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PhD Thesis

SYNTHESIS OF REACTIVE STRUCTURES BY BALL MILLING AND ULTRASONIC CONSOLIDATION

Anastasia Hadjiafxenti

DEPARTMENT OF MECHANICAL AND MANUFACTURING ENGINEERING

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Synthesis of Reactive Structures by Ball Milling and Ultrasonic Consolidation

Anastasia Hadjiafxenti

Research Committee
Associate Professor Claus Rebholz *(supervisor)*
Professor Charalabos Doumanidis *(committee head)*
Assistant Professor Theodora Kyratsi *(committee member)*
Professor Steven Son *(external committee member)*
Professor Alexander Rogachev *(external committee member)*

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Ἡ Ἰθάκη σ᾿ ἔδωσε τ᾿ ὡραῖο ταξίδι.
Χωρὶς αὐτὴν δὲν θά ῾βγαινες στὸν δρόμο.
Ἄλλα δὲν ἔχει νὰ σὲ δώσει πιά.

Κι ἂν πτωχικὴ τὴν βρεῖς, ἡ Ἰθάκη δὲν σὲ γέλασε.
Ἔτσι σοφὸς ποὺ ἔγινες, μὲ τόση πεῖρα,
ἤδη θὰ τὸ κατάλαβες οἱ Ἰθάκες τὶ σημαίνουν.

Κωνσταντίνος Καβάφης

Ithaka gave you a splendid journey.
Without her you would not have set out.
She hasn't anything else to give you.

And if you find her poor, Ithaka hasn't deceived you.
So wise you have become, of such experience,
that already you'll have understood what these Ithakas mean.

Constantinos Cavafy

Preface

The research contained in this PhD Thesis is mainly based on experimental work carried out in the Mechanical and Manufacturing Engineering Department at the University of Cyprus during the period from October 2007 to December 2012. This project was devoted to the synthesis of reactive structures using two processes: Ball Milling (BM) and Ultrasonic Powder Consolidation (UPC), the major and minor parts of this thesis, respectively. Part of the work on UPC was carried out in the Mechanical and Industrial Engineering Department at Northeastern University, Boston/USA, in April and May 2011. The work on BM was funded through a Marie Curie Excellence Team Award from the European Commission for 27 months and through an industrial collaboration with Stuckenbrock Medizintechnik GmbH, Tuttlingen/Germany, for 2 months, while work on UPC was funded by the Cyprus Research Promotion Foundation for 12 months via its Framework Programme for Research, Technological Development and Innovation, co-funded by the Republic of Cyprus and the European Regional Development Fund.

This study was mainly directed towards finding a way of approaching nanoscale multilayer films/foils (MFs) exothermic behaviour (i.e. starting the self-propagating exothermic reaction, SPER, by using a low energy spark from a battery) by producing reactive compacts using BM and UPC, in an approach to decrease costs. MFs are mainly produced through sputtering, which is a relatively expensive and time consuming Physical Vapour Deposition (PVD) method for large scale manufacturing. Therefore, their use is limited to specialty applications which warrant their cost. MFs have been industrially used for many years, especially for the bonding of different materials (e.g. ceramic on metal). Potential applications include soldering, adhesive bonding, polymer memory devices, lab-on-a-chip and hyperthermia for cancer treatment.

Previous work on BM has been mostly focused on High-Energy BM (HEBM), where the high impact energies rapidly produce well-mixed powders within minutes, and intermetallic phase formation (e.g. in the Al-Ni system) during BM or after by uniform heating (e.g. using a hot plate) of green compacts. However, the high local heating during each impact event due to plastic deformation can cause mass diffusion, producing solid-state solutions at interfaces, thus reducing the overall available enthalpies, or increase contamination originating from the steel or tungsten carbide balls used during the process. It is highly desirable to retain most of the reactivity and purity of the powders so that the ignition threshold is sufficiently low, which would enable local ignition with a low-energy spark from a battery as opposed to uniform heating. This is especially important if the materials to be joined cannot be uniformly heated to the required temperatures. Low-Energy BM (LEBM) employed in this study is a viable approach to circumvent this problem by reducing the energy of individual impact events at the expense of processing time. Experiments were carried out in the Al–Ni system, because both powders are relatively inexpensive, and their reactions are highly exothermic and well characterized.

UPC, a relatively new processing technique, was mainly used for the synthesis of Al/Fe_2O_3 and Al/Cu_2O compacts over a wide range of powder ratios at room temperature, but also for the fabrication of Al-Ni compacts at various temperatures and pressures.

The research *objectives* included:

- Implement BM and UPC to create compacts that exhibit exothermic reactions, with desired structures controlled by the processing conditions.

- Develop well-consolidated compacts that allow for easier ignition and maximum heat release.

- Optimize BM and USC parameters to enhance the resultant heat-release upon ignition.

- Evaluate the structural, chemical and thermal properties of powder compacts.

- Study the thermal evolution of ignited powder compacts through Infrared Camera monitoring of the reaction, and evaluate the reaction front propagation using high speed camera analysis.

This work has resulted in the following *highlights*:

- Self-propagating high temperature reactions in compacted pellets of interrupted and continuous low-energy ball milled Al and Ni powders at a composition corresponding to $AlNi_3$, and continuous ball milled powders at a composition of AlNi.

- Formation of a bi-modal structure with nanoscale lamella of Al and Ni with increasing milling time for both $AlNi_3$ and AlNi.

- Ball milled powders cold-pressed into pellets have similar characteristics to MFs in terms of phase formation sequence and exothermic peak shifts.

- LEBM of Al/Ni particles with an overall composition of NiAl can produce powders, which upon cold-compaction into pellets can be locally ignited (in the same way as MFs) using a low energy spark and react in a self-propagating manner with uniform thermal fronts having velocities up to 0.24 m/s.

- Ball milled powders can potentially be incorporated into pure foils or surfaces using rolling to generate thick reactive foils suitable for large scale bonding and can be ignited away from the weld interface using a spark.

- Development of Al-based thermite composites, Al/Fe_2O_3 and Al/Cu_2O, over a wide range of powder ratios at room temperature by UPC. Short processing times and non-requirement of special processing conditions make this process very promising.

The work in this thesis has resulted in six papers to date (four main- and two co-authored); more are planned:

1) **Synthesis of Reactive Al/Ni Structures by Ball Milling**
A. Hadjiafxenti, I.E. Gunduz, C. Tsotsos, T. Kyratsi, C.C. Doumanidis and C. Rebholz
Intermetallics, vol. 18, p. 2219, 2010

2) **The Influence of Structure on Thermal Behavior of Reactive Al-Ni Powder Mixtures Formed by Ball Milling**
A. Hadjiafxenti, I.E. Gunduz, C. Tsotsos, S.M. Aouadi, T. Kyratsi, C.C. Doumanidis and C. Rebholz
Journal of Alloys and Compounds, vol. 505, p. 467, 2010

3) **Exothermic Reaction Characteristics of Continuously Ball Milled Al/Ni Powder Compacts**
A. Hadjiafxenti, I.E. Gunduz, T. Kyratsi, C.C. Doumanidis, C. Rebholz
Vacuum (under revision)

4) **Fabrication, Characterization and Applications of Novel Nanoheater Structures**
Z. Gu, Q. Cui, J. Chen, J. Buckley, T. Ando, D. Erdeniz, P. Wong, A. Hadjiafxenti, P. Epaminonda, I.E. Gunduz, C. Rebholz and C.C. Doumanidis
Surface Coatings and Technology, 2012 (in press);
http://dx.doi.org/10.1016/j.surfcoat.2012.06.095

5) **Spark Ignitable Green Compacts of Continuously Ball-Milled Al/Ni Powders at NiAl Composition**
A. Hadjiafxenti, I.E. Gunduz, C.C. Doumanidis and C. Rebholz
Scripta Materialia (under review)

6) **Ultrasonic Consolidation and Ignition Characteristics of Thermite Composites**
S. K. Pillai, A. Hadjiafxenti, T. Ando, C.C. Doumanidis and C. Rebholz
International Journal of Applied Ceramic Technology, vol. 9, p. 206, 2012

The author's contribution to the papers

In Papers 1-3, I planned and performed all synthesis, completed all the ignition tests using IR and HS cameras, performed all the characterization using SEM, XRD, and DSC, carried out the evaluation/analysis and wrote the papers.

In Papers 4-5, I planned and performed the synthesis and the analysis based on the Ball Milled experiments, i.e. I performed all the ignition tests using HS camera, performed all the characterization using SEM, XRD, and DSC, carried out most of the evaluation and finally contributed to writing the papers.

In Paper 6, I helped planning the experiments, contributed to the ignition tests using HS cameras and performed the characterization using SEM, XRD and DSC.

Acknowledgements

During my PhD studies I have received help from many people to whom I feel grateful. I believe that without their help I might not had the strength and will to finish these studies successfully.

Hence, I would like to gratitude people within the community of the University

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- Dr. Emre Gunduz, without whom I believe I would not have been able to fulfill successfully this PhD. His knowledge and guidance were valuable and he always supported me even from abroad.

- Mr. Kyriakos Roussias and Mr. George Vessiaris for their laboratory help.

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I would also like to thank people outside my research, who were by my side night and day, giving me the strength to move on and finally to be able to finish with this large step in my life. Hence, I would like to thank my family – father, mother, sister and two brothers. I hope in the next years we will rejoice when remembering my stress during the countless weeks and weekends, in addition to the nights I spent at UCY. Last but not least, a person who always supported me, and spend with me plenty of time in the lab, especially the last two years, my husband Doros, who never refused an evening walk to the lab.

Thank you all, I really appreciate your help!

Abstract

Nanoscale and microscale heating sources, produced by methods such as sputtering, chemical reduction and electrochemical deposition, have received increasing attention in recent years as enabling tools for nanofabrication/-manufacturing. These exothermic materials consist of heterostructures made of reactive multi-material systems, e.g. bimetallic aluminum (Al) and nickel (Ni) networks, which upon external ignition release locally concentrated exothermic heat.

Sputter deposited nanoscale multilayer films/foils (MFs) employed as nanoheater sources appear very promising in thermal nanotechnology, since they are stable, reliable, can be ignited relatively easily with a low-energy spark from a battery, and show self-propagating exothermic reactions (SPER). However, the usage of MFs is restricted due to their high production costs (mainly using Physical Vapour Deposition). This thesis was directed towards finding a way of approaching the exothermic behaviour of MFs by producing reactive compacts using mainly Ball Milling (BM), and to a lesser extent Ultrasonic Powder Consolidation (UPC).

Although BM has been used extensively to produce materials Al/Ni compounds with superior high-temperature mechanical properties, here the use of low-energy interrupted and continuous BM to synthesize materials that exhibit SPER is reported. Low–Energy BM (LEBM) was used to mix Al/Ni powders with molar ratios of 1:3 and 1:1, to refine the composite particle microstructures up to the formation of nickel aluminides, and to determine the critical milling time in order to produce ignitable compacts. Experiments were carried out in the Al–Ni system, because both powders are relatively inexpensive, and their reactions are highly exothermic and well characterized. The milled powders were cold-compacted into pellets and ignited along their edges using either a small propane flame source or a low energy spark from a 9 V battery. The reactions were investigated using high-speed optical and infrared cameras to measure the thermal front velocity, local ignition and maximum pellet temperatures, overall sample temperatures during ignition and the time required for ignition. The pellets were characterized using Differential Scanning Calorimetry (DSC) to measure the overall

reaction enthalpies. DSC scans were interrupted between the exothermic peaks. X-Ray Diffraction (XRD) was used to determine the phases that form before and after ignition, and for the interrupted DSC scans to compare the pellet thermal response and the phase evolution to those of vacuum deposited MFs.

LEBM experiments performed on Al/Ni powder mixtures at an atomic ratio of 1:3 showed that highly reactive compacts with nanoscale lamellae can be produced that exhibit similar thermal and phase formation characteristics to MFs with nanoscale bilayer thicknesses, albeit at lower thermal front velocities. Ignition experiments indicated near adiabatic reactions occurring within the pellets, which could be relatively easily ignited with a locally applied small propane torch. LEBM of Al/Ni particles with an overall composition of NiAl can produce powders with similar lamella structures, which upon cold-compaction into pellets can be locally ignited using a low energy spark from a battery and react in a self-propagating manner with uniform thermal fronts having velocities up to 0.24 m/s. The powders can be incorporated into pure foils or surfaces using rolling to generate thick reactive foils suitable for large scale bonding and can be ignited away from the weld interface using a spark. In summary, similarities between BM powder pellets and sputtered MFs were observed. BM has therefore the potential for a novel and economical processing route for generating powders that can be shaped into useful geometries (such as rolled into thin sheets) for thermal manufacturing applications, and they can be an alternative to MFs used for bonding applications.

UPC was mainly used for the synthesis of Al/Fe_2O_3 and Al/Cu_2O compacts over a wide range of powder ratios at room temperature. Powder consolidation was achieved by a multistep procedure involving simultaneous application of pressure and ultrasonic vibrations. The observed reaction characteristics of the composites (ignited using a plasma source) are similar to those of previously reported thermite compacts prepared by a traditional powder metallurgy method. Short processing times and non-requirement of special processing conditions make the ultrasonic powder consolidation process very promising. While further work is necessary to develop this process into a full-fledged powder metallurgy method for reactive powder systems, it is believed that this technique can be used as effectively as that of the existing ultrasonic consolidation methods that are used in layered manufacturing techniques.

Σύνοψη

Πηγές ενέργειας στη νανο-κλίμακα και στη μικο-κλίμακα, παράγονται με μεθόδους όπως βομβαρδισμό με σωματίδια, χημική αναγωγή και ηλεκτροχημική εναπόθεση, και έχουν ελκύσει το ενδιαφέρον τα τελευταία χρόνια ως πιθανά ικανά εργαλεία στη νανο-κατασκευστική και μικρο-κατασκευαστική. Αυτά τα εξώθερμα υλικά αποτελούνται από ετεροδομές φτιαγμένες από αντιδραστικά συστήματα πολλών υλικών, π.χ. διμεταλλικό αλουμίνιο (Al) και διατάξεις νικελίου (Ni), τα οποία μετά από εξωτερική ανάφλεξη, απελευθερώνουν εξωθερμικά, τοπικά συγκεντρωμένη θερμότητα.

Υπερ-λεπτά (στη νανο-κλίμακα) πολύ-στρωματικά υμένια (ΠΥ) τα οποία έχουν εναποτεθεί με βομβαρδισμό, χρησιμοποιούνται σαν νανο-θερμικές πηγές, και εμφανίζονται πολύ υποσχόμενα στη θερμική νανοτεχνολογία, αφού είναι σταθερά, αξιόπιστα, μπορούν να διεγερθούν σχετικά εύκολα με χαμηλής ενέργειας σπίθα από μια μπαταρία και εκθέτουν αντιδράσεις εξώθερμης αυτό-διάδοσης (ΑΕΑΔ). Ωστόσο, η χρήση ΠΥ περιορίζεται λόγω του υψηλού κόστους παραγωγής (κυρίως χρησιμοποιώντας Φυσική Εναπόθεση Ατμού). Αυτή η διατριβή είχε σαν στόχο την αναζήτηση ενός τρόπου προσέγγισης της εξώθερμης συμπεριφοράς των ΠΥ με την παραγωγή αντιδρουσών συσσωματωμάτων χρησιμοποιώντας κυρίως Μηχανική Άλεση (ΜΑ), και σε λιγότερο βαθμό Υπερηχητική Συνένωση Κόνεων (ΥΣΚ).

Παρόλο που η ΜΑ έχει χρησιμοποιηθεί σε μεγάλο βαθμό για τη παραγωγή μειγμάτων Al/Ni με ανώτερες μηχανικές ιδιότητες σε υψηλές θερμοκρασίες, σε αυτή τη μελέτη, γίνεται αναφορά στη χρήση συνεχόμενης και διακοπτόμενης χαμηλής ενέργειας ΜΑ. Η χαμηλής ενέργεια ΜΑ έχει χρησιμοποιηθεί για την ανάμειξη Al/Ni κόνεων, με λόγο μοριακής συγκέντρωσης 1:3 και 1:1, για τον εκλεπτυσμό των μορίων που αποτελούν την μικρο-δομή μέχρι την δημιουργία δομών αλουμινιδίων νικελίου, και τον καθορισμό του κρίσιμου χρόνου άλεσης για την παραγωγή συσσωματώσεων που μπορούν να αναφλεχθούν. Πειράματα με το σύστημα Al–Ni έχουν εκτελεστεί, λόγω του ότι οι δύο σκόνες είναι σχετικά φθηνές, και οι αντιδράσεις τους είναι πολύ εξωθερμικές και καλά περιγραφόμενες. Οι αλεσμένες σκόνες είχαν συσσωματωθεί σε θερμοκρασία δωματίου σε σφαιρίδια και είχαν αναφλεχθεί στο άκρο τους

χρησιμοποιώντας είτε μια μικρή φλόγα προπανίου είτε μια σπίθα χαμηλής ενέργειας από μια μπαταρία 9 V. Οι αντιδράσεις είχαν μελετηθεί χρησιμοποιώντας υψηλής-ταχύτητας κάμερα και υπέρυθρη κάμερα για τον υπολογισμό της ταχύτητας του θερμικού μετώπου, την τοπικής θερμοκρασίας ανάφλεξης και της μέγιστης θερμοκρασίας του σφαιριδίου, της ολικής θερμοκρασίας του δείγματος κατά τη διάρκεια της ανάφλεξης και του χρόνου που χρειάστηκε για τη ανάφλεξη. Τα σφαιρίδια έχουν χαρακτηρισθεί με τη χρήση Διαφορικής Ανάλυσης Θερμιδομέτρησης (ΔΑΘ) για τον υπολογισμό της ενθαλπίας των αντιδράσεων. ΔΑΘ είχε γίνει με διακοπή ανάμεσα των εξώθερμων κορυφών. Διάθλαση με Ακτίνες-Χ (ΔΑΧ) είχε χρησιμοποιηθεί για το καθορισμό των φάσεων οι οποίες έχουν δημιουργηθεί πριν και μετά από κάθε ανάφλεξη, και για τη διακοπτόμενη ΔΑΘ για τη σύγκριση της θερμικής αντίδρασης και των φάσεων σε σχέση με αυτά των υπο-κενό-εναποτιθέμενων ΠΥ.

Πειράματα χαμηλής ενέργειας ΜΑ εκτελέστηκαν σε αναμειγμένες σκόνες Al/Ni με ατομικό πηλίκο 1:3, και έχουν δείξει ότι μπορούν να παραχθούν συσσωματώματα που αποτελούνται από λεπτά-στρώματα στη νανοκλίμακα και τα οποία έχουν υψηλή αντιδραστικότητα. Αυτές οι σκόνες έχουν χαρακτηριστικά παρόμοια σε θερμική ανάπτυξη και χημικό σχηματισμό με αυτά των ΠΥ τα οποία έχουν διπλοστρωματικά υμένια στη νανοκλίμακα, μολονότι με χαμηλότερες ταχύτητες θερμικών μετώπων. Πειράματα θερμικής ανάφλεξης έχουν δείξει ότι σχεδόν αδιαβατικές αντιδράσεις μπορούν να συμβούν στα συσσωματώματα, τα οποία μπορούν να αναφλεχθούν σχετικά εύκολα με την εφαρμογή τοπικά ενός μικρού πυρσού προπανίου. Σωματίδια Al/Ni από χαμηλής ενέργειας ΜΑ με συνολική σύνθεση NiAl μπορούν να παράγουν σκόνες με παρόμοια λεπτά στρώματα στη δομή τους, τα οποία μετά από συσσωμάτωση σε θερμοκρασία δωματίου μπορούν να αναφλεχθούν τοπικά με τη χρήση χαμηλής ενέργειας σπίθας από μια μπαταρία, και να αντιδράσουν με τρόπο αυτό-διάδοσης με ομοιόμορφα θερμικά μέτωπα τα οποία έχουν ταχύτητες μέχρι 0.24 m/s. Οι σκόνες μπορούν να ενσωματωθούν μέσα σε υμένια ή επιφάνειες χρησιμοποιώντας κύλιση για τη δημιουργία αντιδραστικών υμενίων μεγάλου πάχους τα οποία είναι κατάλληλα για συγκολλήσεις μεγάλης κλίμακας και τα οποία μπορούν να αναφλεχθούν μακριά από την επιφάνεια συνένωσης χρησιμοποιώντας μια σπίθα. Συνοψίζοντας, ομοιότητες μεταξύ των κόνεων ΜΑ και των ΠΥ που έχουν εναποτεθεί με βομβαρδισμό έχουν παρατηρηθεί. Επομένως, η ΜΑ είναι μια δυναμική, νέα και οικονομική μέθοδος για τη δημιουργία κόνεων οι οποίες θα διαπλαστούν σε χρήσιμες γεωμετρίες (όπως η κύλιση σε λεπτά υμένια) για εφαρμογές στη θερμική κατασκευαστική, και μπορεί να αντικαταστήσει τα ΠΥ στις συγκολλήσεις.

Η μέθοδος ΥΣΚ χρησιμοποιήθηκε κυρίως για τη σύνθεση Al/Fe_2O_3 και Al/Cu_2O συσσωματωμάτων σε μια ευρεία κλίμακα αναλογίας κόνεων σε θερμοκρασία δωματίου. Η συνένωση κόνεων είχε επιτευχθεί σε μια διαδικασία πολλών βημάτων η οποία ενέπλεκε ταυτόχρονη εφαρμογή πίεσης και υπερηχητικών κυμάτων. Τα χαρακτηριστικά των αντιδράσεων των σύνθετων κόνεων που παρατηρήθηκαν (τα οποία αναφλέγηκαν με πηγή πλάσματος) είναι όμοια με συσσωματώματα θερμιτών στα οποία έγινε αναφορά και τα οποία έχουν ετοιμαστεί με παραδοσιακές τεχνικές μεταλλουργίας κόνεων. Ο μικρός χρόνος επεξεργασίας και η μη αναγκαιότητα ειδικών συνθηκών επεξεργασίας κάνουν την ΥΣΚ μια μέθοδο πολύ υποσχόμενη. Καθώς περαιτέρω έρευνα είναι απαραίτητη για την ανάπτυξη της μεθόδου σε μια μέθοδο μεταλλουργίας κόνεων για αντιδραστικά συστήματα, πιστεύετε ότι αυτή η μέθοδος μπορεί να χρησιμοποιηθεί αποτελεσματικά όπως οι ήδη υπάρχουσες μεθόδους υπερηχητικές συνενώσεις οι οποίες χρησιμοποιούνται σε τεχνικές κατασκευαστικές στρωμάτων.

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Part I

1 INTRODUCTION

Self-Propagating Exothermic Reaction (SPER) was firstly observed and developed in the Former Soviet Union. SPER is also called Self-Propagating High-Temperature Synthesis (SHS), since initially it was used mostly for material synthesis. Members of the Institute of Chemical Physics, in 1967, discovered the phenomenon of igniting titanium-boron mixtures, where they observed a luminous front propagating and clearly separating the initial reactant mixture from a hot solid product [1]. Interpretation and further study of the phenomenon concluded that materials of different chemical character are able to interact under SPER. These materials may be solid, liquid, gaseous or even mixed, and form hard refractory products by self-heating even at very high temperatures. In the 1960's, the identification of material systems that exhibited SPER was a success, before realising that there were so many reactive systems [2, 3, 4]. According to scientists, most interesting were the initially solid substances, which became the objective of research due to velocities and mass transfer differences, with parallel explosive behaviour and lack of gaseous products involved.

Useful refractory compounds like borides, carbides, and silicides were then easier to produce without any special efforts. As expected, the products from the beginning exhibited a notable hardness, allowing for a new approach to the problem of refractory compound synthesis, with high purity products compared to those produced by other methods such as furnace synthesis, but with lower porosity. Moreover, the non-metal and metal compounds, stable at high temperatures, evolved structurally with temperature during the process. Following that realization, there was refractory compound production on the industrial scale, stimulating further development of technological work, even though the compounds required different processing conditions. In 1975, scientists started combining SPER with metallurgy and machine-building technology for sintering, hot-pressing, extrusion, rolling and welding in order to synthesise parts and products of elaborate shape and suitable size with the desired properties.

The interest of scientists in SPER increased between the 70’s and the 80’s, where the number of exothermic-behaviour-related products increased suddenly to over 400 [1]. The unique properties of SPER such as the extremely high temperature, fast heating rates and short reaction times caused interest in the synthesis of materials, especially with potentially controllable microstructure. Synthesis mechanisms and microstructure forming processes were studied, which in some cases included post-combustion treatment, with the purpose of producing materials with desired properties. The mostly used treatment is annealing at temperatures between 800^{o}C and 1200^{o}C, since thermal stresses become minor especially in brittle materials. Of importance are considered the characteristics of green mixture reaction conditions, which are related to the reactant particle size, the particle morphology and size distribution, the stoichiometry, the initial density, the sample size, the initial temperature and the gas pressure. Mostly studied are the front propagation velocity, the temperature as a function of the time profile, and the maximum temperature, with the latter attracting the maximum attention. Ideally, heat losses would be considered negligible and hence complete conversion of reactants would take place, with the maximum temperature reaching the adiabatic temperature. However under non-ideal conditions, the maximum temperature depends on the experimental parameters and the material-particle characteristics.

Experiments indicated that self-propagating reactions are highly exothermic and self-sustaining. However, they do not self-initiate typically without an external ignition source. Another approach is to heat the entire sample up to a certain temperature at which the reaction becomes spontaneous. In the latter case heat-wave propagation is not observed, but the reaction takes place nearly simultaneously everywhere in the reactant mixture. Hence, the reaction characteristics of the concerned materials have to be studied according to the experimental and material parameters for a complete study of the behaviour of the sample during reaction.

Additionally, information of the sample after reaction might also be valuable, since theoretical expectations were eliminated during studies, indicating that modelling oversimplifies the reaction characteristics. One example is the fact that the expected defects and impurities due to the high temperature gradients are not formed during experiments.

The investigation of the ignition of metal porous substances in nitrogen led to the theory of filtration, which exhibited the oscillatory and spin waves of the ignition, important for the chemical stability processes. A stationary interlayer reaction is not trivial and propagates with spatial inhomogeneities. The layer to layer reaction propagation consists of characteristic modes, i.e. the oscillatory and the spin mode. The former is characterised by rapid cyclic displacements and stops, flashes and extinctions, whereas the latter propagates at constant velocity along definite encircling trajectories at one or more reaction spots [5, 6]. Later it became clear that both regimes were manifestations of an unstable condition, due to sensitivity to longitudinal minor perturbations and to transverse perturbations for oscillatory and spin regimes respectively, in general called thermal instabilities [7]. In both cases the layer ahead is heated due to the heat transferred [6].

SPER features are attractive for commercial synthesis with the potential for new materials and lower costs compared to conventional methods of furnace synthesis. The apparatus needed for synthesis is relatively simple, since no equipment is required for bulk heating of the materials, while significant reduction of workspace makes this synthesis feasible outdoors. Additionally, there is a notably small amount of impurities, even lower than those of the initial material, which shows that the material self-purifies. Synthesis temperatures might be higher in comparison to conventional furnaces, which, in addition to the short reaction time, introduce the production of materials and articles directly during reaction. Additionally, the high temperatures result in melting of products presenting more dense products. However, materials synthesis using SPER is favourably lower in cost since synthesis is simple with no additional equipment. Even low-cost materials can be ignited/processed with significant reduction in workspace requirements. The power consumption is the minimum since it utilises heat solely from chemical reaction with no external source, hence feasible outdoors. Presence of metastable phases and unique structures were observed.

For the above reasons, SPER is used for the formation of

a) Abrasive tools, cutting tools and polishing powders
b) Resistive heating elements
c) High-temperature lubricants
d) Neutron attenuators
e) Shape memory alloys
f) High-temperature structural alloys
g) Steel processing additives
h) Electrodes for electrolysis of corrosive media
i) Coatings for containment of liquid metals and corrosive media
j) Powders for ceramic

Modern fabrication technology in the micro- and nano-scale has introduced novel materials with unique geometrical and material structures and capabilities. However, a limitation to future development are the often expensive materials, the toxic chemicals, the requisite research lab-grade instrumentation, the necessary cleanroom environment, the little flexibility and environmental safety. These industrial limitations restrict the utilization of nanostructures and inherit the old technology to the new microscale devices with nanoscale features.

Reaching down to the nano-world, self-assembly of atomic and molecular complexes yields a large variety of random branching trees, such as grain structures in metals and alloys, crystalline dendrites of oxide nano-rods, block copolymers, star fractal polymer networks, and biomolecular constructs of proteins and DNA [8]. Some of them are reactive and could be used in thermal nanotechnology, such as metal and metal oxide nano-powders, sol-gel systems, nanocomposites obtained from mechanical alloying and sputtered multilayer films [9, 10].

The most notable reactive structures are multilayer foils (MFs). Nano-composite foils are manufactured via vapor deposition techniques, e.g. physical and chemical vapor deposition, via electrochemical deposition, mechanical fabrication, evaporation, and magnetron sputtering (the most common technique). Sensitivity of multilayer foils to fabrication of chemically distinct layers is known, which is attributed to the atomic fluxes from each source of layer deposition, while biaxial stresses need to be controlled. Film ignition characterization should follow that of overall thickness, and the thickness of each layer individually. According to Gunduz et al., [11], during ignition of very thick bilayers (thickness in the order of microns), the thermal distance ahead of the flame front becomes comparable to the overall foil size. This leads to the requirement of bulk heating of the foil to start the reaction in the thermal explosion mode for thick bilayers, which was observed experimentally [12, 13]. By adjusting the bilayer thickness, the reaction velocity can be varied between 0.01-30 m/s. The application of MFs as heat sources has been prohibited so far, mainly due to limited control of the heat generation rate.

Most attention has been directed to titanium and molebdenium silicides which have excellent oxidation resistance, high melting points, low density and high electrical and thermal conductivities. Intermetallics of Ti with Ni, Co and Fe require low increase above room temperature to initiate self-sustained reaction. They have shape memory characteristics and have been used in industrial production of sheets, tubes and wires with shape memory in Russia. Aluminides were composed using Ni, Ti, Zr, Cr, Co, Mo, and Cu, with the first two to receive most of the attention. Aluminides have been used as binder for carbides and borides, and on the other hand they have been utilised as intermetallics since they possess high heat of formation and can be produced by exothermic regimes. Aluminides have high plasticity at the reaction temperature, and hence pore-less aluminides can be produced with different methods like hydraulic hot pressing, hot rolling under vacuum, dynamic densification and super-plastic consolidation [1].

Anodized alumina templating offers an affordable non-clean room high rate patterning technique for deposition of nanorods in dense arrays across the layer thickness [14]. Such anodized aluminum oxide membrane display uniform, densely packed hexagonal arrays of cylindrical nanopores with thickness up to 500 μm and diameters up to 250 nm [8]. These nanopores arrays can be used as templates for fabrication of various metallic nanorods. Successive films can be deposited in alumina. Bilayer Al-Ni nanorods were deposited and could be ignited as Al-Ni MFs [14].

Carbon nano-network deposition was shown to produce fractal tree structures with trunks, branches and leafages made of carbon allotropic forms. Branching carbon nanotubes using Ni nanoparticles as active catalyst, was the result with different reaction rates [8].

Nanoheaters of different heterostructures made of reactive multi-materials systems were fabricated by different processing techniques. External ignition allows release of concentrated exothermic heat. Such thermally active structures were fabricated by roll bonding of alternating metal foils stacks and by ball milling or ultrasonically consolidating powders [15, 16]. However, bulk heating of the specimens is required since the layer thicknesses of multilayer foils could not be approached. Metal oxide nano-powders are more widely used compared to the metal powders. The thermite reaction leads to the formation of a more stable oxide and metal composites. However, their processing is difficult due to difficulties in homogeneous mixing, low compressibility, passivation and abnormal self-ignition. Micro-sized powders exhibit intense interaction when the melting of Al is reached, whereas nano-powders are fairly active in solid-state reactions as well. It was observed that the fraction of active aluminum decreases from 99.5% for 20 nm particles to 44% for 30 nm particles, hence decreasing the maximum temperature reached [9].

Sol-gel systems also exhibit exothermic behavior. The advantages of sol gel systems are homogeneous mixing, thin layer formation, short cooling times and higher burning rates from metal and metal oxide nano-powders due to lower conductivity. Disadvantages are the large amount of gas phase products, and the low burning temperatures [9].

By observing the different scientific methods of advanced material formation and the design of very small devices, two different approaches can be presented; the "top-down" and the "bottom-up" approach. The first approach takes a block of material and whittles it away to the object that is wanted; for example, melting metal into shapes. The second approach handles individual atoms and molecules to an assembly, as if creating an atomic building. Having comprehended how mechanisms in nano- and micro-world could work through chemical, physical and biological understanding and the development of new structures of nano-fabrication [17], both approaches could be precise. In this research, the fabrication of cost-effective reactive structures is required and the replacement of the existing relatively expensive structures, i.e. thin films, by low cost structures. Hence, the replacement of a "bottom-up" method, i.e. sputtering, by two, less expensive "top-down" methods, i.e. Ball Milling and Ultrasonic Consolidation, is required.

The advantage of a cost-effective structure of the "top-down" technique intrigues research. However, the disadvantage of a non-controllable technique, which cannot be studied in detail in-situ, might restrict straightforward results. In contrast, a bottom-up technique might be more controllable and the observation of potential problems is more possible, while a top-down technique, like BM, could not be so precise in overcoming the questions that arise through the studies. Hence, the assumption is that cost-effective advanced materials could be formed for industrial applications although parallel difficulties while lowering the scale might result in not well-described materials.

The issues of process robustness, flexibility, throughput, efficiency, affordability, health, safety and environmental sustainability are central in technologies and manufacturing. Regarding yielding low production costs in industrial realization, the non-cleanroom, robust, affordable, continuous manufacturing processes are designed for low infrastructure needs, and for scale-up to multiple parallel production lines.

3 BACKGROUND ON SELF-PROPAGATING REACTION

3.1 Heat Wave-front Characteristics and Reaction Propagation

SPER is characterised by a heat wavefront travelling across the material. The reaction is followed by zones of chemical reactions and various physicochemical conversions, stable or unstable. The temperature profiles of the heat wave-front carry information for the process and the material, and hence scientists devoted effort on the characterisation of the temperature profiles using thermocouples and optico-spectral methods, indicating four types of temperature profiles. These profiles are named narrow zones, wide zones, chemical stages and phase transition as illustrated in Figure 1 [6]. The first case, the Narrow zone (Type I), is the most common theoretical approach, where the wave propagation consists of a heated layer and a narrow reaction zone. The Wide zone (Type II) consists of two subzones, the propagation and the post-reaction where the first one promotes the wave-front displacement. The Chemical stages (Type III) are characterised by two zones of chemical reactions, where the wave-front propagation is affected only by the first zone. Type IV, the Phase transitions, is characterised by the presence of an isothermal region, a plateau that results from chemical reaction and parallel phase transitions, e.g. melting.

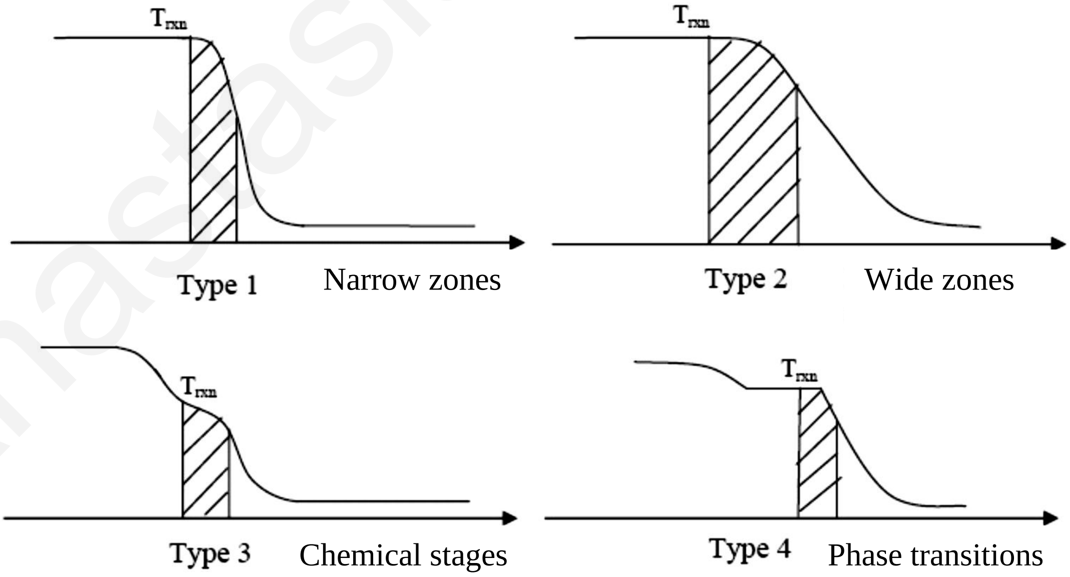


Figure 1: Temperature profiles associated with the heat wave-front [6]

Type I is completely different than the other three profiles, since there is complete conversion of the substance, and the maximum temperature is evaluated by thermodynamic calculations assuming negligible heat losses. In contrast to the other three types, the front velocity depends on the partial conversion of the substance at temperatures lower than the adiabatic temperature. Heat losses and incomplete conversion of the initial reactants affect the temperature, until complete conversion of reactants results due to the presence of a narrow reaction zone. It has to be noted that the temperature profiles cannot completely describe the wave structure, since other parameters are also important to describe during experiments [6].

The last three profiles inhibit the reaction: Type II with the product layers, Type III with phase transformations where the melting point is equal to the temperature that the conversion initiates, and Type IV with multistage spatially separated reactions as complex reactions. The actual temperature profiles may be a combination of several elemental ones. Some computer simulations indicated that the reaction synthesis might be described by initiation of the reaction with a sudden peak which briefly exceeds the adiabatic temperature. However, these profiles resemble early works in reaction of gasses where an ignition model was used [18].

The reaction after igniting a system is a chemical reaction localised in the vicinity of the heat wave-front and propagates throughout the reaction media, converting the reactants into products. Two groups of reaction waves exist; continuous and discrete. The first one can be assumed when the size of heterogeneity is small compared to the thickness of the reaction wave, whereas the second one is characterised by large scales of heterogeneity. During both cases of reaction waves, space distributions of temperature, concentration and density are present, and cannot be described as homogeneous. Nevertheless, the reaction propagates through such systems in a wave-like manner with approximately constant velocity. According to the homogeneous theory, the velocity is constant and slow due to inter-diffusion of the components, while the temperature profile shifts, maintaining its shape. The velocity and the temperature of the reaction wave define the behaviour of the system (e.g. spin).

3.2 Reaction Propagation

Initially, the external heat source is applied at one end of the compact, thus raising the temperature in the immediate layer to the ignition temperature. Once the reaction occurs, the external energy source serves no further purpose and can be switched off. The heat that evolves from the reaction heats up the adjacent reactant layer to the ignition temperature and hence a reaction wave travels through the compact on its own, consuming reactants and forming products. Since some of the heat of the reaction can be self-sustained, and the heat of reaction is used to heat up the adjacent layer, the adiabatic temperature will not be reached. If the reaction is not self-sustained, the compact must be heated to a higher temperature and then the heat which will be needed to raise the temperature of the adjacent layer is reduced, thus promoting self-propagating. However, a reaction might be restricted from being SPER if the heat is conducted away from the adjacent layer before it has time to reach the ignition temperature, usually with reactants with high thermal conductivities and high densities.

Chemical and structural transformations progress during the ignition, while chemical and phase compositions proceed behind the reaction. The phases formed can be characterised by the phase diagram of the system, either as intermediate products or either as final products at the state of local equilibrium. Typically during solid-phase reactions, low reaction velocities correspond more clearly at the phase diagram of the system. The products are mostly in the metastable state, since the reaction velocities are of the order of few millimetres per second, and after sequential chemical conversions, chemical completion away from the heat front forms the final structure. Hence the products do not reflect the phase diagram, since equilibrium phases may form in small amounts or may not form at all. The time of reaction completion is increased when more homogeneous products are formed. Hence, rapid SPER indicate experimentally a non-equilibrium condition which was not described adequately mathematically, since morphology, sample porosity, chemical and phase inhomogeneity and microstructure effects should be taken into account during layer-to-layer reaction. For example, intentional decrease of the maximum temperature results in a flake-structure which is inhomogeneous across the thickness.

Through years of study, researchers noted that the satisfactory operation properties of final products can lead to the chemical products of desired compositions, simple and multi-component materials of desired structure, samples of definite size and form, and products of required operational characteristics [19, 20, 21, 22]. Utilisation of cheap chemical energy instead of electrical energy, and of fast bulk self-heating rather than slow heating through the substance surface, could best describe SPER.

3.3 Microstructure and Reaction

SPER constitutes a gasless synthesis where the product is weakly influenced by changes of the environment, i.e. pressure or inert gases, and depends greatly on the material concentration ratios, reactant particle size, green density and maximum temperature. Microstructural models have also been studied, with variables including the reactant particle size and distribution, the product layer thickness and the combustion characteristics, including the speed and the maximum temperature. The first models that were developed considered that the elementary reaction cell consists of alternating lamellae of the two reactants which diffuse through a product layer to react.

Comparison of the micro-structural characteristics and the reaction wave indicated that coarse powders, larger than 40 μm, approximately correspond to the number of hot spots. In contrast, in case of finer Ti particles, every 3-5 particles form a hot spot. This is a first indication that several parameters of the wave-front strongly depend on the number, size and location of the Ti particles. Of importance is the fact that the typical lifetime of hot spots is at least ten times shorter than the time between consecutive appearances of hot spots in the same area, whereas larger particles cause a delay due to the requirement of preheating. Finally, hot spots have shorter lifetimes in dense samples. Hence, a decrease in reactant particle size does not lead to a quasi-homogeneous reaction; instead, the opposite holds true [23, 24].

The interstices between the zones can be divided according to the physicochemical nature of the initial and final product structures. The driving force of the whole process is the reduction of Gibbs free energy resulting from the formation of new chemical bonding, even at the presence of non-equilibrium conditions. At the final stage of the reaction, the free energy reduces further due to interfacial surface reduction, determining the crystal structure. These physical effects are completed at the end without further chemical compositional changes, and at the presence of quasi-equilibrium conditions. In general, it can be argued that the initial product structure may be defined as that formed during the chemical reaction in the proper zone, which becomes the starting point of the final structure that yields the desired product in the post-reaction zone.

The major physicochemical processes occurring during reaction according to Varma et al.. [1] are:

1. *Heat transfer from the reaction zone to the unreacted particles ahead of the reaction front*
2. *Phase transitions*
3. *Formation of eutectic melts and contact melting*
4. *Melting of reactants*
5. *Spreading of melting phase under the action of capillary forces and due to the reduction of surface tension*
6. *Coalescence of fused particles*
7. *Gasification of volatile impurities and reactants*
8. *Chemical reaction with initial product formation*
9. *Melting of intermediate products*
10. *Melt crystallization upon cooling*
11. *Crystal growth*
12. *Phase transitions in solid products during cooling*
13. *Ordering of the crystal structure.*

Up to the ninth process the temperature increases, and the other four take place behind the reaction front. Since the velocity is approximately constant, the conditions of product formation in the combustion zone are not significantly influenced by the heat losses. Further studies for the structure and material progress during reaction have been done by quenching specimens. Results have shown that there is a rapid increase in grain size that approaches a constant value in the post-reaction zone.

Examination of the Ni_3Al system has own that Ni_2Al_3 and NiAl layers initially appear at the surface of the Ni, and then the Ni_3Al product is formed. However, studies of a quenched Ni/Al system have shown that Ni and Al melt simultaneously and coalesce in the reaction zone, resulting in the appearance of NiAl crystals in the volume of melt. Homogenization of the chemical composition occurs at the post-reaction zone, and was named *reaction coalescence* mechanism by Rogachev et al. [25].

Theoretical results indicated that heterogeneous reaction results in at least one component to remain solid. Heterogeneous reactions occur by diffusion of the components through the solid layer of the product formed along the boundary between the reactants. However, solid state diffusion limited the diffusion rate, but thermal conductivity in the bulk solid material is considered to be significant for the heat transfer of the reaction. The experimental results discussed above indicated that diffusion controlled by mass transfer of the liquid is only observed at a small portion of the systems during the experiments.

The heterogeneous reaction initiates at a temperature related to the melting point of one of the reagents or to its dissociation, and hence is related to the reagent phase transformation and not to any ambient conditions. This correlation is strongly related to the enhancement of diffusion between the reagents. Thus, the thermal and chemical heterogeneity of the reaction media are important to describe the reaction wave propagation of the system, though there are no algorithms, homogeneous or heterogeneous, allowing precise calculations of the reaction velocity of the micro-mixtures without using a fitting parameter. Many of the existing theoretical results explain the experimental data, but none of them provide comprehensive patterns for this complex reaction.

Aleksandrv and Korchagin [26], trying to study the SPER, investigated the reaction between one film and one particle of different systems. They concluded that in all cases melting of the less refractory element initiates the reaction and hence there is not solid-solid reaction. Hence, they proposed the mechanism at which the melting of the less refractory element or eutectic mixture initiates diffusion of the atoms of the molten element into the more refractory elements forming intermediate phases. The reaction continues by the dissolution of phases at the liquid intermediate-phase boundary, with the processes progressing simultaneously and consuming more and more refractory element, while the intermediate phases remain constant. When the concentration represents a saturation level, the final product is reached. Hence, the rate of reaction is governed by the diffusion and formation of intermediate and final products.

It was determined that the interaction between particle-foil components initiated after the appearance of a liquid phase that diffuses into the solid phase. Hence, a primary product layer allows the solid to pass to the liquid phase by dissolution. It is very important that diffusion coefficients of the liquid component exceeded the known values for the bulk bimetallic samples. Structural results are similar to those detected in the quenched reaction zone, which show that fine grains form at the early stages of experiments, followed by coarsening of grains, which takes place in a few seconds. Their agreement suggests that the particle and foil experiments simulate particulate reactant interaction within pressed compacts.

3.4 SPER and different parameters

SPER can occur in two modes, the SHS and the volume synthesis. When heated by an external heat source, the exothermic reaction system initiates through local heating, or uniform heating for the latter one (volume synthesis). SPER is considered to be a well organised wavelike propagation of the exothermic chemical reaction through a heterogeneous medium, followed by desired products, with peak temperatures up to 4000K [18]. The volume reaction requires the sample to be heated uniformly until the reaction initiates, usually for weakly exothermic reaction that refer to preheat requirement before reaction starts. Volume reaction synthesis via various heaters was used in the past to synthesise weakly exothermic systems. Both modes are characterised by extremely high temperatures, fast heating rates and short reaction times. There is no precise tailoring of the product microstructure based on the synthesis mode, the process or the reaction.

The main characteristics that affect the reaction include mean reactant particle size, morphology, size distribution of the reactant particles, reactant stoichiometry, initial density, sample size, initial temperature, and dilution if present. The most commonly described reaction characteristic, which depends on the above main characteristics and on the amount of reacted material, is the maximum temperature. The maximum reached temperature can be assumed equal to the adiabatic temperature if there are negligible heat losses and if there is complete conversion of the reactants, which rarely occurs.

The dependence of the velocity on the particle size of the reactants has been examined by Naiborodenko and Itin [27] for the case of synthesis of NiAl, and it was concluded that the lack of dependence of the velocity on the particle size of Al implies that this element is in the liquid state during reaction. In a subsequent investigation, the same authors [28] suggested that the particle size of both reactants (A1 and Ni) is important in determining the velocity of reaction, despite their conclusion that both metals are molten in the reaction zone. Both observations were summarised at the observation that the wave velocity decreases with increasing Al size for fine Ni particles, and is independent of Al size if coarse particles of Ni are used.

Different laboratory techniques have been designed to study the velocity and the temperature distribution of the samples which exhibit SPER. These methods include pyrometers, heating apparatuses, and pressure and density variation measurements. However, little improvement was observed since difficulties include date acquisition, control, and analysis of the techniques. Merzhanov [29] and Rice [30] generalised several experimental results, and Varma et al., [18] generalised the relationships of Figure 2. It is observed that both reaction temperature and velocity have maximum values when

- the green mixture has the most exothermic reaction
- the initial reactant particle size decrease
- there is no inert diluent
- there is maximum initial temperature
- the sample is larger than a critical value

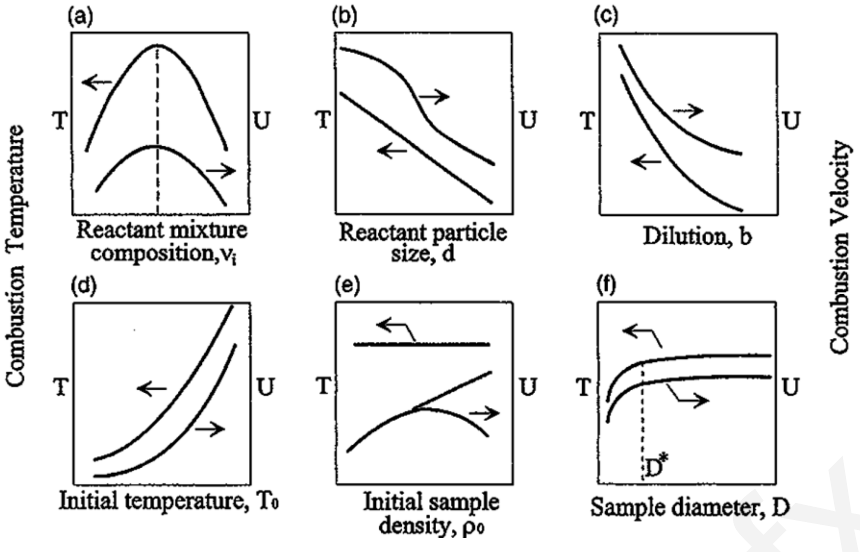


Figure 2: Reaction temperature and heat wave-front velocity as a function of sample parameters i.e. reactant mixture composition, reactant particle size, dilution, initial temperature, initial sample density and sample diameter [18]

Many exceptions have been observed and, hence, it is important to consider each system individually. For example, as shown in Figure 2e, the green density effect on the reaction propagation rate indicates that the reaction velocity increases as density increases, or has a maximum value. Different explanations have been suggested with most scientists attributing the main role to the effect of thermal conductivity, while others suggest the effect of diffusivity to be greater. The reaction propagation rate constantly increases when intimate contact between the reactant particles increases and, hence, velocity increases [23]. Merzhanov et al., [6] suggested that the velocity observed as a function of the green mixture density has a maximum at some intermediate value. As the density is increased the contact between the particles increases, which favours the reaction and propagation. However, as thermal conductivity increases, more heat is lost due to the conduction from the reaction zone to the unreacted area, inhibiting the propagation. These assumptions, even though theoretically based, have not been proven experimentally, but are only based on experimental considerations of the velocity increasing as a function of the green density [1].

Observation of the dependence of wave front velocity as a function of green density of the Ni/Al system for pre-heat treatment and for no previous heat treatment indicates that the samples that were not heat-treated exhibit a maximum, whereas in non- heat-treated samples the velocity increased with increased density. This behaviour changed for different stoichiometric ratios and for different materials. For example, for the same Ni/Al system at a ratio of 3:1, a monotonic increase was observed. The requirement of heat treatment was attributed to different adsorbed gas impurities. In the same experiment, dependencies also included the initial temperature of the sample, which increases the velocity monotonically with increasing initial temperature of the sample. This is due to greater melting and coalescence of particles in the reaction zone, which also increases the sample permeability.

In an early work on the Ti-C, Nb-B and Ti.B systems, it was observed that densities between 0.38 and 0.56 are characterised by a SPER, whereas an oscillatory mode is observed for higher densities. For relative low sample densities, escaping of desorbed gases during the combustion wave is not limited by permeation and occurs without the destruction of the reactant medium structure. By increasing the density, thermal diffusivity increases and hence the velocity increases. At higher densities, adsorbed gases are unable to escape due to low thermal permeability and as a consequence gases are trapped inside the pores, lowering thermal conductivity and forming cracks. On the contrary, in pellets with higher initial densities, the passage of expanding contaminant gases during sample preheating was restricted due to lower permeability, resulting in lower final product density. At lower densities, expanding gases are expelled more easily, increasing the density.

From another point of view, the application of pressure during the reaction or immediately afterwards has shown that high density products are obtained by

a) reaction hot pressing / reactive sintering under compression
b) reaction hot isostatic pressing
c) shock and dynamic compaction
d) high pressure reaction sintering
e) powder injection molding
f) Exo-Melt process for melting and casting
g) reaction infiltration
h) hot extrusion reaction synthesis
i) microwave combustion synthesis

3.5 SPER through modelling

In this project, no theoretical calculations were considered, since for the calculations the complex estimation that involves diffusion control, phase transitions, and multistage reactions result in a complex heat release function. One of the mostly studied subjects, heat wave-front velocity, indicated that heat conduction occurs much faster than mass diffusion. As a result, mass transfer by diffusion may be neglected at the macroscopic scale and an average reactant distribution in the local region may be used. Usually, in computational simulations, thermal and physical properties are the average of reactant and product values. The chemical reaction during the exothermic reaction is controlled only by heat evolution and heat transfer from the reaction zone to the unreacted mixture. Additionally in the heat estimations, melting and evaporation of the reactant might be introduced as a negative heat source, with the phase transformation to be taken into account.

Not many theoretical and experimental results converge to the reaction propagation characteristics, since different experimental conditions correspond to different characteristics. The conclusion is that the unique conditions of reactions lead to very high rates of chemical interaction. Due to the extremely fast heating rates there is not enough time for the completion of the reaction, and intermediate products form with various percentages of chemical conversion [18]. The one reactant melts and spreads out on the surface of the second, which increases the common surface of the two reactants and hence the reaction rate. If the reaction temperature is much higher than the melting point of both reactants, then the reaction rate approaches a critical heating rate. Under those critical heating rates the chemical reaction is relatively slow, since it proceeds by diffusion of melted reagent though the solid layer of the product formed at lower temperatures.

Modelling of only binary elemental systems have been studied extensively [11, 31, 32]. If a binary system of powder mixtures is considered, it can be observed that one substance covered by layers of the others, provides large reactive surface if the particles are small. The real mixtures are more complicated, since the surface of contact is small between the particles, thus failing to provide purely solid state reaction. In the case of a melting agent, the reaction-rate increases due to the melting in the preheating zone and the wettability under the action of capillary forces. The melted agent spreads over the surface of the other agent particles, raising the rate of the reaction process. If the elements do not melt, then solid state diffusion might take place, and the mass transfer of the reactions is compensated by the large contact surface promoting high-rate reaction [3, 33, 34].

Steady state propagation is observed when optimum experimental parameters describe a constant temperature profile. However, when they move away from the optimum, there are unsteady propagation regimes that are described by oscillating and spin reaction synthesis. The reaction regimes are important since they do not only influence the product microstructure but also the properties of the product. Thus, modelling is more complex.

3.6 A closer observation

One restriction to the study of the reaction in detail, could be the thermocouple size, which was shown that it should have a thickness of much less than the width of the reaction in order to be able to characterise the thermal structure, i.e. it should be less than a few micron meters, since the scale of heterogeneity is on the order of the precursor dimensions. In general, an apparatus that could observe the spatial resolution on the micron level and time scale in microseconds should be used, for example high resolution pyrometers. The resolution of the systems for characterisation should be able to test the hypothesis that a flat reaction wave-front propagates in a steady state manner. However, monitoring of the same process with a video camera with micron-resolution indicated that the reaction front has an irregular shape and propagates in a sequence of rapid jumps and long hesitations [23, 24]. It is observed that in conventional magnification, the wave-front appears flat and linearly propagating, whereas at a closer observation it is revealed that the wave front is irregular with convexities and concavities. Results have shown that the microstructure of the combustion front is comparable to the particle shape and size. Heterogeneity increases by increasing the reactant particle size and sample porosity, which makes the sample wave front characteristics more complex. The difference is shown in Figure 3, where the obvious difference indicates the discrete manner propagations during monitoring at different resolutions. Difficulty in measuring the velocity of the wave-front supports the conclusion that the different wave-front points travel with different velocities and hence observed bulk estimated velocity is an average value. According to Mukasyan et al., [23] this indicates that the reaction hesitates most of the time. This concept affirms that the process of reaction is in two steps, a) rapid reaction of the specific local area and b) long ignition delay during which the next reaction cell is preheated. Therefore, while the one region preheats the other propagates, and hence this is named “relay-race”.

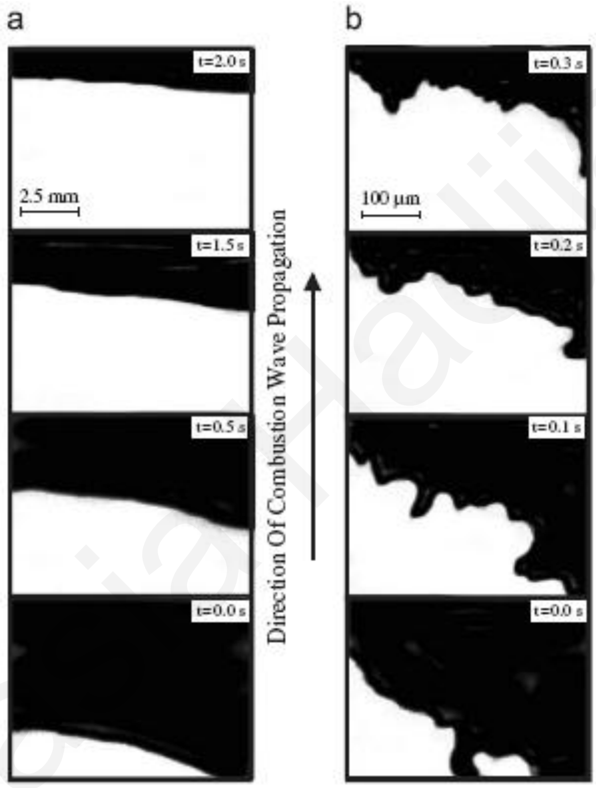


Figure 3: Wave-front propagations [23]

Observation by micro-video analysis also indicated that the temperature is non-uniformly distributed, and there are small bright hot spots randomly spread at the vicinity of the reaction front. This indicated that there are local regions of high temperatures, leading to a virtual propagation of high-temperature along a lateral direction of the front. Hence, the hot regions exceed the average temperature of the reaction front and the reaction rate is much higher. Hot spots were suggested to be present at the locations of the most refractory reactant at the melting point of the other reactant, e.g. at the Ti-Si system, the Si melted at the solid porous media and spread over the surface of Ti. Mukasyan et al., [23] pointed out that the melting point is indicative of the ignition temperature of the system, and while the reaction time is small, the generated heat does not have enough time to dissipate from the local area, causing hot spots which might be greater than the adiabatic temperature of the system. For this reason, criticism has been made of theoretical results, indicating that according to the fundamental theory, the ignition temperature is determined by the balance between reaction heat evolution and heat losses, which can vary from one experiment to the other, and hence the ignition temperature is not a constant value.

The characteristics of the reaction wave front, including velocity and maximum temperature, are affected by the processes that occur during the reaction and are shown in Figure 2 above. The different zones that characterise SPER have been experimentally determined by analysis of the temperature profiles using a thermocouple. The studies have shown that the length of preheating zone varies from 0.05 mm to 0.3 mm, and can reach 20 to 30 mm for multistage reactions. The reaction time can reach 10 s and the temperature up to 3000K. Hence, for these systems SPER is characterized by fast heating rates, short reaction times and very high temperatures.

4.1 Activation energy

SPER can be initiated in MFs by applying locally a small pulse of energy. The energy can be supplied electrically using a spark of a current pulse, thermally using a filament or a hotplate, or optically by using a laser pulse. If sufficient energy is supplied, chemical mixing of layers will accelerate, and heat will be generated fast enough for the reaction to propagate across the specimen. In an alternative method of ignition, a sample can be heated uniformly until a state is reached where the reaction can initiate as self-sustaining.

Activation energy (AE) is the energy required to initiate the reaction, and hence it is leading the chemical reaction of the reaction wave. Thus, it is related to the diffusion in the substance, i.e. high diffusion rate causes a high AE. AE was shown theoretically to increase with temperature increment. However, experimental results indicated initially that intermetallic systems have higher AE than other systems. Furthermore, Knyazik et al., [35] indicated that a reaction of high AE exists below the melting point, of Ti and C systems, and essentially of zero AE above the melting point, which could not be established experimentally. Further study of the AE indicated that a quasi-homogeneous model predicts independence of the sample porosity, since it is related to the elemental process and atomic diffusion in the sample.

AEs vary according to the different methods of the preparation of diffusion couples [36]. Intermediate layer formation, since it includes nucleation and growth, results in higher AEs, whereas bulk diffusion couple studies might also give different results than thin film diffusion couples. Hence, for Ni_2Al_3 the reported AE varies between 98,6 kJ/mol and 126 kJ/mol, whereas $NiAl_3$ AE varies between 119 kJ/mol and 167 kJ/mol. Additionally, AE varies according to the method and the materials used, for example the AE of Ni_2Al_3 of thin films [37] was reported to be 136 kJ/mol. V. Filimonov et al., [38] reported the lowest activation energy for Ni_3Al powder, which was 4.4 KJ/mol, in contrast to previous reported values of 330 kJ/mol and 155kJ/mol. However, the powders processed by this research team were mechanically alloyed, which through plastic deformation of the mixture resulted in a large decrease of the ignition temperature and AE. Other research teams also observed a decrease of AE due to BM, with the decrease to reach almost half of the raw materials [39].

4.2 Adiabatic temperature

A very important parameter is the adiabatic temperature of the reaction, which is the temperature reached under adiabatic conditions. However, the adiabatic temperature value depends on the temperature at which the heat is released and hence it should be specified when reporting the adiabatic temperatures (usually reported at room temperature). The adiabatic temperature exhibits a roughly linear relation to the enthalpy over heat capacity ratio, i.e. $\frac{\Delta H_{298}}{C_{p298}}$. This linearity indicates low sensitivity to heat capacity [7]. Empirically it has been demonstrated that reactions are self-sustained if the adiabatic temperature is higher that 1800K, which is related to ratio $\frac{\Delta H_{298}}{C_{p298}}$ greater than 2000K. Estimation of the adiabatic temperature should take into account melting of the compound, partially or wholly, and phase changes while the related heat capacity is taken into account. The lower adiabatic temperature can be attributed to the dissociation of the formed nickel aluminides and the consequent reduction in overall heat generation.

The adiabatic temperature can be established experimentally only if adiabatic conditions are present. However, heat losses are usually significant and the measured temperatures can be several hundred degrees lower that the estimated adiabatic temperature. An important deviation from adiabatic conditions relates to the geometry of the sample, since it is observed that by increasing the diameter of a cylindrical sample, the temperature increases up to a plateau value and then becomes constant with increasing sample diameter further. Hence, in Figure 4 it is observed that TaC and NiAl have a critical diameter of approximately 15 mm, while MoB has a critical diameter around 25 mm. Increasing the sample diameter increases the ratio of volumetric heat generation to surface heat losses. By increasing the diameter above a critical value the maximum temperature approaches the adiabatic value and the propagation velocity becomes constant. Incomplete reaction often occurs which leads to undesirable product phase composition.

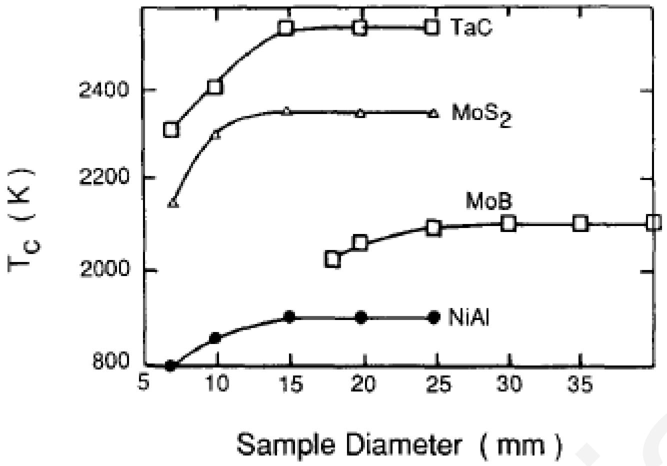


Figure 4: Maximum temperature as a function of sample diameter [7]

The dependence of the heat-wave front is illustrated in Figure 1 and is characterised by a maximum at some intermediate value. However, theory suggests that the velocity under adiabatic conditions should increase with increasing density, since there is a higher thermal conductivity between the particles. This controversy has been explained by various scientists. Varma and Lebrat [1] proposed that two competing phenomena exist, but they were not verified experimentally. As the density increases, intimate contact between the reactant particles increases, which enhances both reaction and front propagation, while an increase in thermal conductivity at higher densities, causes more heat to be lost from the reaction zone, inhibiting the front propagation. Another hypothesis was suggested by Kirdiyashkin et al., [40] who suggested that capillary spreading may control the reaction process due to the molten material.

The Ni-Al binary phase diagram contains Al_3Ni, Al_3Ni_2, Al_3Ni_5, NiAl and Ni_3Al, as shown in Figure 5 [41]. Among those, NiAl and Ni_3Al have the highest melting points and have received the scientific attention due to their relative low densities, good strength, high temperature corrosion, and oxidation resistance. Hence, they are considered candidate materials for high temperature structural and coating applications. An economic route for the production of these phases considered of industrial interest is via SPER. Non-requirement of external pressure, very short processing times, and low temperatures, compared to the melting points of these phases, result in energy savings and thus economic benefits for the industries. The mechanical properties of the intermetallics produced with SPER are equivalent to those by other processing techniques. Experimental and modelling studies of intermetallics keep growing, since the properties of nickel aluminides, in addition to the intermetallic nature, are attractive. Disadvantages of this technique are a) porosity of the products and reactants and b) the limited process control especially due to the very high temperatures reached [41].

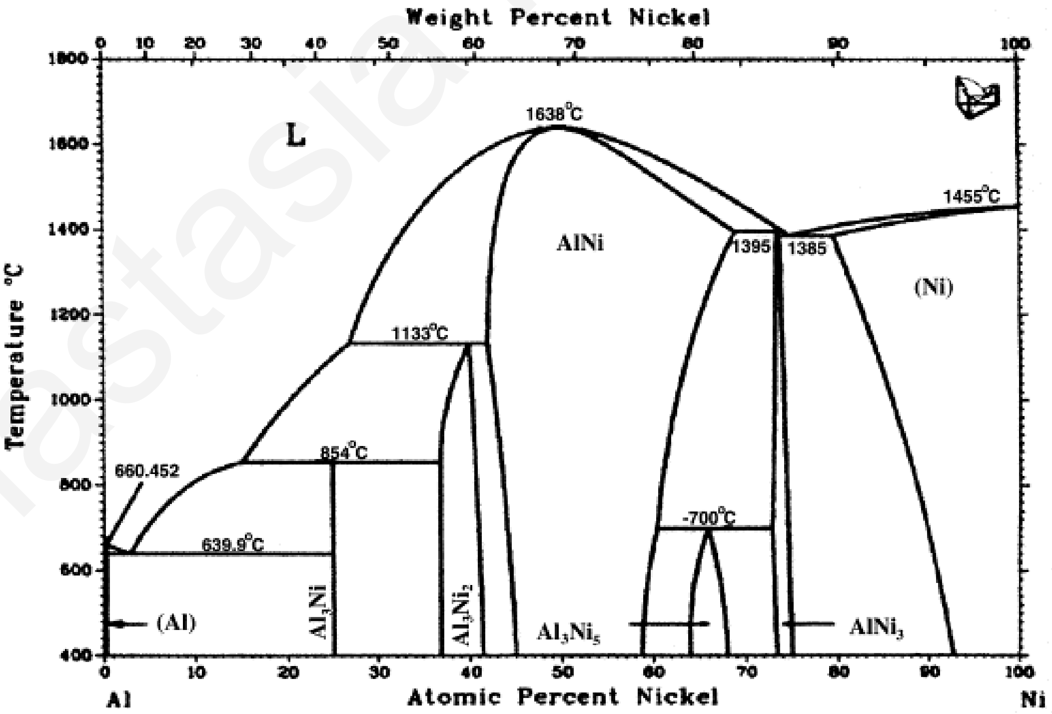


Figure 5: The Al-Ni phase diagram [41]

An important parameter in the reaction synthesis is the adiabatic temperature. The reaction that converts the reactants into products is exothermic and reaction rates can be high enough to assume adiabatic conditions. Therefore, the heat of formation raises the temperature to the adiabatic temperature with zero heat losses. However, when the maximum temperature is measured experimentally, it is found to be equal to or lower than the theoretical predicted adiabatic temperature. Heat losses can be attributed to incomplete reactions, reduced rates, large reactant particles sizes and radial heat losses from compact. The adiabatic temperature is useful in clarifying the reactants and products state. For temperatures lower than the melting points of the products, the reaction occurs in solid state, whereas for higher adiabatic temperature of one of the products, the reaction is in solid-liquid state. For temperatures lower than the boiling point of the reactants the reaction is termed gasless. Thermodynamic parameters of some Al-Ni phases are shown at Tables 1 and 2, whereas Figure 6 indicates the dependence of enthalpy on temperature.

Table 1: Enthalpy of formation, melting temperatures, adiabatic temperatures and ratio of heat capacities for Al-Ni compounds [41]

Compound	**ΔH_f**	**T_m (K)**	**T_{ad} (K)**	**C(R)/C(P)**
Al_3Ni	-150.624	1127	1127	0.24
Al_3Ni_2	-282.42	1406	1406	0.2
NiAl	-118.407	1911	1911	0.48
Ni_3Al	-153.134	1668	1586.5	0.23

Table 2: Specific heat capacity for Al-Ni compounds [41]

Compound	**Specific heat capacity**
Al_3Ni	$43.144+138.406x10^{-3}T+14.611x10^{5}T^{-2}-67.314x10^{-6}T^{2}$
Al_3Ni_2	$106.067+34.303x10^{-3}T-0.001x105T^{-2}+0.003x10^{-6}T^{2}$
NiAl	$41.925+13.6x10^{-3}T-0.033x10^{5}T^{-2}+0.1x10^{-6}T^{2}$
Ni_3Al	$88.491+32.218x10^{-3}T+0.001x10^{5}T^{-2}-0.001x10^{-6}T^{2}$

From X-ray analysis it was determined that the sequence of reaction in the formation of the aluminied includes

$3Al+Ni=Al_3Ni$

$Ni_3Al+Al=Ni_3Al_2$

$3Ni_3Al_2+9Ni=6AlNi_3$

with the main reaction being $Al+3Ni=AlNi_3$. Experimental results, for example studying Ni-Al joints, indicated that in some cases NiAl, Ni_3Al and Ni_5Al_3 phases are not observed [36]. In other cases, for example in powders, only Ni_5Al_3 was not observed, indicating the dependence of the results and the diffusivity variation on the processes. These phases, metastable or not, are followed by the main reaction which takes place above the eutectic temperature, 640^{o}C and includes a liquid phase component. Liquid phase reactions lead to more dense products.

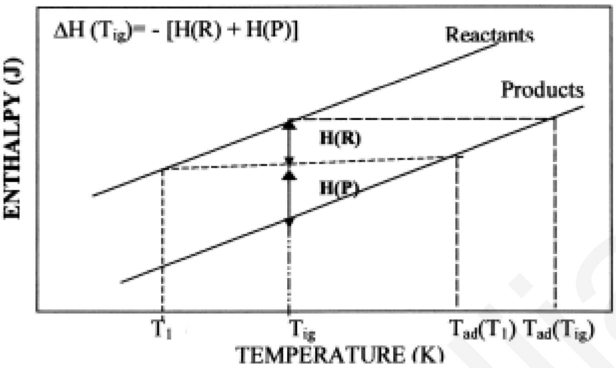


Figure 6: Enthalpy of Al-Ni as a function of temperature [41]

The reaction initiates first by the formation of a transient liquid phase, typically a eutectic or aluminium [12] (eutectic forms at 640°C and aluminum melts at 660°C). The transient liquid then spreads through the compact consuming both the nickel and aluminum. Low heating rates can give rise to the formation of aluminum-rich intermetallics prior to the liquid formation. The melting of aluminum is inevitable in the successful reaction synthesis of Ni–Al, as the melting point is only 20°C higher than the eutectic temperature. The presence of a liquid phase (eutectic or aluminum) during the Ni–Al reaction was found to have a prominent effect on the density of the final product.

Since a liquid is required for SPER initiation, it is important for the low melting point phase (Al) to be interconnected throughout the compact. Liquid causes densification by particle re-arrangement and capillary forces. If there are areas without Al, porosity will arise in areas in which there is no liquid phase at the reaction temperature. This is additionally due to the fact that capillary action of the transient liquid phase will not ensure interconnectivity and promote densification. It is accepted that due to rapid spreading of the liquid Al, pore formation at prior particle sites is common, especially at areas with large aluminum sections and large exotherms.

Hence, it was suggested that the reactant particle size should be chosen correctly in order to have complete reaction [42]. Biggs and Bhattacharya [43] indicated that aluminum should be 2.5 times smaller than the size of nickel particles, hence for Ni_3Al composition, volume fraction of aluminum should be 34%. Similar results were indicated for foils [12].

Although the eutectic Al/Al_3Ni precedes the reaction, thermal analysis indicated that the reaction can proceed at temperatures considerably lower than the eutectic. This is attributed to solid state inter-diffusion which forms predominantly aluminium-rich compound i.e. Al_3Ni and Al_3Ni_2. These reactions are exothermic and take place at lower than the eutectic temperatures for high heating rates [44] resulting in higher porosity due to the liquid spread. Morsi [41] suggested that phases like Ni_3Al that have less Al, have detrimental effects on the ignition temperature, whereas NiAl that have more Al, results in dilution of the exothermic reaction.

The lower the heating rates, the more likely the solid state inter-diffusion occurs. The higher the heating rates, there is loss of process control, and the external surface of the compact is heated more rapidly than the interior. Hence, the reaction initiates at the surface, moving into the interior. Additionally it was observed that:

a) Vacuum gives the best results since it reduces the heat loses to the surroundings, thus maintaining the ignition temperature for slightly longer times [45]

b) The adiabatic temperature increases if melting of one of the products (NiAl) is caused since the reaction kinetics is accelerated [46]

6 BALL MILLED SAMPLES: MICROSTRUCTURES, CHEMISTRIES AND GEOMETRIES

6.1 Introduction

Over the past few decades, Ball Milling (BM) has been used due to its simplicity and inexpensiveness for the production of solid state materials. It is a processing technique that has not totally been characterised, and which can create amorphous materials, nanostructure phases and at its simplest form to mix materials that consist of fine microstructure particles. The power that is given during BM process is capable of mixing powders even of incompatible materials, like Al, Ni, Ti and Fe [47], establishing a simple way for the creation of superalloys of unique microstructure. This power/force is given by rotating the vial that contains the powders-under-process and some balls. Thus, energy is delivered at very high rates via the powder-ball-vial collisions.

BM is also named Mechanical Activation, because it is based on balls that in a vial act as millers due to the huge power density that is provided to the materials [48, 49]. Arrested reactive milling and mechano-chemical activation are also some names that can be found in the literature and which combine the mechanical energy given, the chemical mixing and the activation of atoms due to the energy provided [3, 48]. The power is large enough to refine powders to even nanometer scales and hence mill the powder. This power is delivered as energy to the powder, and as a consequence the results depend on the energy given to the powder. BM is an alternative technique for producing metallic and ceramic powders in the solid state. Using this technique, it was discovered in 1986 [50] that non-equilibrium phases can be produced and even amorphous phases which attracted much attention.

Research on BM has mainly been carried out from the mechano-chemistry viewpoint, which in modern history starts at the end of nineteenth century by Carey-Lee, who had shown that the decomposition and sublimation of mercury and silver halcides is different upon heating and duration in a vial [3]. BM initiated as a way to disperse fine oxides particles in a nickel matrix, and immediately the advantage of producing amorphous phases was observed. Additionally, BM was utilised as a way to extend solubility limits and to prepare intermetallic compounds and amorphous alloys. Nanocrystalline alloys were first observed in high energy millers [51].

The first solid-state reaction was proposed by Goldschmidt in 1885 [3], where a metal oxide was reduced with aluminium in the so-called thermite reaction. The process takes place in a mixture of powder and is initiated by either a high temperature reaction or an electrically heated wire. Merzhanov [52] in 1967 started a more systematic research for SPER for the preparation of refractory compounds. The studies were mostly based on the fact that SPER influences the reaction velocity and product uniformity, and hence in combination with BM the advantage of each method is utilised. In 1982 Chakurov [3] investigated milled powders, Zn, Cd, In, Sn, and Pb, and the abrupt temperature increase inside the vial. Thermite reactions were investigated by Schaffer and McCormick as published in 1991 [53]. They assumed that the powder charge is characterised by an ignition temperature that decreases with milling duration without relating with other quantities. However, further studies indicated that processing the same mixture under different milling conditions helps classify macroscopic aspects of the process. Few reactions have shown unexpected features in the kinetics of SPER within the vial and composition dependence on the ignition time [54].

BM induces chemical reactions and hence mechano-chemical energy results in unique and metastable materials that cannot be prepared by conventional techniques. Parallel BM induces self-sustaining reactions in many exothermic powder mixtures. In the systems of interest initiation of the exothermic reaction does not happen at the beginning of the milling process, but a certain time of milling is required before an exothermic reaction is observed, called activation period. Size reduction, mixing and increase of the chemically active defect sites are comprised during activation period. A critical state is reached and then ignition takes place which propagates throughout the powder.

The easiest published way for detecting ignition is to monitor the temperature evolved inside the vial. Different positions of the thermocouple inside the vial result in different values of the monitored maximum temperature within the same time. The most sensitive and convenient position for placing the thermocouple is in the middle of the top surface, although, the temperature increment measured depends on the temperature distribution within the vial. The main difference with typical SPER is that this is performed in a bulk powder compact, with relatively little heat loss to the environment, while the powder in the ball mill is in close contact with the milling tools, and heat loss to the vial and the balls may inhibit the formation of a self-sustaining reaction front. Additionally, SPER outside the vial can be preheated.

The first metal-metal reaction observation within the vial was in 1990 from M. Atzmon, who combined Ni and Al powders to form NiAl [54]. In his experiment the ignition could not be observed upon continuous milling, but after half hour of cooling period, during interrupted milling. Ignition occurred within one minute resulting in an "interrupted reaction effect" [54]. The reaction could also be observed if a small percentage of Al was replaced with Ti or Fe. Most metal-metal systems are not exothermic enough, as for example $CaAl_2$ which has $-\Delta H / C$ =2980K, exhibiting softness and good heat conductivity of the components.

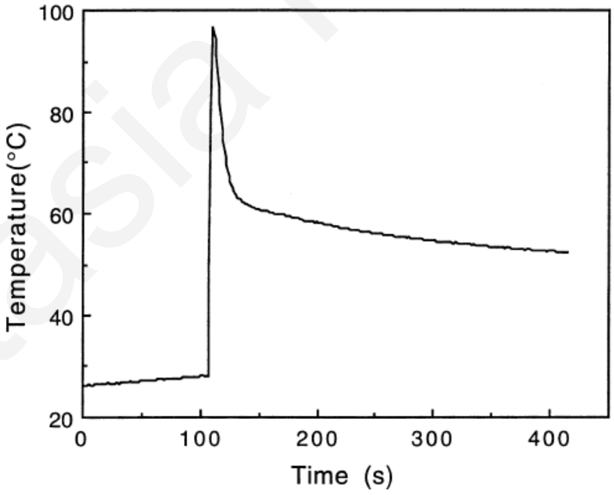


Figure 7: Temperature inside the vial as a function of milling time [3]

The ignition of a system was first detected by measuring the temperature inside a milling vial. Figure 7 shows the temperature increment observed inside a vial milling magnetite-zirconium powders. The reaction can be divided into three steps, (a) the first ~100s that size reduction and mixing take place until a critical state is reached, (b) ignition initiation results in heat release and hence abrupt temperature increase and finally, (c) incomplete reaction of the product, which needs more milling in order to result in a homogeneous product.

BM was used mainly as a way to improve product uniformity, and lower the ignition temperature [55]. BM is a helpful mechanism for further understanding the kinetics and in general the process of milling. Additionally, nanocomposites can be prepared during BM, which are destroyed if high temperature reaction takes place, since it results in large crystallites. Of importance is the conclusion that in order to avoid ignition, energetic materials should be prevented from igniting and hence reacting inside the vial.

Nowadays, the study of material reactivity is taken into consideration not only during milling but also upon milling. Pellets of reactive powder mixtures can be ignited by heating the whole sample uniformly or by local heating that results in a reaction front travelling along the sample. In both cases the ignition temperature is reached in order to initiate the reaction, while the ignition temperature and the propagation velocity can be influenced by mechanical activation. This was observed in different materials like Cr_2O_3 and Al, where the mechanical activation reduced the reaction below the melting point of Al. Similarly, Mo-Si reduced the initiation of the reaction temperature from 800 ^oC to 1200 ^oC. Hence, BM reduces the energy and the equipment cost, by reducing the grain size, formation of lamellar and uniform structures. It could be suggested that BM provides sufficient increase of the material reactivity even at ambient temperatures.

6.2 Diffusion during Ball Milling

Diffusion is a fundamental process during BM. Two mechanisms of diffusivity of atoms take place within the solid at the room or sub-ambient temperatures carried within the vial. Substitutional atoms diffuse by a vacancy mechanism, whereas smaller interstitial atoms migrate by forcing their way between the larger atoms interstitially. Hence, the diffusion process depends on the type of site occupied in the lattice until new alloys are formed. Defect density increases during BM, and therefore, contributes to the homogenization of kinetics.

Diffusion can be presented mathematically by assuming Fick's second law

$$\frac{dC}{dt} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}$$

where C is the concentration of the solute atom element, D the diffusivity at each direction of the solute atom in each direction and t the diffusion time. Hence, the diffusion rate is proportional to diffusivity, which according to Arrhenius depends on temperature

$$D = D_o \exp(\frac{-\mathrm{E}}{RT})$$

where D_o is the materials constant, E is the activation energy, R is the universal gas constant and T is the temperature. For a two element system the diffusivity is a function of the two diffusivities.

During diffusion, an interstitial atom is moved to an adjacent interstice. Thus, high energy barriers must be overcome. The increase in free energy is referred to as activation energy, which for diffusion is equal to the sum of the activation energy to form a vacancy plus that to move the vacancy. During BM, the total activation energy is decreased to the energy of vacancy movement, since the energy of vacancy formation is obliterated.

Diffusivity is greater along a free surface, less along a grain boundary and smaller along a defect-free lattice. Hence, the atoms can migrate easier along a free surface. This is also demonstrated in Figure 8 which shows the diffusion via the surface (smallest slope), the grain boundary and the lattice (largest slope). The surface tends to be a region of relatively high disorder, and hence activation energy is low while lattice activation energy has the highest value. In contrast, diffusion dominates at the surface and is lower in the lattice. As the temperature increases, grain boundary diffusion increases and at higher temperatures lattice diffusion dominates.

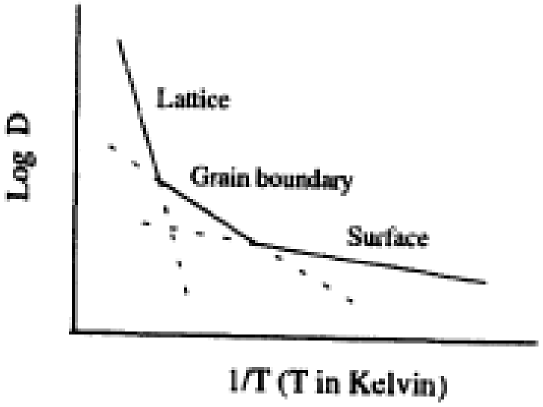


Figure 8: Diffusivity as a function of inverse temperature [56]

BM is a process of repeated cold welding and fracturing of powder particles, which results in a large number of defects and microcracks. Due to the former, the activation energy for diffusion is decreased, and due to the latter, the increased free surfaces cause an increase of the internal energy. A decrease of activation energy is caused also by a temperature increase. BM decreases activation energy by the formation of more free surfaces and grain boundaries, which is equivalent to an increase of diffusion temperature. It can be concluded that a decrease in activation energy and change in diffusion mode are very important for the process.

6.3 Particles and Microstructures

Another phenomenon observed during milling is the grain refinement. As shown in Figure 9, the grain size is reduced from 25 μm to 45 nm after 250 minutes of milling. The results shown indicate Ni and Al mechanical alloying using XRD measurements. Diffusivity increases as the size is decreased, with a dramatic change when the crystalline size reaches nanometres. The diffusivity was estimated by Lu et al., [56] to increase approximately 8 times if the grain size decreased from 20μm to 2μm for the same system and approximately the same temperature. It was estimated by the same authors that diffusivity is the same for a grain size of 25 μm at 1166K and for grains of 55 nm with diffusion temperature of 400K. Due to the decrease of grain size the mode of diffusion changes from surface and grain diffusion to lattice diffusion. Additionally, the thermal diffusion is a steady diffusion process which in addition to the dynamic diffusion process of BM results in continuous diffusion processing. The inter-diffusion layer is soon broken by the alloying process and new surfaces are formed with increased diffusion areas and hence enhanced diffusion kinetics. Thus, an increase of diffusivity is a physical effect, which during BM causes a difference in atom concentration and hence diffusivity changes. It has to be emphasised that due to the dramatic decrease in diffusion temperature and increase in diffusion area, it is possible for some elements, which are very difficult to be diffused using the ordinary powder metallurgy method, to be alloyed at relatively low temperature.

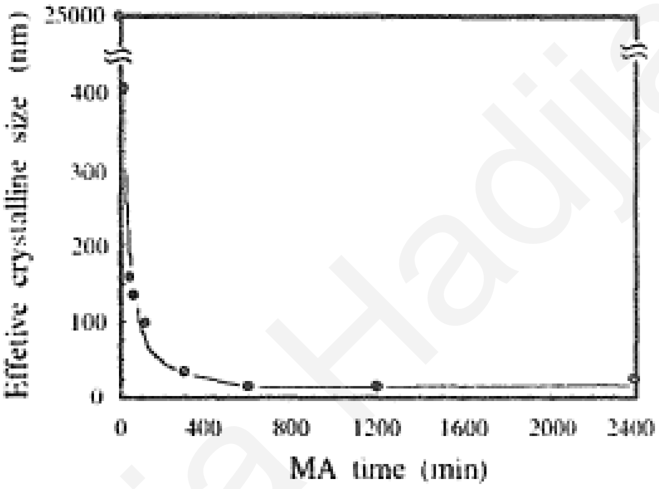


Figure 9: Effective crystalline size as a function of milling time [56]

Solid state reactions involve the formation of one or more product phases. The reaction rates depend on the initial contact area, the diffusion of reactants through the product phases, and on the temperature. BM induces reactions since it was observed that the reaction rates increase with increasing alloying duration [56]. This is due to the repeated fracturing and re-welding of the powder particles which results in an increased contact area and hence an increased reaction area. During BM, a ductile material is usually used which acts as a binder to bind the powder particles together.

Local melting might be achieved by high collision energy. Schaffer an McCormick [53] pointed out that BM minimises the effect of product barriers in the reaction kinetics and hence alloying provides the conditions required for the promulgation of solid state reactions at low temperatures. The maximum temperature monitored inside the vial until 1997 was only 120°C. Hence, the temperature generated by collision was not a dominant factor and is far from reaching the diffusion temperature.

Powder particles during BM are subjected to high energy collision which causes cold welding and fracture. Cold welding and fracture enable the power of contacts with atomically clean surfaces and with minimal diffusion distance. Microstructurally, the BM process can be divided into three stages:

a) The powder particles are cold welded to form a laminated structure. At this stage the chemical composition of the particles varies significantly;
b) The laminated structure is further refined and fracture keeps taking place. The laminated structure becomes even finer and a very fine crystalline size can be observed;
c) The lamellae become finer until they disappear. The chemical composition is achieved for all particles, which finally results in a new alloy with a composition related to the initial powder mixture.

Therefore, it can be argued that BM increases chemical reactivity, even in cold BM which is usually the case.

6.4 Particles and Exothermic Reaction

BM was first applied to metallurgical systems, and nowadays is used to induce chemical reaction to a variety of powder mixtures in a dry or wet processing environment and at different atmospheres. In investigating SPER through BM, three important points [3] should be noted: applications, nanocomposites and mechano-chemical aspects. From an application point of view, BM is useful due to the valuable materials produced as refractory materials and ceramic-metal composite powders. Considering the nanocomposite side, there is more success using BM, but grain growth has to be avoided. Consequently, in the case where materials are characterised by SPER, measures have to be taken in order to prevent ignition during milling which causes grain growth. A new phase is formed by localised ignition of the grains, revealing that SPER comprises not only the wave propagation that is observed, but also multiple reaction effects [57].

BM has been studied extensively, aiming to describe it experimentally and computationally. It has been shown that relaxation of the powders inside the vial, even for thirty minutes, had as a result the change of the sample reactivity [54], and resuming of BM has as a result yielded an exothermic reaction, in contrast to non-stop BM. This change can be explained qualitatively, but not yet quantitatively, and for this reason, scientists tend to admit that the results have not yet totally been understood [3]. Hence, many experiments are published based on BM, showing the different behaviour of materials, the effect of size and relative quantities at mixing and creation of alloys. The dissimilar actions of materials can also be considered in discrete materials. For example, a change in BM parameters, such as the size of the balls, has as a result the creation of crystalline rather than amorphous material. Hence, powder materials, BM, relaxation time and hence temperature, are factors that have to be taken into account for the complete description of a BM process.

In general, the initial product structure may be defined as that formed during the chemical reaction through this reaction, which becomes the starting point of the final structure formation in the post-reaction zone during multistage reactions. A. Varma et al., [18] divided the physicochemical processes before, during and after the reaction in 5 zones, the green mixture, the preheating zone, the reaction zone, the post-reaction and structure formation zone and the final product. Those include heat transfer to green mixture, phase transitions, eutectic melts and melting of reactants, spreading of the molten phase under the action of capillary forces, coalescence of fused particles, gasification of impurities, chemical reaction with initial product formation, melting - crystallization - crystal growth – phase transitions and ordering of crystal structure for the final product formation.

All processes prior to and including the chemical reaction proceed during the rapid temperature increase, as well as during the possible melting of product. The fast progression of the reaction led to quenching methods to study the intermediate processes; methods like quenching in liquid, with shock waves and with copper block. Quenching of 3Ni-Al in Al melt showed that Ni_2Al_3 and NiAl layers initially appear on the Ni surface, followed by the formation of Ni_3Al [58]. The conclusion for Ni-Al was that Ni and Al particles melt simultaneously and coalesce, resulting in the appearance of NiAl crystals [59]. The results demonstrated that the final product for

Ni_3Al is preceded by NiAl and Ni_2Al_3, whereas for Ni-Al the initial product has the same overall phase composition as the final product.

6.5 Modelling and Characterization

Since SPER constitutes gasless synthesis, its theory is based on the comparison of the mass and thermal diffusivities of the solid reactant. The heat conduction, and hence thermal diffusivities, must be much faster than the mass diffusion and hence diffusion at the macroscopic level can be neglected, and an average concentration of the reactant may be used. As a consequence, an average of reactant and product values can be used for physical and thermal properties. Thus, SPER is controlled by heat evolution from the exothermic reaction, and heat transfer from the reaction zone to the initial-unreacted material. Experimentally, the phase transformations have been proven secondary and supplementary to significant thermal effects like melting and evaporation, though they introduce negative heat sources. Heat losses may also be due to convection and radiation.

Various types of kinetics have been introduced through different approaches. The reaction synthesis involves various processes including diffusion control, phase transitions, and multi-stage reactions. If the conversion during the reaction rate is ignored, which is reasonable since the temperature dependence of the reaction rate prevails over concentration dependence, an expression is derived which has been published by Zeldovich and Frank-Kamnetskii in 1938 [60]. The formula determining the effective kinetic constants from experimental data is

$$\ln\left(\frac{U}{T_c}\right) = -\frac{E}{2RT_c} + const.$$

where U is the heating rate, R is the gas constant and T_c is the peak temperature and E is the AE, which can be estimated from the inclination by plotting $\ln(\frac{U}{T_c})$ as a function of $\frac{1}{T_c}$. However, it is not clear if these reported values correspond to actual elementary processes or whether they are the result of complex interaction between transport and reaction phenomena during heat release.

Microstructure models take into account the reactant particle size and distribution and the product layer thickness. The reaction kinetics is implemented through elementary reaction cells consisting of alternating lamellae of the two reactants with diffusion and reaction through a product layer. Flat, rounded, and rounded with solid reactant surfaces (round on a square) cells have been taken into account, trying to analyse the redistribution of energy and the local features of the reaction medium. Novozilov [61] and many others afterwards concluded that the current theoretical results cannot be compared quantitatively with experimental data, since the description mechanism has been oversimplified. For example, most theoretical studies assume an infinitely narrow reaction zone, while the majority of the computations were performed on one- step reactions, along with the fact that the thermo-physical and kinetic knowledge cannot be associated to the heat-wave during the reaction. Hence, A.Varma et al., [18] concluded that new experimental results have to bridge the gap between the mathematical approach and the experimental reality of the process.

Different models were proposed for the explanation of ignition during BM. The characterisation of the powder was mostly related to the temperature at which the self-sustaining reaction initiated upon heating. The kinetic energy of the balls is used to increase the temperature of the powder caught between the colliding surfaces of two balls, and a ball which hits the vial. The highest temperature estimated during the models is the melting temperature of the samples. Schaffer and McCormick [62] suggested that the ignition temperature is larger than the melting temperature, and the ignition does not occur immediately. When the ignition temperature is decreased upon milling, and the ignition temperature reaches a value lower than the melting point, then the reaction starts upon first collision. Several factors contribute to the ignition temperature decrease, such as the decreased particle size, the reactant mixture that reaches a fine scale, the chemically active defects site formation, the dislocations formed, and the interfaces that provide fast diffusion pathways.

Several details have to be taken into account for the reaction model. One factor is the coverage of the balls with a compacted layer of powder. Additionally, calorimetric investigations of the intermetallics or the phases formed during thermally induced reactions have to be studied. Ignition temperature is considered a complex quantity itself, and hence prediction of its value can be related to the determination of the maximum temperature occurring during collisions, the powder properties and the modification of the powder properties during collisions.

Experimental investigations indicated that the temperature decreased during BM, which is a sign that the reaction kinetics cannot be characterised only by a single ignition temperature. Furthermore, the reaction rate also increases gradually along with the heating rate and heat transfer to the environment. The maximum temperature can be characterised by a single value during reaction. Therefore, it is suggested that deeper understanding can emerge from connecting theoretical results with empiricism.

BM and the ignition of a self-sustaining reaction are very complex processes. A full understanding of the process has to include the mechanical operation of the miller, mechanics of individual collisions, chemical processes, structural changes and defect formation. Different approaches were attended, especially for processing of a broader variety of materials and approaching the high exothermicity. Takacs [3] parallelises the problem as a "miniforging event" that follows compression of the powder, thermal and chemical processes. The mechanisms of the mill have to encounter and to relate the global motion of the miller and the motion of balls inside the milling container, rotation or slip, and the mechanics of an individual collision including elastic and plastic deformation of the powder.

BM is hence a complex process that requires understanding of the mechanical operation of the mill, the mechanics of individual collisions, the chemical processes, the structural changes, and the defect formation. L. Takacs [3] "miniforging event" has two outcomes.

a) ignition which leads to SPER – a single agglomerate or a powder layer initiates the reaction;
b) activation of the powders due to collision – comminution, mixing and defect formation take place.

All the parameters have to be taken into account since even a single collision might affect the later course of the process. This problem was initially studied through planetary millers, which through rotation and slip during collision have to be described considering viscoelastic properties as well. This is important considering the viscous resistance of the floating powders and the powder layer of the coating balls. Even the powder layer coating of the balls, frequency of collisions with specific relative velocities and impact parameters, and temperature change during collisions have to be taken into account. The complexity can be also described by the fact that collisions take place between two balls, or one ball and the wall. However, the different assumptions lead to different results, for example, 82K temperature difference was estimated due to different assumptions for the same powder, steel ball and velocity of the ball [50, 63]. Description of the chemical effects should include properties of the powder like the heat capacity, the latent heat of phase formation, the heat conductivity, and the kinetics of the system. However, all these attributes change according to the particle size and the porosity of the particles which change during mechanical activation.

Courtney [64] considered ductile metals important for the development and refinement of a layer structure. Of importance is the fact that trying to model the ignition, one of the most dominant models with predictive ability, assumed that ignition takes place in the miniforging volume, which was assumed to be represented by a thin, flat disk of reactant powder mixture [64]. The assumption did not include the confinement that the collision would create between the surface of the milling balls or a ball and the vial. The model considered that the layer of powder is hit by a ball and the kinetic energy is transferred to the powder as heat increasing the temperature. Mechanical collision takes place while the affected area of the flat-powder-layer is about 0.1 mm. Temperature distributions are limited by the energy balance equation, while density and specific heat, which depend on porosity, incorporate the layer thickness also.

The reaction takes place at the interface, and its rate depends on the specific interface area. Inter-diffusion is a possible reaction mechanism, but the situation is seriously complicated by mechanical activation. Transports along defects can short circuit intrinsic diffusion, drastically increasing the reaction rate. Fresh surfaces are created and brought together repeatedly, making a nucleation and growth mechanism possible. Heat transfer and heat loss also take place, while nonuniformity of the powder is important. The stresses inside the powder are not uniform, but concentrate randomly at points. Those point form hot spots, where the reaction can start even if the average temperature of the powder is not sufficient to initiate a reaction front [65]. It was implicated that any chemical reaction is initiated thermally. However, models considered that the kinetic energy of the balls, which result in local temperature increase, are not sufficient for chemical changes, and only an elevated temperature alone brings about chemical changes. This is not true for mechanical activation. Hence, experimental conditions should be studied for understanding the activation phase which might be related to ignition time.

The theoretical methods that were proposed have been considered incomplete since parameters that are not taken into account include material stuck on the vial and on the balls, while the threshold of individual reaction and material to react as a whole has not been set. In order to verify a theoretical method, experimental results can provide the guidelines not only for utilisation of materials, but also for a complete description of the powder reactivity through a complete characterisation.

6.6 Different Experimental Approach

Vibratory and planetary mills are considered suitable for the research at hand, since milling intensity, frequency of vibrations and rotations may vary easily. Chakurov et al., [66], while studying the ignition time at his vibratory mill, observed that the ignition time is about 2.6 times longer with lower intensity, while the temperature was about twice as large as the one with higher intensity. The milling intensity is adequately characterised by ball-to-powder ratio, which is proportional to energy input. Mechanical activation is related to the amount of absorbed mechanical energy. When the powder is sufficiently activated, statistically there is always a hot spot where ignition initiates. Hence, the ignition time is related to the rate of activation. The inverse proportional relationship between the charge ratio and the ignition time was initially confirmed by Schaffer and McCormick [53], experimentally proved, as shown in Figure 10, that there is also little dependence on the ball material. The experiments took place for TiC and CuO with Fe. However, later they [67] have shown that for alumina and agate the reactions remain gradual, showing that the ball material is also a variable parameter. Possible reasons why there is a difference between the ball-materials is that the impact of lighter materials is weak, and the stress in the reactants is such that they could not be excited, while there might be greater heat losses even if conductivity is greater. However, more experimental studies should take place.

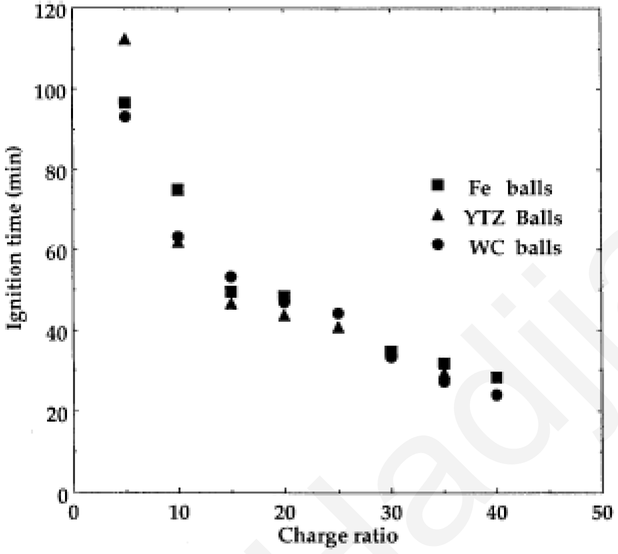


Figure 10: Ignition time as a function of charge ratio [3]

The most important material property is the adiabatic temperature (T_{ad}) or $\Delta H/C$. Hence, it is suggested that the most exothermic materials will have higher T_{ad} and hence higher $\Delta H/C$. Materials with similar reaction heats, adiabatic temperatures, crystal structures, and hence mechanical properties, phase diagrams, e.g. Zr and Hf, are expected to have similar chemical behaviours. However, the study of these elements indicated that the ignition time shortens, with the difference sometimes to be more than one order of magnitude high. This could be explained by studying the diffusion of the nonmetal in the product phase. The difference in diffusion properties can be rationalised by analysing the atomic structure of the relevant compounds.

The dependence of velocity and temperature over reactant particle size was studied above. However, even though the results have shown that the velocity decreases as the particle size increases, the proportionality varies to the diameter as $\sim\frac{1}{d}$, $\sim\frac{1}{d^2}$, or $\sim\frac{1}{d^{1/2}}$. The difference was explained by comparing the adiabatic temperature. The former (inverse linear) proportionality describes systems that have lower adiabatic temperatures than the melting points of the particles, like Ta-C, Ta-B and Nb-B. Systems that the adiabatic temperature is higher than the melting point of one of the reactants are characterised by the second variation (inverse square), like Ti-C, Ti-N, and Ni-Al. For these systems, it was shown that for rather small metal particle size the dependence is different than large metal particle sizes. The latter group (inverse square root dependence) includes mostly intermetallic systems in which the adiabatic temperature is higher than the melting points like Ni-Al and Ni-Ti, and Co-Ti [18].

Reactant particle size has not been studied extensively, even though it is considered important since the wave front velocity decreases while increasing particle size. Some systems, e.g. Ta and TaN, are characterised by independence of the particle size over the velocity and the temperature. This is explained by highly porous and large surface area that act as a large number of discrete nonporous-like fine particles, resulting in the same velocity of fine and coarser particles. The relative low maximum temperature compared to the melting point of the Ta and TaN, constrained the writers to attribute the system behaviour not on the particle size, but on the fact that the coarser particles were more porous with larger surface area at the same time. On the contrary, it has been also experimentally shown, that the ratio of the reactant particle sizes influences the microstructure of the final product. In the 3Ni-Al system, when Ni was 3 to 4 times larger than Al particle size, the microstructure was optimal, which was equivalent to dense final product and maximum material conversion.

One of the most effective and commonly used procedures to modify the synthesis conditions is to dilute the initial mixture with a chemical inert compound. Dilution is an example whereby the reacted system strongly affects the results. The maximum temperature and the heat wavefront velocity are decreased as the amount of dilution is increased for the Hf-B system. However, an exception is the Ni-Al system where a decrease is also noted but with a different trend, since an intermediate area for maximum temperatures indicates that the temperature is constant to the melting point of NiAl for dilution between 11.5% and 35.5%. Even the particle size of the inert diluent influences the reaction characteristics.

Interruption and room temperature aging can significantly alter the kinetics of some mechano-chemical reactions. The interrupted effect was firstly observed by M. Atzmon [54], who indicated that if equimolar mixtures of Ni and Al powders are milled continuously, NiAl forms in a gradual process and no abrupt temperature increase is observed. However, if they are milled and then interrupted, after being aged at room temperature, a SPER ignited within one minute upon resuming milling. Many others indicated this for different materials [53, 68]. However, in some materials, for example the Ti-Si system, the reaction initiated only after two interruptions, i.e. interruptions after 60 hours, again interruption after 48 hours, and then the reaction was observed after 32.5 hours [69]. The interrupted milling depends on the atomic level changes during room temperature ageing. This is explained by the fact that the critical size of the nuclei changes according to the temperature. For higher temperatures the critical size is larger, and hence during cooling at room temperature, the critical size decreased. Therefore, these nuclei growth is aided by the high mobility along defects.

Investigating the defect structure is difficult. An indirect method is to perform thermal analysis after mechanically activating the powder. Forrester and Schaffer [70] have shown that the energy activation of CuO and Fe decreased from 575 kJ/mol to 199 kJ/mol upon milling, suggesting a change from intrinsic diffusion to diffusion along defects. The activation of the powder can be characterised by the mechanical dose (absorbed energy per unit mass) received over a large number of collisions. Therefore, activation can be investigated by evaluating the energy balance of the milling process. Clear understanding of energy transport/dilution is important, as the effects of milling depend both on the total amount of energy transferred to the powder (activation) and the energy involved during collisions (ignition).

7 ULTRASONIC POWDER CONSOLIDATION

Ultrasonic Welding (USW) is a solid state welding process that produces welds by local application of high –frequency vibratory energy. The workpieces to be welded are held together under pressure, and the ultrasound is applied parallel to the work piece surface. Welding is achieved by diffusion of particles from each piece to the other. Among the advantages of USW is the non-requirement of special conditions such as inert gases, which makes this process preferable thanks to its rather low costs.

The ultrasonic vibration is generated in the transducer of the device and is transmitted to the sonotrode tip, until it finally reaches the samples, which are directly in contact with it. The difference between bonding with ultrasonic waves can be observed by studying the material flow. Application of the ultrasonic energy results in material flow, which is increased as the time increases, while gradual bonding between the surfaces to be bonded is achieved. The vibratory action removes surface contaminants to expose fresh material, and the centre of the bond area remains undisturbed to finally achieve a reliable bond. Oxidation and organic membranes on the material break down and disperse by the energy of vibration [71], resulting in a decrease of the process cost.

Ultrasonic welding involves parameters such as

- Static clamping force
- The oscillating shear forces and
- The low temperature rise in the welding zone.

The above parameters depend on factors such as

- the thickness of the welded specimen
- the surface conditions and
- the mechanical properties of the workpieces.

Even if the clamping force is applied perpendicular to the interface, the contacting sonotrode tip oscillates parallel to the surface, resulting in a combination of static and oscillating shear forces. Therefore, dynamic internal stresses are created in the workpiece, having as a consequence elasto-plastic deformation and hence roughening of the surface welded area. Elastic deformation results in reversible metal deformation, whereas plastic deformation results in dispersion of surface films, permitting metal to metal contact at many points, which grow into physically continuous weld areas.

USW takes place at room temperature and produces localized temperature rise. The local temperature increase depends on the machine settings and more precisely on the power provided to the specimen. In contrast, by increasing the clamping force, the temperature decreases and hence appropriate machine settings can be achieved. The low local temperature increment most times results in advantageous non-formation of intermetallics, which is important for keeping the properties of the specimen unchanged. The temperature rise during USW, is higher in metals with low thermal conductivity, and hence less energy is necessary for metals. Aluminium, which is soft and has a high thermal conductivity, is utilised widely as a material binder, and was used in this study for bonding with the harder nickel. Other soft materials can be used as well for good joining, since the lower the hardness, the more efficient is the transfer of the welding energy [72].

Among the advantages of USW is that the pressure requirements are not high, the welding times are very short and the thickness deformations are lower. Disadvantage of USW is the inability to weld thick layers. Hence, the quality of welding depends on the variables of USW like ultrasonic power, clamping force, welding time, ultrasound amplitude, frequency, base metal, and temperature change. All these determine the bonding achieved between the joint surfaces caused by considerable frictional heat from both sliding between the mating surface and ultrasonic vibration.

Metallographic examination of the ultrasonic welds reveals the phenomena that are involved during welding, such as interfacial phenomena, plastic flow and the heat effects that cause recrystallization and diffusion. During welding, atomic diffusion occurs across the interface and the metal recrystallizes to a very fine structure having the properties of moderately cold-worked metal. The two clean surfaces cause the atoms to attract one other and the vibration attains linkages between atoms. A transition layer is created, which can be also referred to as diffusion layer. Hence, welding is achieved by mutual bonding of the materials through atom flow and induced vacancies at the joint boundary. Gunduz et al., [73] state that at the point of welding, the high vacancy concentration observed may enhance diffusion at the weld interface by many orders of magnitude. However, vacancy concentration reaches steady state only in a few micro-seconds, and hence the value of diffusivity might be assumed constant.

Ultrasonic welding has emerged as an effective and potential joining process for several dissimilar or multiphase materials [74], and thus it is used for applications involving monometallic and bimetallic joints. The process is used to produce lap joints between sheets and foils, wires or ribbons and flat surfaces. USW is a production tool in the industry, mainly for aluminium parts and for sealing of parts that cannot be processed by high-temperature joining methods. Spot welding, ring welding, line welding~~,~~ and continuous seam welding, are the four kinds of ultrasonic welding which can be extended to micro-electronics.

Diffusivity of atoms and the plastic deformation of the particles are the two properties of welding that were utilised for consolidation of powders. This is a new utilisation of USW and a unique way to consolidate aluminium and nickel. During the experiments performed, the soft Al deforms to cover Ni grains by filling the voids to achieve full consolidation. Parallel diffusivity is favoured by ultrasonics which increases bonding between the two elements, favouring higher energy release through SPER.

Diffusivity increases at higher temperatures, and as a result full consolidation can be achieved only at higher temperatures. At lower temperatures, full consolidation is far from being observed, and only if the right temperature is approached the consolidation results can be considerable. Theoretical estimations based on Ni and Al atoms indicated that efficient intermixing can only occur at high temperatures which follow after a prior melting step [75].

Ni consolidation is hard to be achieved, and hence it can be argued that in lack of soft Al, consolidation cannot be achieved. This was experimentally observed at the BM powders, where it was observed that the processed powder could not be consolidated. The Al embedded inside Ni to form lamellar structures could not be utilised as a binder for consolidation. Hence, by increasing the Al amount inside the powder, consolidation might be effected.

Therefore, it can be argued that USW can be used for Ultrasonic Powder Consolidation (UPC) easily for the production of pellets with the desired density properties. The short duration times, the non-requirement of special conditions and any special surface treatments are advantageous. A prerequisite, but not a disadvantageous one, is the placement of the anvil and sonotrode below and above the powder, for powder-preservation purposes due to the high energy waves, aluminium or nickel foils. The foils can be thick and are removed from the pellets after ultrasonic processing. However, a small amount of particle diffusion is present, but it cannot be argued that this is essential for the thermal stability results.

Advantage is the fact that only consolidated nano-foils could be ignited using a spark [76]. Hence, the pellets characterised for micro-structure could only be ignited using a torch, indicating that controllable ignition could not be achieved successfully.

The experimental investigations, results and conclusions are presented in detail in the appended papers. Here follows a summary of the main results.

Paper 1:

A. Hadjiafxenti et al., *Journal of Alloys and Compounds*, vol. 505, p. 467, 2010

Paper 1 compares the formation of microstructural refinement and the reactivity of the samples during interrupted BM runs. The increased plastic deformation results in increased grain boundaries and dislocation, which is expected as the number of energy through collision increases. A critical milling time between 10 h and 20 h is believed to offer the reactivity that approaches thin films due to the differences between the two samples. The 10 h sample is characterised by fine lamellar structure and can be ignited within 4.25 s after a small propane torch ignited it at the edge of the pellet. A heat wave-front that requires 0.7 s to travel across the pellet characterises the reactivity of the 10 h sample. In contrast, the 20 h sample cannot be ignitedand only the part of the sample in contact with the flame reaches high temperatures. It is more likely that the formation and refinement of the lamellar structure permit the rapid initiation of SPER during the collision events. It has been speculated that ball milled powders equivalent to the 20 h samples in this study show the formation of a single phase $AlNi_3$ with the absence of superlattice peaks, which is then attributed to this phase being disordered.

Closer examination of the XRD results reveals that the samples milled for up to 10 h are characterised by Al and Ni before ignition tests. The aluminum and nickel peaks are increasingly broadened due to the formation of the fine lamellar structure and the internal stresses. After ignition tests, the powder compacts rapidly react and melt partially at the interfaces to form AlNi, which is followed by excessive aluminum diffusion into the nickel layers to form $AlNi_3$ and extended solid solutions.

Thermal analysis indicated exothermic peaks at low temperatures. The increasing milling time results in the formation of additional peaks and peak shifts towards lower temperatures, related to further mixing and lamellae refinement. The 5 h sample shows two peaks, the 7 h milled sample exhibits three peaks and the 10 h milled sample shows four major peaks indicating that the lamellar structure. The 20 h milled sample shows only one small peak which might correspond to a relaxation process such as stress relief or recrystallization. All the samples show the large endothermic peak associated with the melting of $AlNi_3$.

The low ignition sensitivity of the samples milled for up to 10 h, compared to sputtered nanoscale multilayer foils, is probably due to the remaining nickel particles which might act as heat sinks, as well as persisting voids, lack of good thermal contact during cold compaction of the powders into pellets.

Paper 2:
A. Hadjiafxenti eta al., *Journal of Alloys and Compounds*, vol. 505, p. 467, 2010

Paper 2 is a more detailed study of interrupted BM and indicated that two categories of samples are present. The first category includes samples milled for up to 14 h. Reaction was only observed after sample temperature (ST) reached values in the vicinity of initial temperature (IT). The recorded maximum temperature (MT) was near the maximum calibration limit of the IR camera. The second group of samples consist of pellets ball-milled for more than 14 h. These samples exhibited SPER relatively fast without requiring a substantial increase in ST with IT values near the melting temperature of Al. The reaction modes observed using an IR camera indicated that for the first category, the temperature of the entire pellet reached high temperatures before the reaction initiated, indicating the requirement of preheating. In contrast, the second category was characterised by a sharp flame front that travelled rapidly across the pellet.

The microstructure of samples milled for less than 14 hours indicated that initially the softer Al particles mechanically mixed with micro-welded Ni fragments, fragmentation of the Ni particles follows parallel to more boundary welding and shear deformation. Further milling results in finer microstructure features due to the hardening of the Al-rich matrix, and hence more efficient load transfer to the Ni particles1. Longer milling durations, above 14 h, resulted in finer lamellar structures, composed of thin layers of Al and Ni along with the remaining larger highly deformed Ni particles, as also described in *Paper 1*.

By correlating ignition tests and microstructure, it is indicated that increasing milling time resulted in a substantial decrease in the required ignition time due to smaller diffusion distances across the more refined lamellar structures. The first category of samples is observed for microscale sputtered multilayers and powder mixtures, where the large diffusion distances prohibit a sustained reaction. In the second category of samples, observed in sputtered nanoscale multilayers, the flame-front is able to self-propagate due to shorter diffusion distances across adjacent layers and faster intermetallic growth.

Ignition results in the formation of AlNi and $AlNi_3$ intermetallic compounds. The relative peak intensities of the intermetallics vary with milling time. For lower milling times, the local composition within lamella are closer to AlNi composition as some of the Ni remains separate, which would reduce the formation of $AlNi_3$. With increasing milling time, more of the Ni is incorporated into the lamellae through mixing, increasing the local compositions closer to $AlNi_3$, resulting in increased amounts of this phase. Ni peaks remain in all of the ignited samples, so the phase transformation is never complete after the reactions.

DSC traces show that increasing milling time results in additional peaks as well as a general peak shifting trend towards lower temperatures, related to further mixing and lamellae refinement, as discussed in *Paper 1*.

The flame front velocities measured for the second set of ball milled samples indicated that increased pellet density, due to better thermal contact between particles, results in a weak exponential increase in velocity. The lower porosity not only directly increases the rate of heat transfer due to reduced thermal resistance between particles, but also the diffusive mass transfer across particles. Of importance is the fact that there was no dependence of the MT on the measured densities, suggesting that reaction heats are not affected and the effect is only kinetic.

Paper 3:

A. Hadjiafxenti et al., *Vacuum* (under revision)

Paper 3 investigates continuous BM of Al/Ni at a ratio of 1:3. SEM, BSEM and profilometry images indicated that increasing the milling time resulted in particle size reduction, accompanied by the refinement of the microstructures with decreasing amount of pure Ni layers. Increased mechanical mixing consequently results in more uniformly distributed lamella, possibly due to the formation of Ni-rich solid solutions with Al as the solute, which, as stated in *Papers 1 and 2*, are work-hardened by the impact events during BM.

Ignition tests revealed that all samples had IT values higher than the melting point of the Al eutectic at around 900K, indicating that the reactions did not start until an Al-rich liquid formed. A reduction in ST at ignition and MT was observed with milling time. The images of the samples milled for 5 to 7 h indicate that the cooling due to the sample support was significant enough to affect the thermal wave front, which lost its uniformity when it passed beyond the halfway point on the pellets. The observed decrease in thermal front velocity with milling time can be attributed primarily to two counteracting effects. The refinement of the lamellar microstructure with increasing milling time, which increases the overall reactive surface area and decreases the diffusion distances across lamellae, increases the thermal front velocity, as observed in multilayer foils. The decreasing overall sample temperatures required for the ignition of the samples with increasing milling times results in higher thermal gradients ahead of the front and this cooling effect reduces its velocity.

Of importance is the fact that even if there is particle size reduction with increasing milling time, the densities quickly reach a steady average value of ~4.7 g/cm^3 beyond 2 h of milling (nominal density = 7.35 g/cm^3). Therefore, the effect of particle size on densities was negligible for most of the samples and the velocity decrease with milling time can be attributed to enthalpy losses during milling due to solid-state diffusion.

XRD analysis of the samples was performed before and after ignition tests. Before ignition tests, only Al and Ni was observed for samples up to a milling duration of 8 h, which also contained small amounts of AlNi, indicating that the particles partially reacted during milling. The Al peaks in the XRD spectra broadened significantly with increasing milling time indicating nanoscale refinement of their grains. This was also accompanied by a decrease in peak sizes, before vanishing revealing that almost the entire Al had to be mixed into the Ni-rich solid solution before AlNi could form. This indicates significant amounts of mixing beyond the equilibrium solubility limits occurring and that the nucleation of the AlNi phase is preceded by the formation of the Ni-rich solid solution. XRD patterns after ignition tests point out to a mixture of Ni, AlNi and $AlNi_3$ in different proportions with no remaining Al. Samples with low milling time had the highest amount of Ni with some AlNi and traces of $AlNi_3$. The amounts of Ni and AlNi decreased, whereas the amount of $AlNi_3$ increased with increasing milling time, similarly to interrupted BM (*Papers 1 and 2*).

Thermal analysis indicated that all samples exhibited numerous exothermic peaks which shifted to lower temperatures with milling time up to 4 h, and remained stationary afterwards with diminishing heat outputs. Interrupted DSC analysis was performed on the samples to identify the phase formation. Before the first exothermic peak only Al and Ni are present. The available pure Al decreased, while Al_3Ni, AlNi and $AlNi_3$ consequently are formed, followed by endothermic peaks corresponding to the melting of the remaining phases, $AlNi_3$ and Ni.

Paper 4:
Z. Gu et al., *Surface Coatings and Technology*, 2012 (in press)

Paper 4 is a joined publication on nano-heaters, which demonstrates reactive nanostructures that can generate localized heat through controlled ignition. In this paper, demonstration of (a) synthesis of Al–Ni bimetallic nanoparticles by a galvanic replacement reaction method using Al nanoparticle templates, (b) fabrication of Al–Ni nanowire structures by a two-step process involving electro-deposition and thermal evaporation, (c) fabrication of Al–Ni composites by a novel ultrasonic powder consolidation method, using Al and Ni nanoparticles as source materials, and (d) synthesis of nanostructured Al–Ni powders by low energy ball milling with microscale Al and Ni powders. The author of this thesis mainly contributed to part d.

In *Paper 4,* continuous BM of Al and Ni at ratios of 1:3 and 1:1 is compared. Both compositions indicate that most of the plastic deformation initially occurs within the softer Al matrix, into which thinner sections of Ni shear off and mix under intense ball impact events. The Al matrix eventually hardens sufficiently to transfer impact loading into Ni layers, which results in their deformation and thickness reduction. Powder mixtures with 1:3 molar ratio show the formation and relatively rapid refinement of lamellae, consisting of alternating layers of the constituents. Further milling results in a slower gradual refinement of the lamellae, but some thicker Ni layers remain until NiAl starts to form after 8 h. Powder mixtures with 1:1 molar ratio show a similar evolution but at a slower lamella refinement rate. This composition can be milled for much longer, up to 13 h, until NiAl formation is present. This can be attributed to the higher amount of aluminum that can accommodate the plastic deformation.

Continuous DSC scans of the samples up to 1773 K are observed. Samples with an overall composition of Ni_3Al exhibited various exothermic peaks followed by endothermic peaks starting at around 1653 K, corresponding to the melting of the remaining Ni-rich solid solution and Ni_3Al. Samples with the NiAl composition show similar exothermic peaks, which tend to move to lower temperatures with more milling time. However, in contrast to the 1:3 molar ratio, they lack the endothermic peaks at the highest temperature measured, indicating that no pure Ni or Ni-rich solid solution remains and the transformations to the NiAl phase is complete.

XRD analysis of as-milled powders for different durations for 1:1 and 1:3 molar ratios indicated that both samples exhibit sharp peaks at low milling times, indicating they have relatively large grains up to this point. With increasing milling time, the peaks widen for both Al and Ni, as their grain sizes decrease due to lamellae formation upon deformation. Further milling results in intensity reduction of Al peaks while Ni peaks remain unaffected. This is possibly due to solid state diffusion of Al into Ni, forming Ni-rich solid solutions. For the 1:3 molar ratio sample, Al peaks totally disappear after 6 h due to the higher amount of Ni present, which can accommodate the entire Al. First signs of NiAl peaks appear after 7 h, which are more clearly visible at 8 h. The solid state diffusion is more limited for the 1:1 ratio samples, where some Al remains up to 13 h when NiAl starts forming during milling. Therefore, substantial solid diffusion of Al into Ni appears to be necessary to start forming the NiAl phase during milling. Furthermore, the overall composition does not seem to have an effect on phase selection.

Paper 5:
A. Hadjiafxenti et al., *Scripta Materialia* (under review)

Paper 5 is based on continuous BM of Al/Ni at ratios of 1:1, investigating the observations of *Paper 4* in more detail,

XRD analysis of as-milled powders indicated that there are only Al and Ni present for the samples milled up to 13 h of milling time. Further milling indicated that there is significant broadening in the Al and Ni peaks, pointing to grain refinement and increasing amounts of strain. A rough estimation using Scherrer's formula revealed that average grain sizes of Al and Ni can go below 10 nm. The Al peaks are still present when NiAl starts forming during milling, revealing that there is a solubility limit to how much Al can be incorporated into the Ni-rich phase.

DSC scans showed results similar in terms of phase formation sequence to other studies using high-energy BM and magnetron sputtered foils In contrast to experiments with an Al/Ni ratio of 1:3, there is phase formation before the first exothermic peak. $NiAl_3$ is the first phase to form, whereas as the milling time is increased, the concurrent formation of Ni_2Al_3 and NiAl occurs. Samples milled for more than 6 h fully reacted up to 1100K, whereas up to 1700K only AlNi is present for all the samples. No endothermic peaks for Ni were observed, indicating full transformation to the AlNi phase.

Using different heating rates, Kissinger analysis was performed to determine the activation energies for the first peaks of the specimens milled for 10 h, 11 h and 12 h, which yielded 108.8, 101.9 and 100.0 kJ/mole. The peak maximum temperatures could be lower by almost 20 degrees, and closer to those in magnetron sputtered foils with bilayer thicknesses of 40 nm. Therefore, it appears that although the kinetics of growth are similar, the reaction barrier is lower.

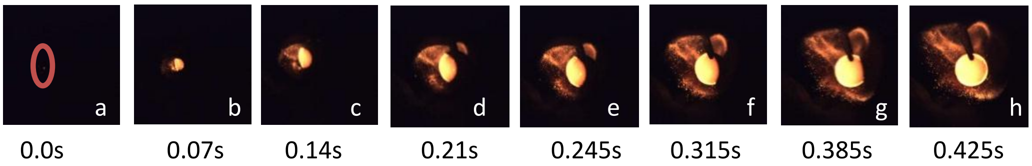


Figure 11: High-speed camera images of the thermal front for a spark-ignited pellet (Al/Ni 1:1, BM for 11 h)

The 11 and 12 h powder-pellets could be ignited using a spark from a 9 V battery. The formation of a self-propagating thermal front traveling between 0.2 and 0.24 m/s among different BM runs is shown in Figure 11 for the 11 h specimen. The pellets were fragile and edges tend to fall apart during handling. The 12 h samples had lower velocities around 0.14 m/s. The front velocity is considerably smaller than in multilayer foils, which can be expected as the cold-compacted pellets have no metallurgical bonding and have very low thermal conductivities. Furthermore, the porosity within the pellet (32 %) would reduce the volumetric energy density. Of importance is the fact that ignition using a spark, as for thin films, is achieved. The velocities in Al/Ni thin films vary from 0.01-30 m/s, whereas the velocities in BM-powder compacts (11 h and 12 h) vary between 0.1-0.24 m/s.

Paper 6:
S. K. Pillai et al., *International Journal of Applied Ceramic Technology*, vol. 9, p. 206, 2012

In *Paper 6* powder mixtures of Al/Fe_2O_3 and Al/Cu_2O at varying compositions were ultrasonically consolidated at different equivalence ratios. It was observed that for mixtures with Al >75 wt%, single welds were sufficient to form homogenous powder consolidates, for 50 < wt%, Al<75, double weld were required, and for lean mixtures of Al, 30 <wt% Al <50, the process was repeated three times to form dense structures. SEM images of Al/Fe_2O_3 and Al/Cu_2O compacts indicate that Fe_2O_3 and Cu_2O particles are uniformly distributed in the Al matrix.

The ignition of the pellets was characterized by a significantly large emission of light, indicating very high temperatures. The reaction velocities of Al/Fe_2O_3 are observed to increase and then to decrease, as the Al weight percentage increased. The propagation velocities upon ignition of the Al/Cu_2O compacts were found to be larger than that of the Al/Fe_2O_3 compacts of same equivalence ratio, by an order of 10.

SEM observation of the samples after ignition test indicated needle-like single crystals, believed to be resulting from the vaporization and solidification of iron among thermite reaction. XRD analysis of the ignited Al/Fe_2O_3 samples, indicated the presence of hercynite (FeAl2O4), along with a-Al_2O_3 and a-iron. XRD analysis of the ignited Al/Cu_2O, revealed the presence of $CuAlO_2$.

In contrast to BM-samples, the thermal stability of the compacts did not indicate any exothermic peaks at low temperatures. The first peak observed was an endothermic peak occurring at around aluminum melting point, followed by the exotheric peaks at temperatures above 1100K.

9.1 Ball Milling Experiments

Experimental observations indicate the uniqueness of each material system individually. The variety of experimental results published in literature arise through the different milling parameters which include the properties of the materials (particle size, hardness), the quantity of the materials, ball to material ratio and the materials used for milling (tungsten, steel or aluminum). Additionally, they arise from the properties of the systems which include rotational speed and duration in a dual or single vial system. These differences reinforced the scientists' efforts to quantify the results which indicated a detailed description that could only characterize the sensitivity of the system. Equations consider only the kinetic energy of the balls aiming to study the impact of the balls on the powder. Furthermore, the overall impact of the balls on the powder, the degree of filling of the vial, the velocity, the energy during collision events and, finally, the overall energy is considered [77, 78].

The effort to quantify the results during the experiments was unsuccessful since the materials that stuck in the vial were an indication that the energy given could not be estimated precisely since the material quantity decreased. This was further verified when observing the differences between the experiments between *Paper 1* and *Paper 2*, since the energy given to the 4 h samples in both experiments was estimated to be equal. However, there were vast differences between the two specimens which indicated that even the interruption and the material removed during processing affected the correlation of the experiments and the precise quantification of the energy.

Literature indicates that the structural, chemical and thermal behaviour of the materials produced could have similarities with other materials produced under different conditions. Correlation between the experimental results observed using High-Energy BM (HEBM) and Low-Energy BM (LEBM) could not be doubted. The small duration of the experiments performed using HEBM resulted in high energy impact on the materials, in contrast to the ones that required long processing times using LEBM, which gradually milled the processing materials. The different energy input reveals properties of the materials which cannot be observed unless a step-by-step procedure is followed. For example, a simple observation of thermal analysis graphs between the papers published by Cardellini et al., [79] and Hadjiafxenti et al., [80, 81] indicate that there is a similarity in the thermal behaviour of some specimens but with different energy input. Additionally, some characteristics of the materials that might be of interest could be skipped.

The results observed through this study do not cancel those of HEBM but reinforce the utilisation of a step-by-step observation using LEBM. Furthermore, the results could be extended to HEBM for manufacturing in industry. Relatively short synthesis durations can be achieved through HEBM and can result in an even less time-consuming and cost-effective product. A possible fabrication restriction could be the requirement of pure inert atmosphere in order to decrease the contamination during milling.

Summarizing, the results observed in the BM experiments showed that the excess energy provided to the powders allow plastic deformation and formation of dislocations and defects. The consequence of this mechanical energy is a lamella structure and smaller activation energy due to the surplus diffusion. BM decreases the ignition temperature, expands the flammability limits, favours complete reaction of reagents to products, exhibits repeatable results without the influence of ageing parameters, and releases energy through nano-structure and oversaturated solid solutions. The energy provided cannot be quantified due to the material stuck on the vial walls. The powder studied and analysed did not include material removed from the vial walls. Only loose powder from the vial was studied.

9.2 Ultrasonic Powder Consolidation

Introduction

Ultrasonic welding (USW) facilitates rapid joining of materials without requirements of special conditions like inert air, vacuum or excessive heating. Ultrasonic powder consolidation (UPC) is an USW technique applied to create compacts of particulate materials, producing green compacts that do not require further sintering at elevated temperatures for full metallurgical consolidation, or any other special treatment, since ultrasonic vibrations fracture and displace surface contaminants such as oxide layers on Al powder, allowing metal surfaces to come in contact and form a metallurgical bond.

Preliminary UPC experiments with Al and Ni powders indicated that full densification and metallurgical consolidation is possible for Al/Ni 1:1 only at 90MPa and 300^{o}C [15]. The objective of this study was to evaluate the UPC processing conditions for Al/Ni at ratios 1:3 and 1:2 such as full density-consolidated compacts are formed. For achieving this purpose, compact specimens were produced at various pressures and temperatures, both with the application of ultrasonic vibrations. Differences in the density of the compacts are discussed with respect to processing conditions.

Experiments

The materials used in this study were 325 mesh aluminum (99.5% pure) and 325 mesh nickel (99.8% pure) powders, respectively. UPC experiments were performed with the experimental setup depicted in Figure 12, which consisted of a die and a punch, both made of a 0.78 mm think steel sheet, placed on a hot plate. The die hole and the punch had a diameter of 3.40 mm. Powders, placed in the preheated die and held under a desired uniaxial pressure normal to the die for 30 s, were subjected to ultrasonic vibrations in open air for 1 s using a STAPLA Condor ultrasonic welding unit, at a fixed frequency of 20 kHz with amplitude of 10 μm.

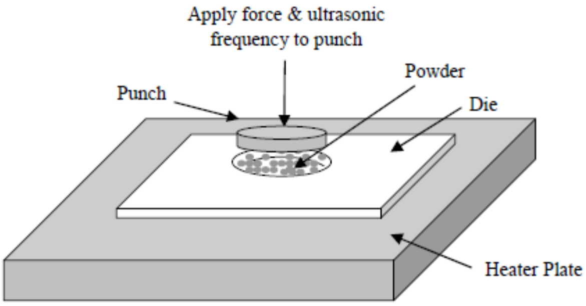


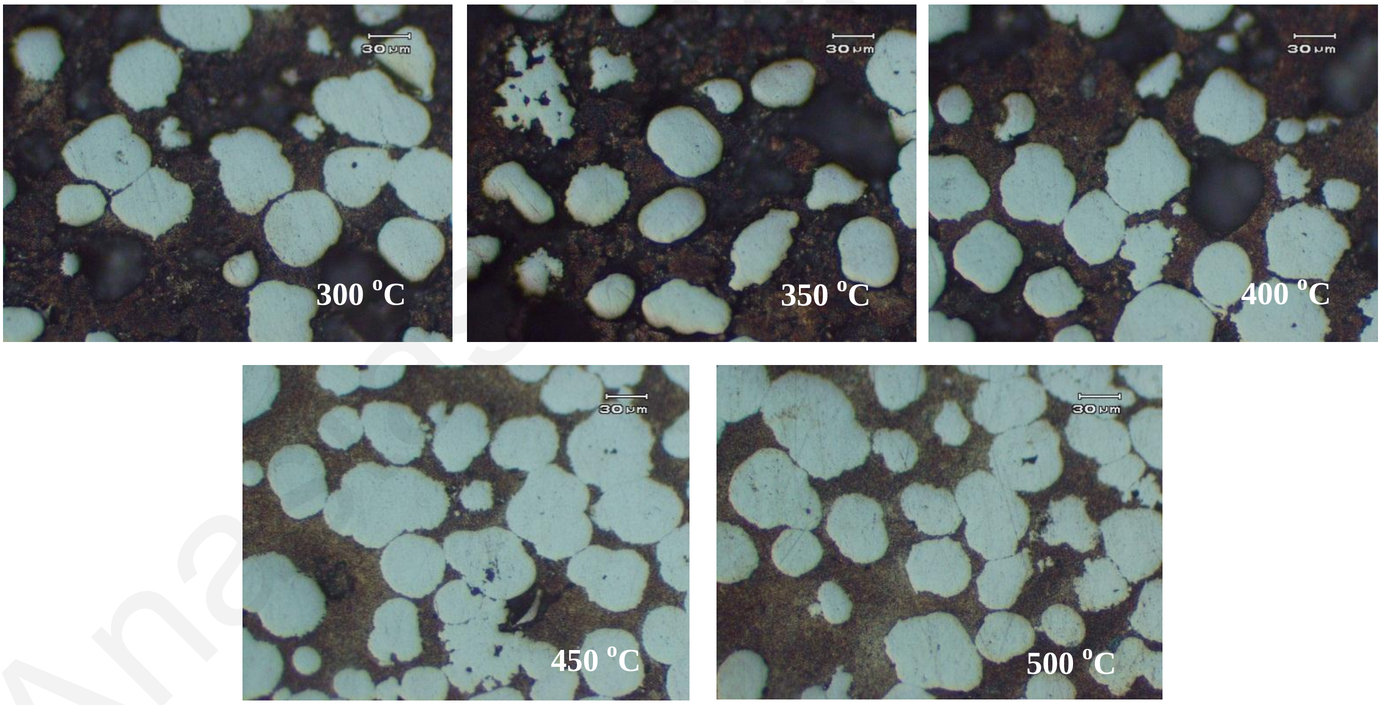
Figure 12: Experimental set-up [16]

Results

Table 3 indicates some of the parameters used for the Al/Ni 1:3 consolidation. It is observed that full consolidation occurs only at 450^{o}C and 500^{o}C at 84.2 MPa. In Figure 13, the compacted sample microstructures under 84.2MPa are shown. The two samples were compacted at temperatures 450^{o}C and 500^{o}C, and have densities of 98.5% and 99.6% respectively.

Table 3: Summary of consolidation experiments

	300 ^{o}C	350 ^{o}C	400 ^{o}C	450 ^{o}C	500 ^{o}C
250 lbs- 84.2 MPa	x	x	x	v	v
300 lbs- 101.1 MPa	x	x	x	x	x



98.5% density **99.6% density**

Figure 13: Microstructure of samples consolidated at Al/Ni ratio of 1:3

Powder compacts with mixtures of Al/Ni 1:2 were also compacted at 84.2 MPa and 500^{o}C. Previous experiments with a ratio of 1:1 indicated compaction at 90 MPa and 300^{o}C [15, 16]. The significance temperature difference, with the experiments at ratio of 1:2 and 1:3, is attributed to the amount of Ni. The soft Al-particles are easier to be compressed in contrast to the hard Ni-particles. This can be observed in the last two fully-compacted samples, which have few areas of Ni-particles connected, reinforcing the opinion that mostly Al is acting as binder. Experiments with nano-particles were also performed. Unfortunately, in contrast to the ratio 1:1, those samples were not consolidated, but easily broke. This is attributed to the lack of Al-bonding-particles, which "hold" the particles together.

A really interesting experiment was the effort to consolidate BM powder. The milled sample is shown in Figure 14 (Al/Ni, at ratio 1:3, milled for 4 hours). The laminated structure did not allow consolidation of the sample, indicating work-hardened milled samples. The fact that the milled sample is not consolidated indicates that during milling the small and hard pieces of Ni embedded in the soft Al matrix allow hardening of the powder. Additionally, the dislocation generation within the crystal structure of the materials results in an increasingly saturated material with new dislocation which prevents nucleation. The Al atoms take positions in the Ni non-brittle lattice, which, due to the severe plastic deformation, exhibit a structure with increased number of dislocations. Plastic deformation occurs as a consequence of work done on the material through consequence collisions and impact. Hence, the energy provided to the materials results in a work-hardened structure which cannot be bonded due to lack of a soft bonding agent.

The milled sample, at a ratio 1:3, was mixed with Al, which is the most common bonding agent for the compact total ratio to be 1:1. Unfortunately, this sample reacted during UPC, indicating the reactivity of the sample formed. Hence, the combination of BM and UPC methods was not successful, since the energy from the sample was not released at the moment it was required, but during processing and, therefore, this approach cannot be utilized for nano-heater purposes.

Conclusions

UPC was applied to produce Al-Ni composites from elemental powders. The results showed that the residual porosity in Al-Ni consolidates decreased with increasing temperature and pressure. Al/Ni compacts were fully densified with good interparticle metallurgical bonding at temperatures of 450°C and 500°C with uniaxial pressures as low as 84.2 MPa. The composite microstructure consisted of Ni particles distributed in an Al matrix. Powder compacts are low-cost and capable for infrastructure, health-safe and environmentally friendly.

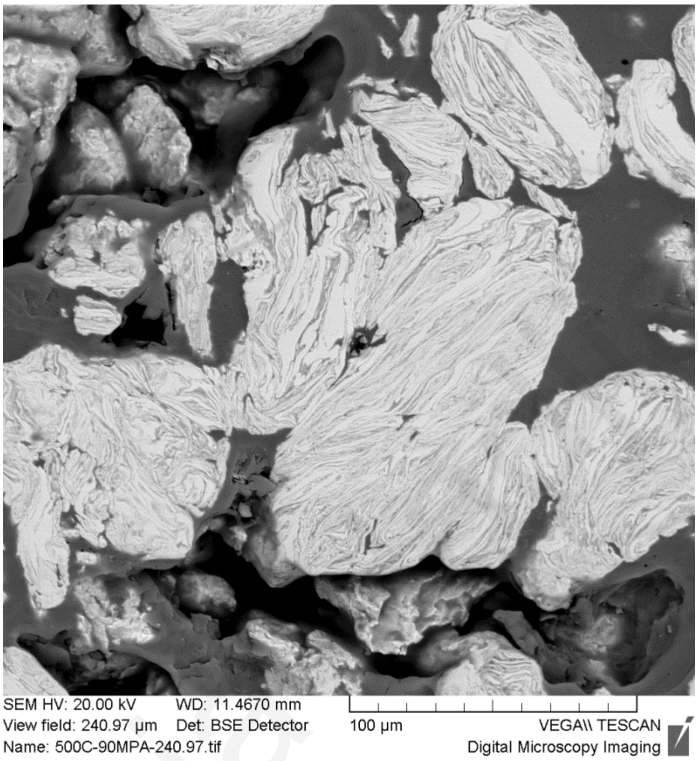


Figure 14: Ball milled samples after compaction – High in porosity

10 SUMMARY & CONCLUSIONS AND FUTURE RESEARCH & POTENTIAL APPLICATIONS

10.1 Summary & Conclusions

A major target of this thesis was to produce reactive Al-Ni compacts through Ball Milling (BM), to refine their particle microstructures up to the formation of nickel aluminides, and to determine the critical milling time necessary to produce compacts with lamella structures, similar to the nanoscale structures observed in sputtered multilayer films/foils (MFs), ignitable using a low-energy ignition. For this purpose, low-energy interrupted and continuous BM was carried out on Al/Ni powders with molar ratios of 1:3 and 1:1 to synthesize materials that exhibit self-propagating exothermic reactions (SPER). Low-Energy BM (LEBM) was selected in this study as a viable approach to reduce the energy of individual impact events at the expense of processing time. Additionally, LEBM was employed since it is highly desirable to retain most of the reactivity and purity of the powders so that the ignition threshold is sufficiently low, which can enable local ignition with a low-energy spark from a battery, as opposed to uniform heating. This is especially important if the materials to be joined cannot be uniformly heated to the required temperatures.

Initial studies on BM of Al/Ni with a ratio of 1:3, where some powders from the mixture were removed after certain intervals, in interrupted BM runs, the total mass was reduced with each sampling point. Such changes increase the ball to powder mass ratio, affecting the reproducibility of the results and complicate comparisons of equivalent milling energy with other work. BM of Al and Ni causes extensive mechanical mixing and the formation of nanoscale lamellar microstructures with increasing milling time. With a ball to material weight ratio of 5.1:1 and a rotational speed of 300 rpm, 16–18 h of milling time produce easily ignitable powder mixtures (using a small propane torch) with little intermetallic formation that exhibit self-propagating reactions, comparable to magnetron sputtered nanoscale multilayers. The reaction velocity increases with compacted pellet density due to enhanced thermal contact among the particles.

Following up these initial studies, continuous BM of Al/Ni with a ratio of 1:3 were carried out for different durations, where the ball to powder mass was held constant. Results showed that reactive compacts can be formed that exhibit similar thermal and phase formation characteristics to sputter deposited MFs with nanoscale bilayer thicknesses, albeit at lower thermal front velocities. BM produces near optimum microstructures after 4 h of continuous milling under the selected milling conditions, with nanoscale lamellae and some remaining relatively thick Ni layers, suggesting that the thermal characteristics of the powders can be improved by using smaller Ni particles in the starting mixture. BM beyond the optimum point increases the solid-state diffusion of Al into Ni-rich solid solutions that negatively impacts the heat output and the thermal wave velocity. The ignition experiments indicate near adiabatic reactions occurring within the pellets milled at 4 h, which can be relatively easily ignited with a locally applied heat source (using a small propane torch). It was suggested that an overall composition of AlNi could be potentially behave identical to MFs, ignitable using a low energy spark.

Additional continuous BM experiments were carried out on powders with an overall composition of AlNi. The results showed that microstructural refinement with increasing milling times increases reactivity, and pellets produced using 11 and 12 hours milled powders can be ignited locally using a low energy spark from a battery and react in a self-propagating manner with uniform thermal fronts having velocities up to 0.24 m/s (for a pellet porosity of 32 %). Using different heating rates for the 10 h, 11 h and 12 h samples, Kissinger analysis was performed to determine the activation energies for the first exothermic peaks, which yielded 108.8, 101.9 and 100.0 kJ/mole, which are close to values published very recently for high-energy ball milled powders. However, the peak maximum temperatures were lower by almost 20 degrees (~500 K), and closer to those in MFs with bilayer thicknesses of 40 nm (~498 K). Therefore, it appears that although the kinetics of growth are similar, the reaction barrier is lower. This might be due to less interfacial mixing compared to the high-energy ball milled powders. This would also explain the higher ignitability of low-energy ball milled powders in this study, where the relatively sharper interfaces can promote phase nucleation.

In summary, similarities between low-energy ball milled Al/Ni powder pellets and sputtered MFs were observed. BM has therefore the potential for a novel and economical processing route for generating powders that can be shaped into useful geometries (such as rolled into thin sheets) for thermal manufacturing applications, and they can be an alternative to MFs used for bonding applications.

As a second powder processing method, Ultrasonic Powder Consolidation (UPC) was used in this work to mainly produce thermite composites with a wide range of Al/Fe_2O_3 and Al/Cu_2O ratios by the application of ultrasonic energy as cylindrical pellets with a clean, safe and efficient consolidation process at ambient conditions. For oxide-rich compositions, multiple welds were used to synthesize dense pellets. The observed reaction velocities and the reaction products of the composites prepared by this fast process were found to be in good agreement with that of a prior research on compacts of similar compositions and geometry.

Initial work on UPC of Al/Ni powders with a molar ratio of 1:3 showed that full consolidation occurs only at 450-500^{o}C and an applied pressure of 84.2 MPa. This is in contrast to powders with an overall composition of AlNi, where full consolidation occurs under similar applied pressures at already 300^{o}C. This big temperature difference is attributed to the larger amount of Ni, since the soft Al particles are easier to be compressed in contrast to hard Ni particles.

The exothermic reaction provides utilization of internal energy of the system for heat release. The reaction takes less than a second and results in a high-purity product. The short duration of the reaction does not allow change of the specimen shape, even if melting is believed to take place at some of the powder compacts. The density of the products changes by only ten per cent after reaction and, hence, the slight compact growth can be taken into account if the specimens are used in sensitive components. The non-involvement of gaseous product could be a benefit despite the fact that particle spreading is observed during the reaction of the spark-ignitable compacts. In contrast, materials that can be ignited using a small torch do not exhibit particle spreading, but require flame utilisation, whereas possible preheating might restrict their usage in industry. However, it can be argued that each specimen produced could be used in industry if the temperatures necessitated reflect those of the specimen (IT and MT).

Focusing on the spark-ignited specimens, the functionality problem of the compacts might be their fragility. The utilisation of these specimens could be broader if the non-requirement of a flame is taken into consideration, but their handling could be easier if fragility is overcome. Additionally, for industrial usage, the temperature of the specimens should be precisely calculated parallel to the velocity evaluation, reaction time and ignition delay time. These powder compacts could be produced in industry in an inert atmosphere, either by LEBM, which takes a few hours, or by High-Energy BM (HEBM), which needs only a few minutes.

10.2 Future Research & Potential Applications

Further research could be focused on some of the following topics:

- Decrease processing times of LEBM by using smaller Ni powder sizes, since most of the mechanical energy in the initial stages goes to reducing the harder Ni particle sizes (the softer Al particles readily experience severe plastic flow). This increases the required milling times for mixing. Preliminary results with smaller Ni particles (3-5 μm) in the initial mixture with an overall composition of AlNi have showed that the required milling times can be reduced to 6 h as opposed to 12 h to form similar structures.
- Carry out detailed studies on the effect of pellet porosity on thermal front velocities. The front velocity of continuous LEBM experiments on powders with an overall composition of AlNi was found to be considerably smaller than in MFs, but this was expected as the cold-compacted pellets have no metallurgical bonding and can have very low thermal conductivities.
- Compare the microstructural refinement with increasing BM times and the reactivity from low-energy and high-energy ball milled powders, to better understand the effect of the local heating during each impact event due to plastic deformation, which can cause mass diffusion and produce solid-state

solutions. This might include Transmission Electron Spectroscopy (TEM) studies.

- Use spark ignitable low-energy BM Al/Ni powder mixtures cold-pressed into pellets for bonding trials; compare their properties to MFs.
- Incorporate powders into pure foils or surfaces using rolling to generate thick reactive foils suitable for large scale bonding, ignitable away from the weld interface using a spark.
- Study in more detail the influence of powder shapes/sizes and processing parameters for UPC. Initial studies have shown that Al/Ni flake composites, which exhibit a uniform distribution of Ni flakes in a fully densified Al matrix, can be produced at 250°C and 80 MPa uniaxial pressure in 1 second.

In terms of *potential applications*, reactive nanostructures that can generate localized heat through controlled ignition can be applied to a wide range of applications where spatial and temporal control of heat can allow for thermal actuation-based processing improvements or enable new features or abilities. Besides the widely used sputtered MFs with multiple alternative Al–Ni layers, various new nanostructures have been fabricated in the last several years using, for example, BM and UPC, as employed in this study. In general, applications for reactive nanostructures can be classified into joining, melting, and ablation.

Potential applications include:

- Bonding/joining of different materials and sealing for microelectronics and power applications.
- Self-sintering powders (with pre-mixed BM Al–Ni particles) under electrical actuation, etc.
- Reactive nanostructures embedded into polymer films, fibers or rods to allow for melting and reshaping parts as part of new functions or for degradation, e.g. in disposable self-heating fabrics and membranes for military materials, biocatalytic processing substrates, and self-repairing polymer-matrix composites.

- Ablation of biomaterials (e.g. cancer cell walls and cauterizing blood vessels) through the use of created intense heat.

- Energetic materials for defense applications, which bring to fruition the promise of nano-materials for a unique contribution to this field.

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