulated as before with the first reaction and ignition temperature taken from the first noticeable exothermic peak. This exothermic reaction consumes the endothermic melt of aluminum, but the onset of aluminum melt remains consistent. Although the reaction timing has changed with the added aluminum in the matrix composition, the ignition temperatures remain constant with matrix composition and reinforcement percentage as shown in Table 4. The shift in onset temperature for these reactions is only a few degrees compared to the discrepancies as large as 50 ºC for similar compositions tested in the helium environment.

3.3 Experimental Theoretical Comparisons

3.3.1 Helium Results vs. Theoretical

It is difficult to objectively compare the theoretical results and the experimental results produced from testing in a helium atmosphere, because of the scattering of data points and the uncertainty associated with pellet compact composition and density. In addition, the theoretical model was based on the

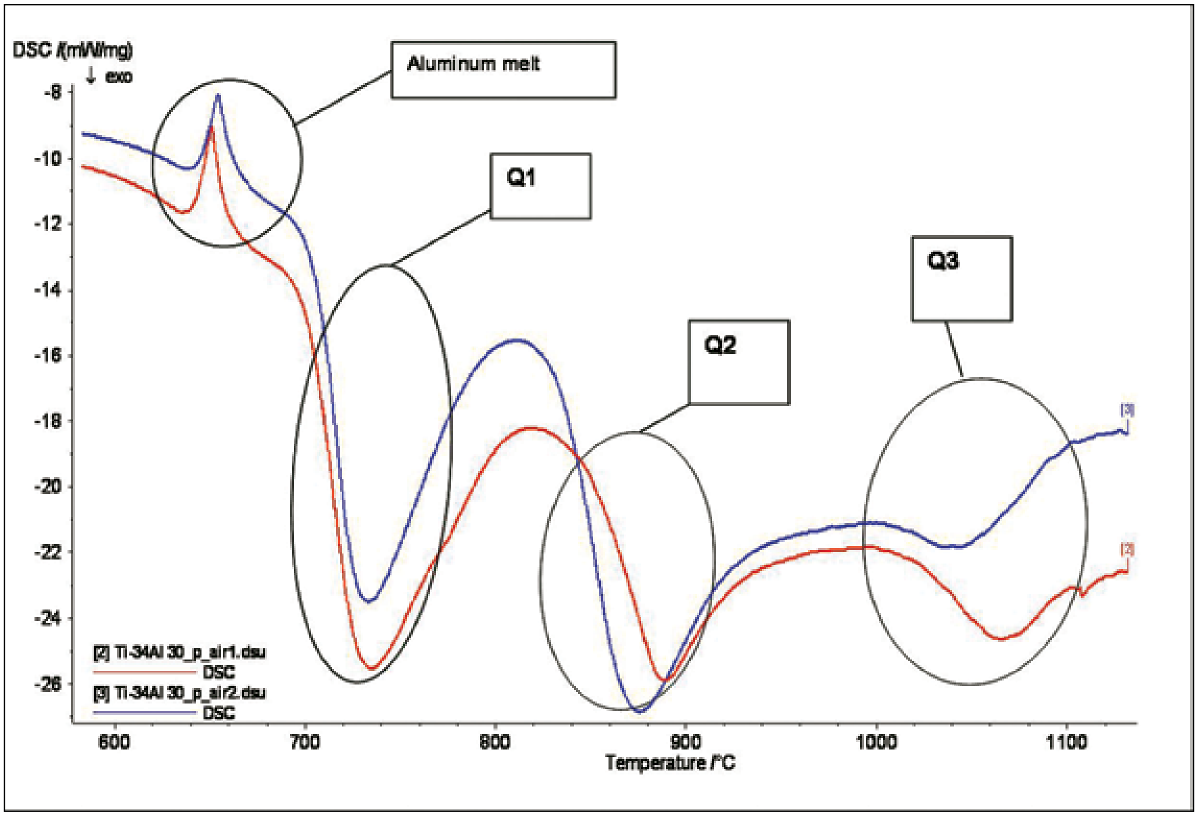


Figure 6. DSC trace for Ti-34 + 30 volume percent TiB_2 tested in air

assumption of 1 mole of products, and adiabatic conditions during the reaction and we have not proven those conditions occured. Comparing the theoretical and experimental values of heat of reaction as a function of atomic percent Al, as shown in Figure 8, reveals the data is an order of magnitude apart.

Also, neither the 34 nor 43 atomic percent Al follows the trend that was present in the theoretical model. However, the 50 atomic percent Al data does follow a downward trend similar to the same downward trend in the model

3.3.2 Air Results vs. Theoretical

The values obtained from the air atmosphere reactions also cannot be compared directly to the values determined by the theoretical model for several reasons. First, the actual reaction products found in the air reacted compositions can not be determined without further analysis, such as x-ray diffraction, electron discharge spectroscopy, or other elemental/compound characterization techniques. Also, the theoretical models were based on the assumption that no heat was lost to surroundings and that reaction ignited when the aluminum melted as we see did not happen to some compositions tested in air. However, it was recognized that the values of heat of reaction obtained from the air atmosphere experiments are an order of magnitude larger than those found using the helium atmosphere, thus closer to the theoretical values. This suggests that the reaction occurred at a greater fraction of its potential in air.

Table 3. DSC reaction heats for compositions tested in air atmosphere

Atomic % Al	Vol % TiB_2	Experiment 1 (J/g)			Total heat (J/g)	Experiment 2 (J/g)			Total heat (J/g)	Avg. heat (J/g)	standard deviation in % of avg.
		Q 1	Q 2	Q3	Q total	Q 1	Q 2	Q3	Q total		
50	30	1074.0	1375.0	457.9	2906.9	1415.0	959.6	278.0	2652.6	2287.0	7.86
50	50	1854.0	506.1	90.1	2450.2	1525.0	800.3	269.7	2595.0	2365.1	4.33
34	30	935.5	566.8	202.3	1704.6	807.5	1008.0	156.4	1971.9	1795.0	10.53
34	50	1786.0	365.8	270.0	2421.8	1535.0	350.2	184.1	2069.3	2250.1	11.08

Table 4. DSC ignition temperatures for compositions tested in air atmosphere

Atomic % Al	Vol % TiB2	Experiment 1 Ignition Temperature °C	Experiment 2 Ignition Temperature °C
50	30	542.1	555.10
50	50	544.4	540.90
34	30	702.6	705.60
34	50	708.2	707.00

4. Conclusion

4.1 Testing Repeatability and Theoretical Correlation

Results from the DSC testing machine indicate that a helium atmosphere provides inconsistent results in both ignition temperature and heat of reaction that are counterintuitive to trends predicted by the theoretical models. This inconsistency along with very large discrepancies between the theoretical and measured heats of reaction suggests that reactions are being suppressed by the helium atmosphere, and not allowed to go to completion. On the other hand, results from the DSC in an air atmosphere provided better consistency in ignition temperature, along with considerably higher heats of reaction which were much closer to predicted values. Also, these results qualitatively followed the trends produced by the theoretical models. However, more data needs to be gathered to verify these findings.

4.2 Reaction Oscillation/Propagation

Both helium and air atmospheres produced reaction curves that demonstrated multiple exothermic reactions. The exothermic peaks in the helium atmosphere appeared as small oscillations in the DCS trace, indicating that the reaction was short lived. In comparison the exothermic peaks in the air atmosphere showed pronounced separation and larger/longer oscillation peaks, indicating that the reactions were slower and or allowed to go to completion.

5. Future Work

The unexpected discrepancy arising from the change in atmosphere during testing leads to a need for more characterization of the reaction kinetics and the evolution of final product. To accurately determine a reliable trend, more data needs to be taken for each matrix composition and reinforcement percentage already tested in the air atmosphere. Although two samples of each composition resulted in uniform reaction parameters and repeatable ignition temperatures, more tests should be taken to establish a uniform distribution and narrow the standard deviation. In addition, different matrix compositions should be tested to define a trend in the shifting ignition temperature.

Finally, due to the oxidizing atmosphere, the product of the reaction is questionable. In theoretical models the product was assumed to be solely a composite of matrix material, Ti_3Al and TiAl, and its reinforcement phase, TiB_2. Because the sample exhibits oxidation in the air atmosphere, the product may con-

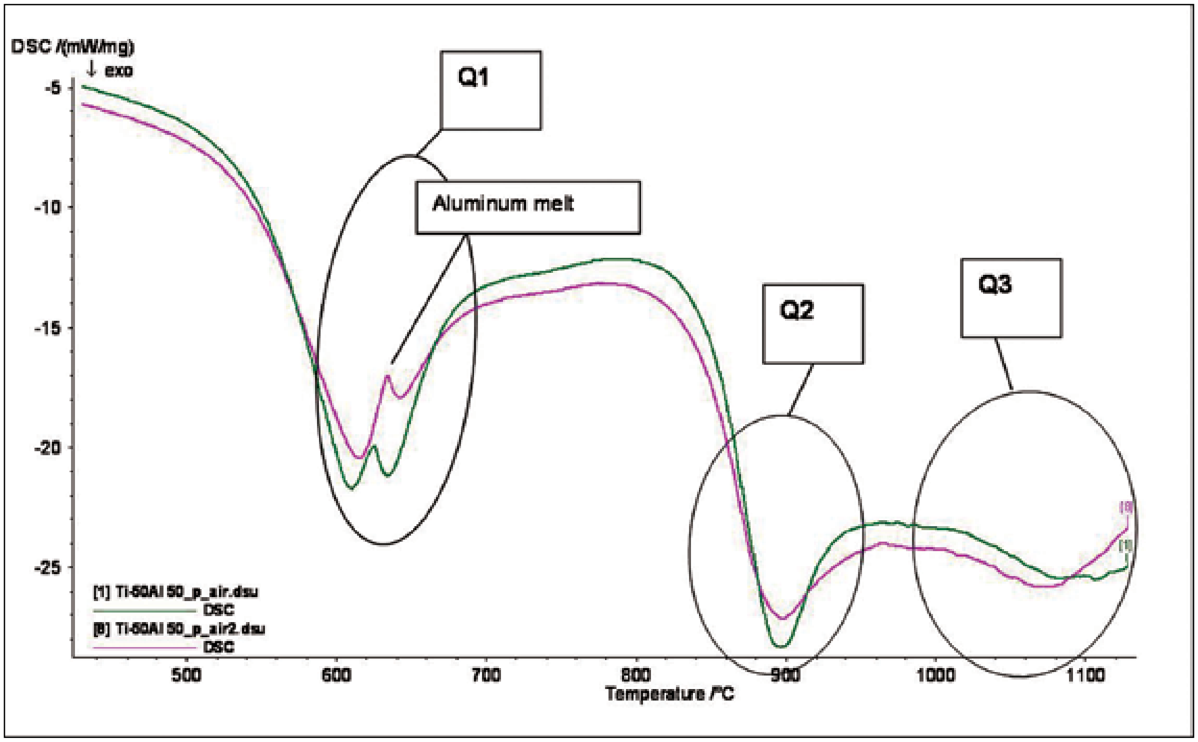


Figure 7. DSC trace of Ti-50Al + 50 volume percent TiB_2 in air atmosphere

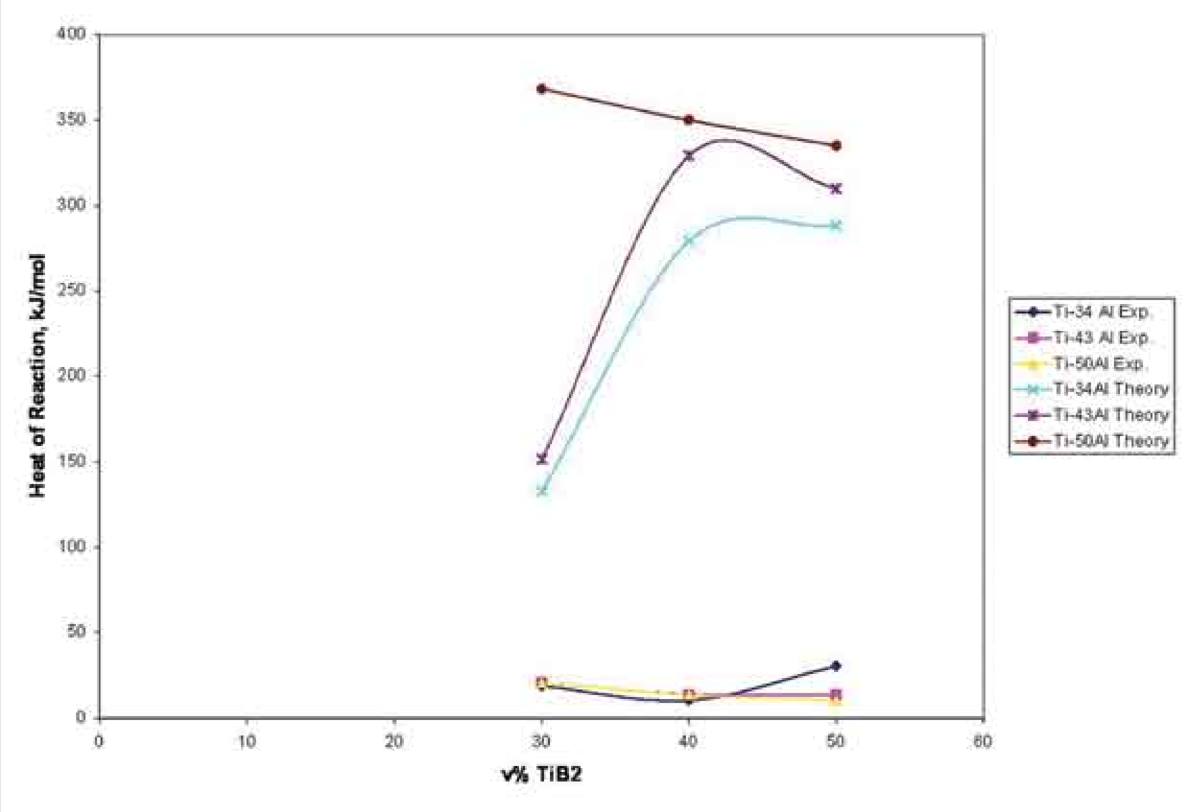


Figure 8. Comparison of theoretical variations of reinforcement with experimental variations of reinforcement

tain a percentage of alumina, Al_2O_3. This was not considered in earlier models and without proper molecular weight values, the conversion from DSC data in J/g to J/mol is inaccurate and a direct comparison would be invalid.

Overall characterization on intermediate products should be done using X-ray powder diffraction and SEM. X-ray data can be used to confirm constituents at phases of reaction completion. SEM analysis can confirm structure and size of phases and may allow further insight into formation of final reinforcement phases. The presence of three separate reaction fronts should allow for these characterization techniques at each phase of reaction to be analyzed.

Lastly, care should be taken in sample preparation. Possible sources of error may occur in sampling of blended powders. Given the small amount of sample needed for DSC testing, an accurate representation of the overall constituent powders may not be present. To improve testing scenarios, samples should be pressed to near testing weights and care should be taken to mix only small batches of material with accurate scales to insure proper ratios.

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