Optimisation of the microwave assisted SHS of intermetallics in single mode applicators

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Short Abstract—Microwave assisted Self propagating High temperature Synthesis (SHS) of NiAl intermetallic in single mode applicator has been optimized by means of electromagnetic field numerical simulation and Design of Experiments techniques. The optimized synthesis conditions have been applied to the reactive sintering of NiAl on titanium substrates, evidencing the formation of a hard dendritic layer, belonging to the Ni-Al-Ti system. The dendritic layer could not be directly formed using conventional (resistance) heating.

Keywords: microwave assisted SHS, intermetallic, NiAl, titanium

I. INTRODUCTION

A relatively economic route for the production of intermetallics in bulk form is Combustion Synthesis (CS) or Reaction Synthesis (RS), a process used for decades to obtain ceramics and their composites, benefiting of the widely acknowledged energy and economic savings [1-5]. Reaction synthesis (combustion synthesis) is a process which uses the exothermic reaction of reactants, properly ignited to spontaneously transform into products. Depending on the mode of ignition, the process can be subdivided into Self-propagating High temperature Synthesis (SHS) in which a reactant compact is typically ignited at one end, and thermal explosion, in which the whole volume of the compact is heated to the ignition temperature. Both methods of ignition have been used in the past in the fabrication of nickel aluminides, and recently the use of microwaves to ignite CS has been reported for the NiAl intermetallic [6]. The direct microwave absorption, within the skin depth, of the metal powders, can not completely explain the microwave-matter interaction. In case of metallic powder compacts immersed in relatively high intensity electromagnetic field, other phenomena can occur, leading to a more pronounced and deeper heating of the conductive material, like arcing and plasma formation [7,8]. Moreover, the oxide layer which can be present on the metallic powders can give a further heating contribution by dielectric heating [9]. One of the main drawbacks in using microwaves to ignite the CS lies in its intrinsically low reproducibility. Many factors affect the way a load can be heated in a microwave applicator, and small compositional unhomogeneities (variations of electric, magnetic or dielectric properties), or non-controllable electromagnetic field distributions contribute in perturbing the heat generation. Aim of the present work is the optimisation of the Microwave Assisted Combustion Synthesis (μwACS) of intermetallics in a single mode applicator, in order to achieve the highest yields, energy efficiency and process reproducibility. An application of the method to the synthesis of NiAl and to the reactive sintering of NiAl compacts on Ti substrates is presented as well.

II. NUMERICAL SIMULATION TO OPTIMISE THE SYNTHESIS CONDITIONS

The software Concerto 4.0 (Vector Fields, U.K.) has been used to numerically simulate the heating behavior of a metallic powder compact in a microwave single mode applicator, based on the WR340 waveguide geometry. The aim of the modeling step, preliminary to the experimental activity, is to determine the most suitable refractory support to be used during Microwave Assisted Combustion Synthesis. As a matter of fact, the refractory deeply influences the heating behavior and the energy efficiency of the whole process, since it can absorb or reflect microwaves, as well as modify the electromagnetic field distribution around the sample. The model is composed of a rectangular metallic enclosure (microwave applicator) containing a 70 mm diameter disc upon which lies a 30 mm diameter silicon carbide disc and an optional third graphite disc, 20 mm of diameter. The SiC disc, acting as an auxiliary absorber, is used to increase the temperature of the load, placed on top, in order to improve its microwave coupling efficiency. This setup has demonstrated, in a previous work [10] that the presence of an auxiliary absorber helps improving the reproducibility of the results, while a direct microwave absorption by the metallic powder compact is more prone to arcing and lack of homogeneity. The material of which the base disc is constituted has been varied from a total reflective behavior (metal), to a lossy (SiC) or to a transparent (Al2O3) one. The length of the applicator can be varied as well, to simulate the presence of a movable plunger, while the remaining dimensions (86 x 43 mm) are fixed. On one side of the applicator is positioned a port excited sinusoidally in the fundamental TE10 mode, simulating the magnetron, operating at 500W power, 2.45 GHz frequency. Four different configurations have been tested, namely a metallic, a low-loss, a lossy disc, and a low loss disc having a third graphite disc on top. The presence of a different support material (base disc) will affect the heating behaviour of a load positioned on the top of the SiC element, as shown in fig. 1. This difference can be quantitatively evaluated integrating the calculated SAR values over the second disc volume, as depicted in fig.2. The best conversion of microwave power into heat occurs in case of alumina as a refractory support. The presence of a thin graphite disc on the top of the SiC disc slightly worsen the efficiency, while the presence of a lossy material lowers the power...
available to heat the SiC disc of more than one order of magnitude, while the metallic support lowers the electric field intensity in the SiC disc, as well as drastically changing the impedance matching of the system.

Figure 1. SAR envelope (W/kg) of the SiC disc layer nearest to the reacting Ni-Al powders, placed on (from left to right): a metallic disc, a low-loss disc, a lossy disc, and a low loss disc having the third graphite disc on top.

Figure 2. SAR in the SiC disc volume as a function of the base disc material and of the presence of the optional third graphite disc.

III. EXPERIMENTAL

A. NiAl synthesis

The software Design Expert v.6 was used to reduce the number of experiments needed to gather information regarding the optimization of the SHS of NiAl. Independent variables were: microwave forward power (500, 1500 W), sample mass (3, 5 g), sample forming pressure (50, 150 MPa), atmosphere (Ar, air) and support material (SiC, graphite). Dependent variables were ignition temperature, ignition time and a calculated merit factor proportional to the amount of NiAl obtained. A two level factorial fractional (1/2) design was chosen, leading to 16 experimental conditions, repeated for two blocks. Ni carbonyl powders (99% pure, 5-7 μm in diameter) and Al gas atomized powders (99.8% pure, 10-50 μm in diameter) were mixed in a Al₂O₃ ceramic jar for 30 minutes under vacuum in a 1:1 atomic ratio. Successively, to compact the powder mixtures, an uniaxial pressure of 50 or 150 MPa, in a cylindrical metal mould, was applied; the diameter of the compacted samples was 20 mm. A microwave TE10n single mode applicator operating at 2.45 GHz was used to start the SHS. Forward and reflected power were monitored by means of a directional coupler, while a 3-stub tuner and a movable short circuit were used for impedance matching purposes during the whole test runs. A 3 kW magnetron, water cooled, was used to feed the applicator, interposing a 3-port circulator to protect the generator from the reflected power. The magnetron forward power was set to constant power (500 or 1500 W) for all the runs. Reacted samples were subjected to optical microscopy and Scanning Electron Microscopy (SEM) to evidence the microstructure evolution, while phase analysis was performed by means of X-Ray Diffraction analysis (XRD). EDS (Energy Dispersive x-ray microanalyzer Spectroscopy), attached to the SEM, was used to confirm the absence of potentially deleterious unhomogenous regions, presenting a Ni/Al ratio different from 1. A merit factor was defined as the ratio between the NiAl XRD main peak intensity and the sum of the NiAl and Al₂O₃ main peak, the latter if present.

B. Reactive sintering of NiAl compacts on Ti substrates

The optimized synthesis conditions previously determined for the SHS of NiAl intermetallics were applied to reactive sintered Ni-Al (1:1 atomic ratio) powder compacts on Ti and Ti6Al4V discs. The high temperature involved in the synthesis can be higher than the titanium melting point, thus leading to the rapid formation of ternary Ni-Al-Ti intermetallic compounds. In order to compare microwave assisted SHS with conventional SHS methods, reactive sintering tests have been performed in a resistance heating furnace, maintaining unaltered the experimental conditions (atmosphere and system geometry) and applying similar heating rates to the reacting powders, when possible.

IV. RESULTS AND DISCUSSION

Microwave assisted SHS of NiAl intermetallic was successful in all the experimental conditions considered, despite some pronounced differences in the final products aspect and composition. The variation of the synthesis conditions allowed to investigate the influence of the main variables, as depicted in fig. 3.
From the experimental results, it can be inferred that:

- Ar flux increases the NiAl yield, as well as reaction time. This can be explained considering the prevention form the oxidation offered by the Ar flux, but also its cooling effect on the sample's surface.

- the use of SiC, without any further conductive layer, leads to the highest reproducibility of results and the highest NiAl yield. The SiC, as a matter of fact, is governing the early stages of heating and constitutes a somewhat fixed load which is able to partially compensate the sample's properties variation. Moreover, the higher temperature surrounding the sample improves the propagation of the reaction from the ignition points.

- a lower forming pressure increases the microwave coupling and thus reduces the synthesis time. This phenomenon can be ascribed to a slightly higher microwave penetration in a partially dense compact, and a lower thermal conductivity of the sample, which, thus, dissipates less heat to the environment.

Integrating the forward and reflected power curves as a function of time, and dividing by the NiAl mass obtained, it has been possible to quantify the specific energy consumption. Fig.4 summarizes the calculation results, evidencing that the specific energy consumption is lower in case of use of the SiC alone and without Ar flux, leading to an average 3.1 Wh/g of synthesized NiAl. Despite the presence of an auxiliary absorber, the lower reflected power, as well as the improved synthesis conditions, allow the obtainment of the highest energy efficiency.

When the optimized experimental conditions (in terms of NiAl yield, i.e. using SiC and Ar flux) are applied to the microwave assisted synthesis of the intermetallic on a reactive layer, like titanium and its alloys, there is the formation of a dendritic layer, whose composition belongs to the Ni-Al-Ti system [11]. This dendritic layer is not observed after conventional SHS performed in the same conditions. The dendritic layer is not homogenous, compare spectra 1 and 2 in fig. 5, and its titanium content progressively decreases moving from the substrate to the region where the NiAl powders compacts were placed. A NiAl free zone, obtained avoiding to completely cover the titanium substrate with the reacting powders, allowed to determine that there is no diffusion of titanium, the ternary dendritic region being formed exclusively by liquid NiAl diffusion in the titanium. This issue can explain the different microstructure observed when performing the SHS on titanium by microwaves rather than conventionally.

In conventional SHS, the temperature of the furnace is raised up to the temperature needed to ignite the reaction. As soon as the reaction starts, the high temperature due to the exothermic reaction tend to invert the heat flow, so that the newly formed intermetallic transmits heat to the surrounding environment. During microwave treatments, instead, energy can still be conveyed to the newly formed NiAl during and after the synthesis, and heat can still be generated inside the liquid NiAl phase, thus partially compensating the heat losses towards the cooler surroundings. This phenomenon could help slowing the solidification of the newly formed NiAl (and its compounds presenting different stoichiometry [12]) maintaining it in the liquid state for longer time, thus favoring its diffusion and reaction with the titanium substrate. From an application point of view, this peculiar aspect of microwave assisted SHS leading to reactive sintering of the starting Ni and Al powders presents numerous advantages, like the possibility of joining titanium parts with minimum overall heating of the parts (only the joining region is heated directly), or cladding titanium with layers presenting interesting mechanical properties. Fig. 6 shows the results of a scratch test, at 1N constant load, conducted on the interface regions among the titanium substrate, the dendritic layer, and the synthesized NiAl. The dendritic layer present a lower friction coefficient.
(yellow curve), as well as higher hardness, deducible from the residual depth curve (green) and from fig. 7. In addition it can be observed that the dendritic region is completely crack-free, and presents some crack-stopping capabilities, as evidenced in fig. 7, where a crack from the NiAl region is not able to completely propagate through the dendritic layer.

Figure 6. Scratch test (1N) on the dendritic interface: Pd= penetration depth of the indenter during the scratch test; Rd= residual depth of penetration after the test; friction= friction coefficient.

Figure 7. Vickers microhardness indentations on the titanium substrate, on the dendritic layer and on the NiAl intermetallic

V. CONCLUSIONS

Coupling the numerical simulation of the SHS of metallic powder compacts with a proper Design of Experiments can help reducing both the modeling and the experimental time required to optimise the process. An application of this approach to the synthesis of NiAl is presented, aimed at achieving the highest process reproducibility, yield and efficiency. Once the best synthesis conditions have been determined, the reactive sintering of NiAl on titanium substrate has been performed, both conventionally and by microwave heating. In the first case, no adhesion was observed between the substrate and the newly formed NiAl, while in the second case a pronounced dendritic layer, of composition belonging to the Ni-Al-Ti system, was formed. Its formation can be ascribed to the possibility offered by microwaves of conveying energy to the molten NiAl during synthesis and cooling, thus slowing its solidification and favoring its reaction with the titanium substrate. The dendritic layer present interesting mechanical properties, like low friction and high hardness, as well as crack-stopping capabilities.

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