Combustion synthesis of reactive nickel-aluminum particles as an innovative approach for thermal joining applications

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Abstract. Reactive systems, which are widely used in combustion synthesis, represent a promising solution for challenging joining tasks. They are able to undergo a self-sustaining, highly exothermic reaction when exposed to an external energy source. Reactive foils are the only systems that are currently commercially available. However, their industrial use is limited due to the brittle nature of the material and the restriction to planar geometries. Reactive particles represent a more flexible format, but are currently not commercially available. Therefore, a two-step electroless plating process has been developed to synthesize nickel-aluminum core-shell structures. These structures function as microreactors, which provide the energy for the thermal joining process. Ignition tests with electromagnetic waves were performed in order to investigate the overall reactivity. Energy input and particle size significantly influence the activation and the reaction behavior of the core-shell structures. Furthermore, a general approach to use reactive particles as a heat source in joining applications is proposed.

1. Introduction
Combining materials with dissimilar thermo-physical properties, like fiber-reinforced plastics, light metals or ceramics, within only one component is an effective means for functional and lightweight design. Both are becoming increasingly important in the automotive and aerospace industry as the reduction of mass, fuel consumption, and emissions have become core demands [1]. The manufacturing of hybrid joints is a major challenge in production engineering and requires efficient, adaptable, and innovative joining techniques. Reactive systems, which can function as a heat source in the thermal joining of distinct materials, represent a promising solution to meet these demands.

1.1 Characteristics of reactive systems
Reactive systems gained increased attention in the past few years by both, academia and industries [2; 3]. The unique ability to undergo a self-sustaining, highly exothermic reaction is successfully used in the field of combustion synthesis for producing advanced materials [4]. The exothermic reaction can be initiated by a locally confined energy input, e.g. an electrical impulse, mechanical impulse, or laser radiation [5; 6]. Moreover, the activation energy can also be provided by a volumetric energy input, e.g. uniform heating in an oven [7] or electromagnetic waves [8]. These two basic reaction modes are denoted as self-propagating high temperature synthesis (SHS) and thermal explosion (TE) or volume combustion synthesis (VCS) [9]. Generally, a reactive system is composed of at least two reactants in a defined stoichiometric ratio which determines the amount of the released energy [10]. Besides a great variety of diverse reactants, the combination of nickel and aluminum is of growing
interest due to the beneficial characteristics of the reaction product [11; 12]. Nickel aluminides can be used as highly resistant coatings [13] or as lightweight material, since for example nickel aluminide (NiAl) features a low density combined with high strength as well as good oxidation and corrosion resistance [14]. These promising material properties gave rise to various sophisticated investigations in order to understand the mechanisms and kinetics of the combustion synthesis [15; 16]. The heat of reaction for the formation of NiAl, released within only a few milliseconds, results in a maximum temperature of 1810 °C [16] and motivates the use of the reactive system Ni + Al in thermal joining processes.

1.2 Joining with reactive systems

The research focus for joining with reactive systems is currently on reactive foils, also known as multilayer systems [17; 18]. Reactive foils consist of alternating layers in the range of nanometers of at least two metallic components. The thicknesses of the single layers and the overall thickness of the reactive foil significantly influence the reaction behavior [19]. Depending on the manufacturing process, which can be either cold rolling [20] or magnetron sputtering [21], the number of single layers ranges between a few up to thousand layers. The ignition of the reactive multilayer system via an electrical or mechanical impulse (SHS mode) leads to the formation of a reaction wave expanding circularly from the point of initiation with a maximum speed exceeding 10 m/s [22]. Consequently, maximum reaction temperatures are reached within and only for a few milliseconds and thus allow joining of thermosensitive materials.

In the context of thermal joining, the reactive multilayer system is placed between the two joining partners, an adequate joining pressure is applied and an external energy input is used for ignition. The released energy serves as a heat source, which melts the surface layers of low-melting materials. For high-melting materials, the joining partners are coated with an additional solder layer in order to form an adhesive bond [23]. Joining distinct materials, like different metals [24], metal and ceramic [25], or bonding on wafers [26] has been studied by many researchers. Reactive multilayer systems, consisting of nickel and aluminum, are commercially available under the trade name NanoFoil®. However, there are several disadvantageous characteristics of the multilayer systems for joining processes, such as the brittle nature of the material, the limitation of applications to planar geometries and the lack of automation of the joining process [27].

A promising approach to combine the beneficial reaction properties and overcome the restrictions of multilayer systems are reactive systems in a more flexible format, namely reactive particles. Heterogeneous, stoichiometric mixtures of distinct powders are commonly used for the combustion synthesis of advanced materials [3]. Yet, there are additional forms of reactive particles, which are under scientific investigation. The basic structure is similar to the multilayer system described above and consists of two metallic reactants which are able to undergo an exothermic reaction. The main difference is that reactive particles are reactive themselves as they combine both reactants within one particle. The morphology can be described as core-shell structure, as shown in figure 1a), or as lamellar composite, as shown in figure 1b). The former are synthesized via wet chemical processes [15; 28] whereas the latter are synthesized via ball milling [29] or by shredding cold rolled multilayer systems [30].
The exothermic reaction can be initiated similarly to multilayer systems. In contrast to multilayer systems or pressed pellets, loose particles are not in direct contact with each other. Therefore, the second ignition mode (TE mode) plays an important role in activating the reactive system. In order to guarantee the ignition, particles can be uniformly heated in an oven [31] or exposed to electromagnetic waves [32]. Electromagnetic waves are well absorbed by metals [33], such as nickel and aluminum. It has been shown that microwave radiation allows selective heating of reactive powder mixtures and has a positive effect on the reaction characteristics [8; 32].

The joining process for reactive particles is the same as with reactive multilayer systems. The ignition of the reactive particles between the desired joining partners results in an energy release which can be used to join via welding, bonding, or adhesion. Despite numerous studies on the reaction behavior of compressed powder mixtures [14; 31] and of lamellar composites [34], comparatively little attention is being paid to reactive core-shell structures and to joining via reactive particles.

Therefore, this research focuses on reactive core-shell structures and on joining via reactive particles in general. A two-step wet chemical process to synthesize reactive core-shell structures is studied. Furthermore, a general approach to combine the beneficial characteristics of microwave ignition in the thermal joining process with reactive particles is presented.

2. Experimental procedure
The synthesis of reactive nickel-aluminum core-shell structures requires the following chemicals: nickel(II) chloride (Sigma-Aldrich, 98 %), ammonium chloride (Sigma-Aldrich, 99.998 %), sodium citrate dihydrate (Sigma-Aldrich, ≥ 99 %), sodium fluoride (Fluka, ≥ 99 %), nickel(II) acetate tetrahydrate (Sigma-Aldrich, 98 %), glycolic acid (Sigma-Aldrich, 99 %), ethylenediaminetetraacetic acid tetrasodium salt hydrate (Sigma-Aldrich, ≥ 99.0 %), hydrazine hydrate solution (Fluka, 78-82 %) and sodium hydroxide (Honeywell, ≥ 98.0 %). All chemicals were used as received. Elemental aluminum powder (d50 = 23.5 µm, 99.7 % purity) was purchased from New Materials Development.

2.1 Wet chemical synthesis
Reactive nickel-aluminum core-shell structures were synthesized in a two-step electroless plating process. First, the oxide layer of the elemental aluminum powder was removed and substituted with a thin nickel layer. Second, the initial thin nickel layer was coated with additional nickel until a stoichiometric ratio of 1:1 was reached and reactive particles, which can be considered as microreactors, were obtained.

As mentioned before, the first step is a pre-treatment of the elemental aluminum powder, which is covered with an oxide layer as it is not handled under an inert gas atmosphere. Moreover, the pre-treatment serves to remove possible contaminations, activate the surface for subsequent nickel coating and prevent further oxidation [35]. The composition of the pre-treatment solution is shown in table 1.
Table 1. Composition of the pre-treatment solution for elemental aluminum powder [35].

| Chemical                  | Formula                      | Pre-treatment solution |
|---------------------------|------------------------------|------------------------|
| Nickel(II) chloride       | NiCl₂                        | 30 g/l                 |
| Ammonium chloride         | NH₄Cl                        | 7 g/l                  |
| Sodium citrate dihydrate  | C₆H₅Na₃O₇·2H₂O              | 20 g/l                 |
| Sodium fluoride           | NaF                          | 0.5 g/l                |

The purpose of the second step is to deposit more nickel onto the pre-coated particles. The advantage of electroless plating processes is that coatings can be deposited precisely and uniformly. Besides, the composition of the deposited material plays a significant role as it is supposed that impurities affect the reaction characteristics of the core-shell structures and hence influence the thermal joining process. Therefore, the selection of the reducing agent is of major importance. It has been shown that phosphorous (e.g. sodium hypophosphite) or boric (e.g. sodium borohydride or dimethylamine borane) reducing agents lead to significant co-deposition of phosphor and boron [36]. In this study, hydrazine is used as reducing agent since it allows nickel depositions with high purity.

Table 2. Composition of the plating solution for pre-treated aluminum powder [37].

| Chemical                  | Formula                      | Plating solution |
|---------------------------|------------------------------|------------------|
| Nickel(II) acetate tetrahydrate | C₁₂H₁₄NiO₄·4H₂O           | 40 g/l           |
| Glycolic acid             | C₂H₄O₂                       | 60 g/l           |
| EDTA tetrasodium salt     | C₁₀H₁₂N₂Na₄O₈·4H₂O          | 25 g/l           |
| Hydrazine hydrate solution| N₂H₁₂·H₂O                   | 100 ml/l         |

2.2 Ignition tests
To test the reactivity of the synthesized core-shell structures, ignition tests with electromagnetic waves were carried out. Based on the internationally defined ISM-frequencies (industrial, scientific, and medical applications), microwave heating was applied at a frequency of 2.45 GHz.

3. Results and discussion
In this section, the results of the wet chemical plating process are shown and discussed. In addition to that, a general procedure for joining with reactive particles in combination with microwaves is presented.

3.1 Synthesis and ignition of reactive core-shell-structures
The starting point of the two-step plating process is elemental aluminum powder with a mean particle diameter of 23.5 µm. In contrast to the material data sheet, particles do not have a spherical but an irregular shape as demonstrated in figure 2. Furthermore, particles significantly vary in size and feature small adhesions of elemental aluminum on the surface.
In order to obtain reactive core-shell structures, the pre-treated particles were plated with nickel until a stoichiometric ratio of nickel and aluminum of 1:1 was reached. The scanning electron micrograph in figure 3a) presents the nickel plated particles. Due to the broad particle size distribution of the elemental aluminum powder, the synthesized core-shell structures vary in size as well. Furthermore, the formation of agglomerates during the plating process is visible. The metallographic section in figure 3b) demonstrates that the deposited nickel layers are closed and uniform. The composition of the nickel layers was examined with the help of energy dispersive X-ray spectroscopy and does not feature any significant amounts of impurities due to the efficient pre-treatment and the beneficial characteristics of the chosen reducing agent. However, the broad particle size distribution results in core-shell structures with individual compositions even though the overall stoichiometric ratio of nickel and aluminum of the synthesized batch was adjusted via the process parameters to 1:1.

The reactivity of the synthesized core-shell structures was tested with microwaves at a frequency of 2.45 GHz and an output power of 800 W. The reaction during microwave heating takes place after five to ten seconds and can be described as a short lighting of the particles. Yet, not all particles were ignitable which is probably due to the limitation of the output power of the experimental setup, as smaller particles were ignitable. Moreover, pressed pellets were also not ignitable even though the loose powder itself reacted in an exothermic way. Further studies to investigate the reaction characteristics of reactive core-shell structures have to be conducted. For this reason, a general approach for thermal joining with reactive particles, which are ignited with the help of microwave energy, is presented.
3.2 Thermal joining with reactive particles

As reactive particles can be used as a heat source in thermal joining of similar and dissimilar materials, further investigations on the ignition of core-shell structures via microwave heating are required. In order to have precise control over the energy input, a test rig as shown in figure 4 is set up.

![Figure 4. Schematic representation of the thermal joining process with reactive particles via microwaves (not drawn to scale).](image)

Microwaves are guided directly into the joining zone and allow efficient heating of loose powder or pressed pellets. The electromagnetic waves are adjusted in such a way that exposure times can be reduced. Interesting challenges, that have to be addressed, are process monitoring during microwave heating, the cause-effect relationship between core-shell structures and microwaves and the application of reactive particles to freeform surfaces. Generally, joining with reactive core-shell structures can be realized via welding, soldering, or adhesion.

4. Conclusions

Thermal joining with reactive systems is a promising approach in the field of production engineering and lightweight design. As reactive particles represent a flexible format that can be adapted to the specific joining task, a two-step electroless plating process to synthesize reactive core-shell structures has been developed. Reactive nickel-aluminum core-shell structures with high purity have been obtained. The reactivity of the system was proven with the help of ignition via microwave energy. Further studies regarding the synthesis of the reactive core-shell structures are required in order to obtain defined particles. Furthermore, a general approach to ignite reactive particles via microwave energy, which allows for an efficient transfer of energy into the joining zone, has been shown.

References

[1] Koffler C 2014 Life cycle assessment of automotive lightweighting through polymers under US boundary conditions *Int. J. Life Cycle Assess.* **19** 538–545
[2] Merzhanov A G 1995 History and recent developments in SHS *Ceramics International* **21** 371–379
[3] Morsi K 2012 The diversity of combustion synthesis processing *J. Mat. Sci.* **47** 68–92
[4] Merzhanov A G 2004 The chemistry of self-propagating high-temperature synthesis *Journal of Materials Chemistry* **14** 1779
[5] Moore J J and Feng H J 1995 Combustion synthesis of advanced materials *Prog. Mat. Sci.* **39** 243–273
[6] Fritz G M, Spey S J, Grapes M D and Weihs T P 2013 Thresholds for igniting exothermic reactions in Al/Ni multilayers using pulses of electrical, mechanical, and thermal energy *J. Appl. Phys.* **113** 14901
[7] Thiers L, Mukasyan A S and Varma A 2002 Thermal explosion in Ni-Al system *Combust. Flame* **131** 198–209
[8] Rosa R, Veronesi P and Leonelli C 2013 A review on combustion synthesis intensification by means of microwave energy *Chem. Eng. Process.* **71** 2–18
[9] Varma A, Rogachev A S, Mukasyan A S and Hwang S 1998 Combustion Synthesis of Advanced Materials: Principles and Applications Adv. Chem. Eng. 24 79–226

[10] Ansara I, Dupin N, Lukas H L and Sundman B 1997 Thermodynamic assessment of the Al+Ni system Journal of Alloys and Compounds 247 20–30

[11] Naiborodenko Y, Lavrenchuk G and Filatov V 1982 Self-propagating high-temperature synthesis of aluminides Sov. Powder Metall. Met. Ceram. 21 909–912

[12] Philpot K A, Munir Z A and Holt J B 1987 An investigation of the synthesis of nickel aluminides through gasless combustion J. Mat. Sci. 22 159–169

[13] Rasmussen A J, Agüero A, Gutierrez M and José Landeira Østergård M 2008 Microstructures of thin and thick slurry aluminide coatings on Inconel 690 Surface and Coatings Technology 202 1479–1485

[14] Pascal C, Marin-Ayral R and Tédenac J 2002 Joining of nickel monoaluminide to a superalloy substrate by high pressure self-propagating high-temperature synthesis Journal of Alloys and Compounds 337 221–225

[15] Andrzejak T, Shafirovich E and Varma A 2007 Ignition mechanism of nickel-coated aluminum particles Combust. Flame 150 60–70

[16] Zhu P, Li J and Liu C 2002 Reaction mechanism of combustion synthesis of NiAl Mater. Sci. Eng. A 329-331 57–68

[17] Politano O, Baras F, Mukasyan A S, Vadchenko S G and Rogachev A S 2013 Microstructure development during NiAl intermetallic synthesis in reactive Ni–Al nanolayers Surface and Coatings Technology 215 485–492

[18] Gunduz I E, Fadenberger K, Kokonou M, Rebholz C and Doumanidis C C 2008 Investigations on the self propagating reactions of nickel and aluminum multilayered foils Appl. Phys. Lett. 93 134101

[19] Knepper R, Snyder M R, Fritz G, Fisher K, Knio O M and Weihs, T P 2009 Effect of varying bilayer spacing distribution on reaction heat and velocity in reactive Al/Ni multilayers J. Appl. Phys. 105 83504

[20] Battezzati L, Pappalepore P, Durbiano F and Gallino I 1999 Solid state reactions in Al/Ni alternate foils induced by cold rolling and annealing Acta Mater. 47 1901–1914

[21] Barbic T W and Weihs T P 1994 Method for fabricating an ignitable heterogeneous stratified metal structure US Patent 5,547,715

[22] Alawieh L, Knio O M and Weihs T P 2011 Effect of thermal properties on self-propagating fronts in reactive nanolaminates J. Appl. Phys. 110 13509

[23] Duckham A, Levin J and Weihs T P 2006 Soldering and brazing metals to ceramics at room temperature using a novel nanotechnology Advances in Science and Technology 45 1578–1587

[24] Wang J, Besnoin E, Knio O M and Weihs T P 2004 Investigating the effect of applied pressure on reactive multilayer foil joining Acta Mater. 52 5265–5274

[25] Grieseler R, Welker T, Mueller J and Schaar P 2012 Bonding of low temperature co-fired ceramics to copper and to ceramic blocks by reactive aluminum/nickel multilayers Phys. Status Solidi 209 512–518

[26] Braeuer J, Besser J, Wiemer M and Gessner T 2012 A novel technique for MEMS packaging Sens. Actuators A-Phys. 188 212–219

[27] Boettge B, Braeuer J, Wiemer M, Petzold M, Bagdahn J and Gessner T 2010 Fabrication and characterization of reactive nanoscale multilayer systems for low-temperature bonding in microsystem technology J. Micromech. Microeng. 20 64018

[28] Mukasyan A S, White J, Kovalev D Y, Kochetov N A, Ponomarev V I and Son S F 2010 Dynamics of phase transformation during thermal explosion in the Al–Ni system Physica B 405 778–784

[29] Takacs L 2002 Self-sustaining reactions induced by ball milling Prog. Mater. Sci. 47 355–414
[30] Stover A K, Krywopusk N M, Gibbins J D and Weihs T P 2014 Mechanical fabrication of reactive metal laminate powders J. Mater. Sci. 49 5821–5830
[31] Wu W W, Gubarevich A V, Wada H and Odawara O 2011 Volume combustion synthesis of NiAl as applied to ceramics joining International Journal of Self-Propagating High-Temperature Synthesis 20 94–99
[32] Rosa R, Colombini E, Veronesi P, Poli G and Leonelli C 2012 Microwave ignited combustion synthesis as a joining technique for dissimilar materials J. Mater. Eng. Perform. 21 725–732
[33] Buchelnikov V D, Louzguine-Luzgin D V, Xie G, Li S, Yoshikawa N, Sato M, Anzulevich A P, Bychkov I V and Inoue A 2008 Heating of metallic powders by microwaves J. Appl. Phys. 104 113505
[34] Kawanaka H, Taguchi M, Hirose S and Ogura S 2016 Reactive powder, bonding material using reactive powder, bonded body bonded with bonding material and method for producing bonded body US Patent 20160121395A1
[35] Ramaseshan R, Seshadri S and Nair N 2001 Electroless nickel-phosphorus coating on Ti and Al elemental powders Scr. Mater. 45 183–189
[36] Mallory G O and Hajdu J B 1990 Electroless plating (Orlando, Fla) The Society p 4
[37] Dini J W and Coronado P R 1967 Thick nickel deposits of high purity by electroless methods Plating 54 385–390