Electroplating of aluminium microparticles with nickel to synthesise reactive core-shell structures for thermal joining applications

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Abstract. Reactive particles represent a promising alternative for effectively joining components with freeform surfaces and different material properties. While the primary application of reactive systems is combustion synthesis for the production of high-performance alloys, the highly exothermic reaction can also be used to firmly bond thermosensitive joining partners. Core-shell structures are of special interest, since they function as separate microreactors. In this paper, a method to synthesise reactive nickel-aluminium core-shell structures via a two-step plating process is described. Based on an electroless process, the natural oxide layer of the aluminium particles is removed and substituted with a thin layer of nickel. Subsequently, the pre-treated particles are electroplated with nickel. The high reactivity of aluminium and the oxide layer play a significant role in adjusting the process parameters of the Watts bath. Additionally, the developed experimental set-up is introduced and the importance of process control is shown. In order to achieve reproducible results, the electroplating process was automated. Ignition tests with electromagnetic waves demonstrated that the particles undergo an exothermic reaction. Therefore, they can be used as a heat source in thermal joining applications.

1. Introduction
A mere invention does not automatically lead to innovation, as the latter depends on whether an idea is successfully put into industrial practice or not [1]. Combustion synthesis is nowadays considered as an established production technology to efficiently synthesise high-performance materials [2; 3]. Apart from the main objective of alloying, the occurring highly exothermic reaction has also attracted interest in academia and industries. The released energy can be used as a heat source and therefore represents a promising approach for thermal joining applications. Multi-material designs and thus hybrid joints are gaining importance in the field of production engineering due to their lightweight potential. Consequently, inventive and innovative joining strategies are required.

1.1. Reactive systems as innovative heat source
The combinations of elements (e.g. Ni + Al, Ti + 2B, Hf + C, etc.), which are used in combustion synthesis, are denoted as reactive systems. In a specific stoichiometric ratio, the reactants are able to undergo a self-sustaining, exothermic reaction. During this reaction, the reactants can either be in a solid, liquid or gaseous state depending on the respective adiabatic temperatures [4]. The ignition of a reactive system is of major importance, since it significantly influences the combustion mode. Generally, it can be distinguished between two combustion modes: the self-propagating or propagation mode [5] and the thermal explosion [6] or volume combustion synthesis mode [7]. Together with the fact that the term self-propagation high temperature synthesis (SHS) is often synonymously used with the term
combustion synthesis as well as the self-propagating mode, it becomes evident that a vast variety of terms is present in scientific publications. In case that the reaction is initiated by uniform heating (e. g. in a conventional oven, with electromagnetic waves [8] or in an induction furnace [9]), the thermal explosion mode occurs. If the energy input is not homogeneous, but locally confined to a certain point or area (e. g. induced by a mechanical impact [10], a heated wire [11] or a laser impulse [12]), a planar, self-sustaining reaction wave propagates through the reactive system which is referred to as self-propagating mode. Aside from the initiation, the reaction behaviour is also influenced by the morphologic structure of the reactants. Most common in combustion synthesis are powders or pressed pellets [2]. In addition to that, reactive foils, also denoted as multilayer systems, have attracted increased attention over the past decades. An overview over the different structures is depicted in figure 1.

As illustrated in figure 1 a), multilayer foils and particles can be considered as the two basic forms of reactive systems. Moreover, the category of particles can be further subdivided into homogeneous mixtures of particles, lamellar composites and particles with a core-shell structure (see figure 1 b)). The structure of the reactive system as well as the morphologic form significantly influence the reaction characteristics like the reaction rate, the ignition temperature or the maximum combustion temperature. Taking into consideration that multilayer systems, which consist of alternating layers of two metals in the range of nanometres, differ from particles with dimensions in the millimetre range by several orders of magnitude, the previous statement becomes most obvious.

1.2. Reactive joining with nickel and aluminium
While a great variety of reactive systems exists, the combination of nickel and aluminium has attracted particular attention. The ordered crystal structures in nickel aluminides result in low densities, high melting points, high mechanical strengths as well as comparatively good oxidation and corrosion resistances [13]. Due to these excellent material properties, nickel aluminides are not only used as lightweight construction materials, but also in order to influence the combustion characteristics of propellants [14] or as elaborated coatings [15]. Although experimentally determined values for the reaction enthalpy vary, a value of $-62 \pm 2$ kJ/mol corresponds to most publications [16; 17]. Furthermore, maximum reaction temperatures of up to 2083 K [18] are reached within milliseconds or seconds, which forms a promising basis for thermal joining applications. The idea of using the released heat of reactive systems as a joining technology has led to sophisticated research efforts [19]. To the present day, reactive multilayer systems consisting of nickel and aluminium represent the only system that is commercially available (trade name NanoFoil®). Different intrinsic structures and characteristics, namely the bilayer or the overall thickness, strongly influence the reaction characteristics [20] and thus can be an effective means to adapt the desired reaction enthalpy to a specific joining task. However, this valuable joining concept features certain disadvantages. Due to the brittle nature of the multilayer systems, the geometries of the joining partners are limited to even surfaces. In addition to that, the comparatively low degree of automation [21] combined with high manufacturing costs because of the physical vapour deposition process impede the industrial application. Reactive particles, which provide the advantageous characteristics of reactive systems as well as an increased flexibility for joining geometries, represent a promising alternative to multilayer systems.
Pellets of homogeneous mixtures of nickel and aluminium powders have been used to join nickel base superalloys [22; 23] or refractory ceramics [24]. However, comparatively little attention is being paid to reactive core-shell structures. Research efforts in the field of core-shell particles, also denoted as clad particles, are limited and mainly focussed on the reaction behaviour [25–27] for the use in propellants or combustion synthesis. Every single particle represents a reactive system and thereby contributes to the reaction during the joining process. Thus, the synthesis of core-shell particles, which forms the basis for the resulting combustion characteristics, must be further studied.

1.3. Electrochemical synthesis of reactive particles

Reactive core-shell particles are commonly synthesised via wet-chemical coating processes, with aluminium as the substrate and nickel as the deposited material. In contrast to the electroless deposition [28], the electroplating of aluminium powders with nickel is not properly described. Generally, aluminium particles are suspended in a nickel ions containing electrolyte and electroplated with nickel as soon as they come into contact with the cathode. In a continuous process, the suspension is circulated so that the particles repeatedly collide with the cathode [29; 30]. A discontinuous process consists of three steps: sedimentation, electroplating and stirring [31]. First, particles settle onto the cathode. As soon as the circuit is closed, particles are electroplated. Finally, vigorous stirring separates agglomerates, which formed during the electroplating step.

For aluminium particles with a natural oxide layer, a specific pre-treatment is required, since the particles have to be electrically conductive. In addition to that, numerous parameters influence the deposition of nickel on aluminium particles and therefore have to be taken into consideration. Figure 2 shows essential parameters for obtaining reactive core-shell particles.

![Figure 2. Essential parameters for the electroplating of aluminium particles with nickel.](image)

TAKESHIMA et al. [29] present a continuous process to obtain coated aluminium particles with diameters ranging from 0.1 to 10 µm. On the contrary, Ylı[31] describes a discontinuous process without any restrictions regarding the particles size, but does not explicitly mention aluminium particles to be suitable for electroplating. Therefore, this research focusses on the electrochemical synthesis of reactive core-shell particles, which are composed of aluminium as a substrate and nickel as coating. A two-step wet-chemical process is studied, which consists of an electroless pre-treatment for the removal of the oxide layer and a discontinuous electroplating process.

2. Experimental procedure

The pre-treatment of the aluminium particles (New Materials Development GmbH, 6.9 µm and 23.5 µm, 99.7 % purity) requires the following chemicals: nickel(II) chloride hexahydrate (Alfa Aesar, 99.3 %),
ammonium chloride (Sigma-Aldrich, 99.998 %), sodium citrate dihydrate (Sigma-Aldrich, ≥ 99 %) and sodium fluoride (Fluka, ≥ 99 %). The electrolyte is a common Watts bath and consists of the following chemicals: nickel(II) chloride hexahydrate (see above), boric acid (Sigma-Aldrich, 99.7 %) and nickel(II) sulphate hexahydrate (Sigma-Aldrich, ≥ 99.95 %). All chemicals were used as received.

2.1. Pre-treatment and electroplating of nickel

Prior to the electroplating, it is essential to remove the natural oxide layer of the aluminium particles. The pre-treatment solution is based on RAMASESHAN et al. [32] and serves to remove possible contaminations as well as to prevent further oxidation by substituting the oxide with a layer of nickel. The adapted composition for the electroless pre-treatment at room temperature is shown in table 1.

| Chemical                        | Formula                  | Pre-treatment solution |
|---------------------------------|--------------------------|------------------------|
| Nickel(II) chloride hexahydrate | NiCl₂·6H₂O               | 30 g/l                 |
| Ammonium chloride              | NH₄Cl                    | 7 g/l                  |
| Sodium citrate dihydrate       | C₆H₅Na₃O₇·2H₂O          | 20 g/l                 |
| Sodium fluoride                | NaF                      | 0.5 g/l                |

Subsequently, aluminium particles are electroplated with nickel until a stoichiometric ratio of 1:1 is reached. Table 2 describes the composition of the electrolyte solution, which is a Watts bath.

| Chemical                        | Formula                  | Electroplating solution |
|---------------------------------|--------------------------|-------------------------|
| Nickel(II) sulphate hexahydrate | NiSO₄·6H₂O               | 300 g/l                 |
| Nickel(II) chloride hexahydrate | NiCl₂·6H₂O               | 20 g/l                  |
| Boric acid                      | H₃BO₃                   | 20 g/l                  |

2.2. Experimental set-up

The electroplating of the aluminium particles with nickel requires a specific experimental set-up, which guarantees that the aluminium particles are in contact with the cathode. In this study, a discontinuous three-step process patented by YIH [31] was used. A schematic representation of the experimental set-up is depicted in figure 3. An automated process control allows to adapt the time-related parameters sedimentation, electroplating, and stirring time. Uniform heating is ensured by a heating jacket which encloses the glass cylinder with the electrolyte solution. The cathode is made out of aluminium so that the oxide layer, in this case, can prevent nickel deposition [31].
3. Results and discussion
Before discussing the electroplating process, the oxidation of aluminium, which can be found in common literature, but is not mentioned in the patents cited above, is studied. This phenomenon is of crucial importance for the laboratory- and industrial-scale synthesis of reactive core-shell particles.

3.1. Reaction of aluminium particles
Aluminium particles are also under investigation due to the oxidation of aluminium in aqueous solutions and the resulting formation of hydrogen. Starting with the overall reaction equation, the occurring reactions can be described as follows [33]:

\[
\begin{align*}
2\text{Al} + 6\text{H}_2\text{O} & \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \uparrow \\
\text{Al}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2\text{AlOOH} \\
\text{AlOOH} + \text{H}_2\text{O} & \leftrightarrow \text{Al(OH)}_3
\end{align*}
\]

Since the reaction shown in equation (1) is both a source for hydrogen and highly exothermic with a heat release of 16.95 kJ/g [34], aluminium particles are suitable for energy and hydrogen storage. The oxide layer on the aluminium particles and its reaction with water (see equation (2) and (3)) as well as low temperatures inhibit further oxidation and are hence considered disadvantageous [33; 35].

As it can be consequently anticipated that the suspension of the aluminium particles in the aqueous Watts electrolyte solution will result in the formation of hydrogen, preliminary studies with only deionised water and aluminium particles (6.9 µm and 23.5 µm) were conducted. It was investigated how the ratio of the mass of aluminium particles to the volume of water, the temperature of the suspension, a pre-treatment, the particle size and stirring influence the subsequent electroplating process.

It was found that a high ratio of the mass of the aluminium particles to the volume of the water, stirring and a smaller particle size promote the formation of hydrogen. In contrast to that, lower temperatures ranging from 318 to 323 K and a pre-treatment of the aluminium particles impede the exothermic reaction. Furthermore, the formation of hydrogen in the electrolyte solution is weaker.

3.2. Electroplated core-shell structures
In order to obtain reactive core-shell particles, the pre-treated aluminium particles are electroplated with nickel until a stoichiometric ratio of 1:1 is reached. The pre-treatment took place at room temperature.
and no significant formation of hydrogen was observed. A scanning electron micrograph of the pre-treated aluminium particles is shown in figure 4. In order to avoid further or a new formation of Al₂O₃, the particles were directly added into the electrolyte solution after washing.

![Figure 4. Scanning electron micrograph of a pre-treated aluminium particle.](image)

Based on the preliminary studies, on experiments with a Hull cell and on the information given in the cited literature, essential parameters were identified and varied within a specific range as listed in table 3. It is recommended to adjust a current density over 5 A/dm² and to vary the height of the sediment layer from 1 to 30 mm depending on the particle size [31].

**Table 3. Parameters for the electroplating process.**

| Parameter                      | Value or range |
|-------------------------------|----------------|
| Stirring time                 | 10 s           |
| Sedimentation time            | 120 s          |
| Current density of the cathode plate | 5 A/dm²      |
| Electroplating time           | 150 s          |
| Sediment layer height         | 1 – 10 mm      |
| Temperature                   | 323 K          |
| Stirring speed                | 500 rpm        |
| Number of cycles              | 50             |

At first, particles with a diameter of 23.5 µm were studied at a temperature of 323 K and a sediment layer height of 10 mm. The results of the electroplated aluminium particles are illustrated in figure 5.

![Figure 5. Scanning electron micrographs of the metallographic section of the electroplated aluminium particles (dark grey) with nickel (light grey).](image)
Even though the aluminium particles are electroplated with nickel, the coating only results in some core-shell particles (see figure 1 a)). The thickness of the nickel layer as well as the uniformity of the nickel shell differ (see figure 1 b)). As significant hydrogen formation was observed during the electroplating process, no proper sediment layer could be formed, which led to the circumstance that particles were not constantly in contact with each other during the electroplating step.

Moreover, particles with a diameter of 6.9 µm were investigated. In order to reduce the expected increase in the hydrogen formation due to the smaller particle size, the height of the sediment layer was reduced to 3 mm. The result is shown in figure 6.

![Figure 6. Scanning electron micrograph of the metallographic section of the electroplated aluminium particles (dark grey) with nickel (light grey).](image)

The formation of hydrogen and thus the movement of the suspension could be reduced. As a result, a more uniform layer of nickel was deposited onto the aluminium particles. However, there are still particles without any nickel shell and agglomeration was enhanced. After the electroplating process, a significant amount of nickel could be found on the cathode as well as adhering aluminium particles. Ignition tests with microwaves at a frequency of 2.45 GHz were used to demonstrate the reactivity. However, the described inhomogeneities led to an irregular combustion. Consequently, the electroplating process must be further investigated to determine the cause-effect relationships between electroplating and hydrogen formation to obtain reactive core-shell particles.

4. Conclusions
Reactive systems are not only successfully used in combustion synthesis for the production of high-performance alloys, but do also represent a promising approach for joining different materials like metals, ceramics and plastics. The combustion characteristics and thus the released energy of a reactive system strongly depend on the morphologic structure of the reactants. In contrast to multilayer systems, particles provide an increased flexibility for joining geometries. In addition to that, reactive particles, with each single particle being reactive, are of great interest as a tailored heat source in thermal joining applications. Thus, a two-step wet-chemical process for the synthesis of reactive core-shell particles has been developed. The occurring oxidation of aluminium in aqueous solutions and the resulting formation of hydrogen significantly hamper electroplating. On the basis of experimental studies it could be demonstrated that the production of reactive core-shell structures is possible. However, further studies to investigate the cause-effect relationships must be performed to obtain a stable and safe process.
5. References

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