# Microwave ignited combustion synthesis of intermetallic compounds, modelling and experimental results

E. Colombini, R. Rosa, P. Veronesi, A. Casagrande

*The process of Combustion synthesis (CS) is based on the highly exothermic reaction by reactants, which, if properly ignited, spontaneously turn into products. The aim of this work is to study the CS of β-NiAl formed starting from Ni and Al (1:1 at. %) powders activated by microwaves at 2.45 GHz. Numerical simulation is used to obtain data otherwise difficult to be measured experimentally and to develop a predictive model of microwave ignited and sustained CS of metal powder compacts. The simulation couples an electro-thermal model with a chemical model, required to study the exothermic reaction between powders. A simplify model was obtained and validated, neglecting volume changes, to study compositional and temperature change and reaction kinetics during the CS. It allowed to demonstrate how microwave application, during and after, synthesis could control the cooling rate of products and hence the microstructure of the newly formed intermetallics.*

Keywords:
combustion synthesis, intermetallics, microwaves, numerical simulation

## INTRODUCTION

Intermetallics are extremely promising materials to improve the performance of engines, pumps, heat exchangers, furnace components, tools and dies parts [1]. These properties make them suitable for high temperature structural and coating applications, despite a relative intrinsic brittleness [2]. Among intermetallic compounds, aluminides, are regarded as promising candidates for the next generation of high temperature, high performance structural and coating materials.

The Ni-Al phase diagram (Figure 1) contains five intermetallic compounds ($Al_3Ni$, $Al_3Ni_2$, $Al_3Ni_5$, NiAl, $Ni_3Al$). Among these, NiAl and $Ni_3Al$ have received an increasing scientific attention [3] and NiAl is one of the most attractive, having a high melting point (1638 °C), a low density (5.91 g $cm^{-3}$), an excellent oxidation resistance and a good thermal conductivity (75 W $m^{-1}$ $K^{-1}$)[4]. Thus, it represents a good compromise between a relatively low density and the capability to withstand high temperatures.

A possible synthetic route to produce high purity intermetallics, and in particular, aluminides, is Combustion Synthesis (CS) [5]. Combustion synthesis (CS) exploits the propagation of a combustion front across the reactants mixture. The reaction starts at a triggering or ignition temperature and it is sustained by self-heating of the unreacted portion of the mixture, associated with the release of exothermic heat of formation [6-7]. There are basically two different ways to trigger CS: Self-propagating High-temperature Synthesis (SHS) mode or Thermal explosion (TE) mode. In the SHS mode the reaction is ignited at one end of the reactive sample and it self-propagates through the reactants in the form of a combustion wave at very high velocities. In the TE mode, the whole volume of the sample is heated uniformly in a controlled manner, until reaction takes place essentially simultaneously throughout the volume.

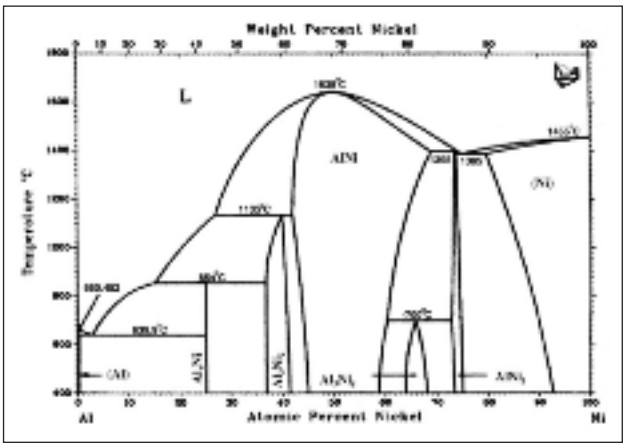


**FIG. 1** ***Phase Diagram Ni-Al [3].***
*Diagramma binario Ni-Al [3].*

All Combustion Synthesis reactions ignited by conventional heating techniques usually show an inversion of the heat flow before and after the synthesis: initially heat is transferred from the ambient to the reactants; after ignition, the usually extremely high temperatures of the newly formed products cause the reversal of heat flow. For this reason, as soon as the reaction occurs, it is no longer possible to continue to transfer heat by conventional heating from the external heating source to the reaction zone. The use of microwaves heating selectivity, instead, is expected to lead not only to a more rapid temperature increase of the whole re-

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action zone, but also to a continuous energy transfer during and after the ignition [1].
The aim of the present work is to experimentally study and to numerically simulate the microwave ignited combustion synthesis of intermetallic based materials. Numerical simulation of the process is used to overcome the difficulty - or impossibility - to perform non perturbative temperature measurements during microwave initiated CS. Numerical simulation, thus, is used to estimate the heating and cooling rates in each portion of the reactants and products volume, as well as of the surrounding substrates and supporting materials. In this work, a simplified multi-physics model, neglecting volume change of the reactants, of the microwave-assisted combustion synthesis of Ni and Al metal powders to form the NiAl intermetallic between metal substrates has been realized and validated, considering the following reactions [9]:
(1) $Ni + 3Al \rightarrow NiAl_3$
(2) $NiAl_3 + Ni \rightarrow Ni_2Al_3$
(3) $Ni_2Al_3 + Ni \rightarrow 3NiAl$

## NUMERICAL SIMULATION

The numerical simulation of the microwave assisted CS requires to couple an electro-thermal model (electroheat, considering microwave power generation and heat transfer) with a chemical model (reactions 1-3), the latter necessary to study the exothermic reaction between powders and account for a further heat generation term. In this way it is possible to obtain a simplified model to study compositional and temperature variations, as well as reaction kinetics during the CS. The software used to simulate the system is Comsol Multiphysics 3.5a.
The electromagnetic part of the model is based on two different geometry, namely an axial-symmetrical microwave cavity fed by a TEM coaxial cable, and a prismatic microwave applicator, based on the WR340 waveguide. The latter reproduces the experimental setup used and described in next section. The sample (pressed disc mixture of Ni+Al powders) is placed, in both cases, in the region of expected maximum of electric field. This configuration allows to attain rapidly ignition condition in comparison with maximum magnetic field configuration, as demonstrated by the authors in a previous work [10]. The model geometry and dimensions are shown in Figure 2.
To simulate microwave heating, the built-in RF application mode of Comsol was used. Boundary conditions are of perfect electric conductor, except for the microwave input (port, with power of 600 - 1200 W range, at 2.45 GHz.)
Due to the lack of reliable high temperature data on magnetic and dielectric properties of reactants and products at 2.45GHz, the electromagnetic pat of the model has been solved independently on the thermal one, in stationary conditions, to calculate

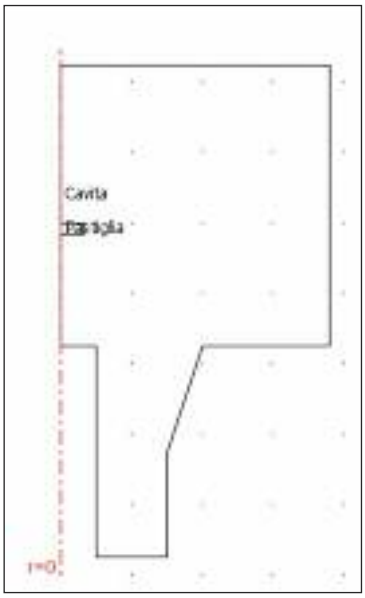


**FIG. 2**
***2D Axial-symmetric model, coaxial feed (bottom).***
*Modello 2D assial-simmetrico, applicatore alimentato da conduttore coassiale (in basso).*

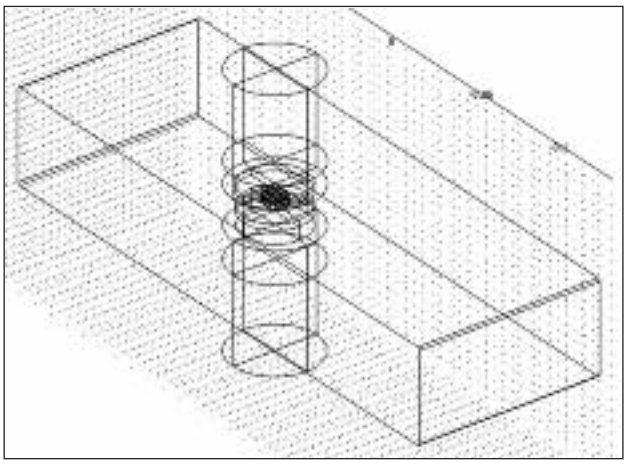

**FIG. 3** ***3D model, based on WR340 waveguide.***
*Modello 3D, configurazione basata sulla guida d'onda WR340 (86x43mm).*

the power density generated in the load, by microwave heating, and to be used as source term in the heat transfer equation. Heat developed by microwaves is used as input value to activate CS of Nickel and Aluminum powders. CS is described using the predefined Comsol Reaction Lab module. This module requires kinetic parameters such as Arrhenius pre-exponential factors, A, and energy activation, E, as well as thermodynamic factors (e.g.

| Reaction | A | E [kJ mol$^{-1}$] [11] | H [kJ mol$^{-1}$] [11] | S [J mol$^{-1}$ K$^{-1}$] [11] |
|---|---|---|---|---|
| 1) $Ni+3Al \rightarrow NiAl_3$ | 8.4 [12] | 135 | -151 | -110.7 |
| 2) $NiAl_3 + Ni \rightarrow Ni_2Al_3$ | 4.06 [13] | 119 | -433.4 | -247.1 |
| 3) $Ni_2Al_3 + Ni \rightarrow 3NiAl$ | 0.07 [13] | 76 | -637.6 | -190.5 |

**TAB. 1**
***Kinetic and thermodynamic parameters.***
*Parametri termodinamici e cinetici delle reazioni*

| Element | Cp [J mol$^{-1}$ K$^{-1}$] [7] [11] | $C_0$ [mol m$^{-3}$] |
|---|---|---|
| Ni | 25.52 | 45000 |
| Al | 24.3 | 45000 |
| $NiAl_3$ | 53.49 | 0 |
| $Ni_2Al_3$ | 75.95 | 0 |
| NiAl | $(41.925+(13.6e\text{-}3\cdot T)-(0.033e5\cdot T^{-2})+(0.1e\text{-}6\cdot T^2))$ | 0 |

entropy, enthalpy and specific heat) and physical data (concentration, density and molecular weight) of the 1-3 reactions and individual elements. Table 1 shows used data and, when available, references used.
Concentration is calculated by stoichiometry, according to real geometric dimension obtained measuring a powder compact produced in laboratory according to the procedure described later in the text .
An average porosity, about 30%, is considered. This value is applied to specific heat (4), density (5) and thermal conductivity (6), according to equations:

(4) $C_{p\_real} = C_{p\_theoretic} \cdot (1 - \%porosity)$

(5) $\rho_{real} = \rho_{theoretic} \cdot (1 - \%porosity)$

(6) $k_{real} = k_{theoretic} \cdot [(1-\%porosity)/(1+(\%porosity/2))]$ [13]

Results obtained by the chemical model simulation are shown in figures 4-5.
In Fig. 4 it is possible to notice the rapid temperature increase due to CS ignition, occurring when the microwave power generated in the load increases the temperature up to the ignition temperature. It is not evident any cooling after reaction occurred because in the chemical part of the model no heat loss is implemented.
Fig. 5 shows the time-dependent concentration of the reacting species and products, demonstrating that, according with experimental and literature [9] results, NiAl is the only product at the end of the reactions 1-3.

## EXPERIMENTAL STUDY

Nickel (≈ 3 μm, 99,7% purity) and Aluminium (≈ 200 mesh, 99% purity) powders were provided by Aldrich Milan, Italy. The powders have been mixed in $Al_2O_3$ agate jar for 30 minutes under vacuum, with ratio 1:1 at%. Disc-shaped compacts have been prepared by inserting the powder mixtures into a 20 mm diameter mould and applying 140 MPa of uniaxial pressure. In this way, a series of compacts with diameter of 20 mm and weight of 3-5 g are prepared for further microwave processing, between two grade 2 titanium discs. The objective is to achieve a reactive synthesis with the titanium support, as described in a previous work [16].
Heating was carried out in a single mode applicator, which is constituted bya magnetron generator (with an output power level ranging from 300 to 3000 W) connected to a three-ports circulator and to a three-stubs tuner, both based on the WR-340 rectangular waveguide geometry (86 x 43 mm section). During the synthesis a pressure of 0.8 MPa is applied to reduce product porosity. The pressure is obtained by application of two low-loss (i.e. not generating heat when exposed to microwaves) refractory cylinders during combustion synthesis, inserted trough two circular ports (circular waveguides under cut-off condition, so as to microwaves does not propagate to the surrounding environment) placed at upper and lower side of cavity. This configuration allows both to minimize perturbation of the electromagnetic field distribution and to apply the load on the upper side of powder compact [17]. A fixed microwave power is directed towards the pressed sample, which is placed at cavity centre, where the electric field is predominant, as a result of TE10(n) mode in the cavity.
Synthesized sample have been cut in order to investigate microstructure and chemical composition by optical microscopy as well as by ESEM (Quanta-200 Fei, Oxford Instruments) and X-rays (EDS, Inca-350, Oxford Instruments).
The optical microscope images shown in figure 6 and 7 show the cross sections of NiAl (left part of the micrographs) obtained by power application of 600 W and 1200 W, respectively, in the case of titanium substrate (right part of the micrograph).

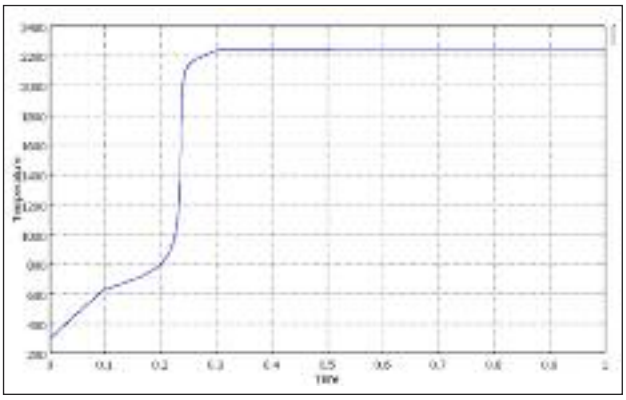

**FIG. 4** ***Temperature [K] vs time[s] (Reaction Engineering Lab).***
*Curva temperatura vs tempo ottenuta da modulo chimico.*

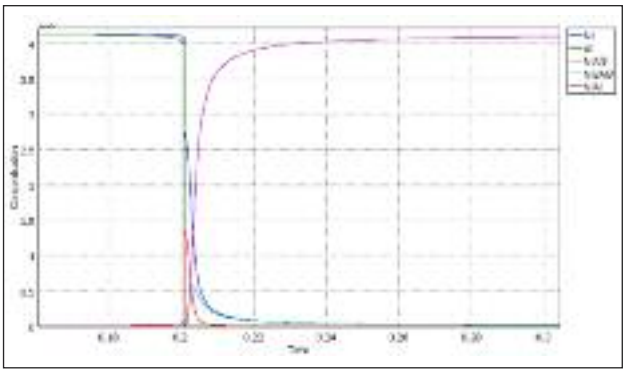

**FIG. 5** ***Species concentration variation during CS.***
*Variazione di concentrazione delle specie.*


**FIG. 6** ***Microstructure sample treated at 600 W.***
*Microstruttura campione trattato con 600 W.*

In both cases, chemical etching with glyceregia for 10 s evidenced the presence of a dendritic intermediate layer (dark regions of figure 6 and 7) with presence also of eutectic microstructures, as shown in a previous work [17-18]. The ESEM-EDS analyses showed the presence of Ni, Al and Ti in this intermediate layer, suggesting that during CS, reactions between the substrate and the reactants occurred. The zones presenting only NiAl formation (left part of figures 6 and 7) exhibit a typical solidification structure, with equiaxial grains growth, confirming the achie-

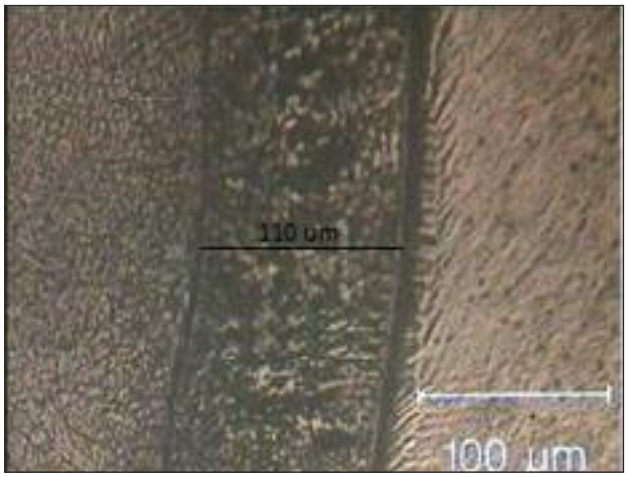


**FIG. 7** ***Microstructure sample treated at1200 W.***
*Microstruttura campione trattato con 1200 W.*

vement of temperature, during synthesis, in excess of the melting temperature of NiAl. Thus, at the very end of CS, the newly formed phases are in the liquid state and this can favour the rapid reaction between the molten NiAl and the Ti substrates, leading to the generation of the intermediate layer, where formation of eutectics in the Ni-Al-Ti system occurs. In particular, in the Ni-Al-Ti system, the liquid phase can exist down to 905°C [7].
The intermediate layer thickness shown in figure 6 and 7 results higher the higher the microwave power applied, thus suggesting a direct interaction of such layer with the microwave field, with possible heat generation occurring selectively in this layer (the titanium substrate can be considered microwave reflective). Hence, the measured thickness difference of the intermediate layer can be ascribed to a different reaction time between the newly formed intermetallics and the Ti substrate. Such reaction time is influenced by the time of existence of the liquid phase, which, at its turn, depends on the microwave power generation in this layer.

## DISCUSSION

In order to understand the dependence of the intermediate layer thickness on the microwave applied power, numerical simulation has been performed varying input power. Results, shown in table 2 and in figure 8 in case of the 3D model, demonstrate that the increase of power, as expected, leads to a proportional increase of resistive heating (time averaged) and of the square root of electric field maximum value.
Figure 9 shows that the zone with higher electric field intensity effectively corresponds to the position of the sample. In these conditions, the extremely high electric field values can lead to arcing, with uncontrollable and localised ignition of the CS. In order to avoid such occurrence, maximum microwave emitted power before CS must be carefully controlled.
Figures 10 and 11 show calculated heating and cooling curves in the centre of the sample (green line) and in the centre of titanium support (blue line) at 600 W and 1200 W, respectively. In

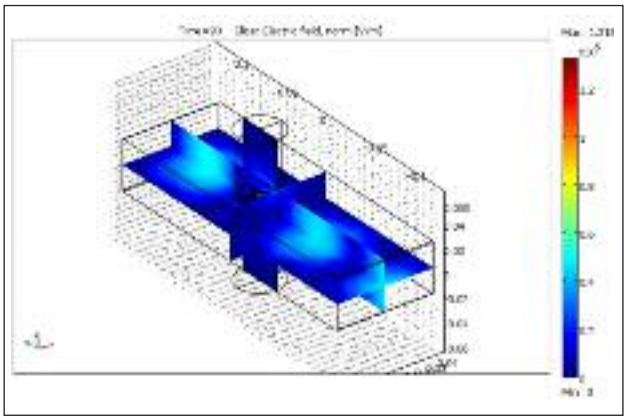

**FIG. 8** ***Electric field distribution [V m$^{-1}$], at 600 W, in the WR340 based applicator.***
*Distribuzione del campo elettrico [V m$^{-1}$], 600 W di potenza in ingresso.*

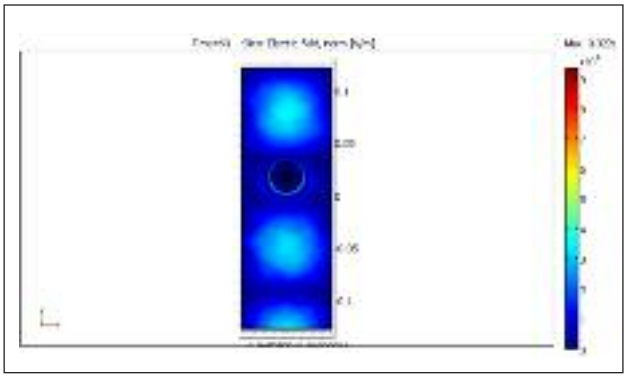

**FIG. 9** ***Particular to show the sample position on maximum of Electric field distribution [V m$^{-1}$].***
*Particolare, mostra la posizione del campione nel massimo del campo elettrico [V m$^{-1}$].*

this simulation microwaves are stopped as soon as CS takes place.
Increasing microwave power decreases the ignition time of CS, which occurs approximately after 22 s at 600 W and after less than 12 second at 1200 W, but the maximum temperature reached is poorly affected by the different ignition power. Also cooling rate depends on initial power, with sample exposed at 600W reaching 905 °C (the minimum eutectic temperature in the ternary Ti-Ni-Al phase diagram) after only 1 second after CS completion, while in case of 1200W power, this temperature is reached 4 seconds after CS completion. Moreover, if microwaves are delivered during and after synthesis, i.e the microwave generator is kept on even after CS completion, the cooling rate further decreases, as shown in figures 12-13, where microwaves are stopped after 60 s and the permanence at temperatures in excess of 905°C lasts almost 60 seconds after CS completion.
The latter aspect is a distinctive feature of microwave heating, where volumetric heating generation on sample allow to slow

| Input Power [W] | Resistive Heating, Time Average [W m$^{-3}$] | Electric Field [V m$^{-1}$] |
|---|---|---|
| 600 | 2.307e7 | 7.812e4 |
| 1000 | 3.846e7 | 9.271e4 |
| 1200 | 4.614e7 | 1.016e5 |

**TAB. 2**
***Resistive heating (time average) in the load and electric field maximum value at different power levels in the coaxial applicator.***
*Valore della densità di potenza nel carico e valore del massimo del campo elettrico a diversi valori di potenza emessa dal generatore nella configurazione con applicatore coassiale.*

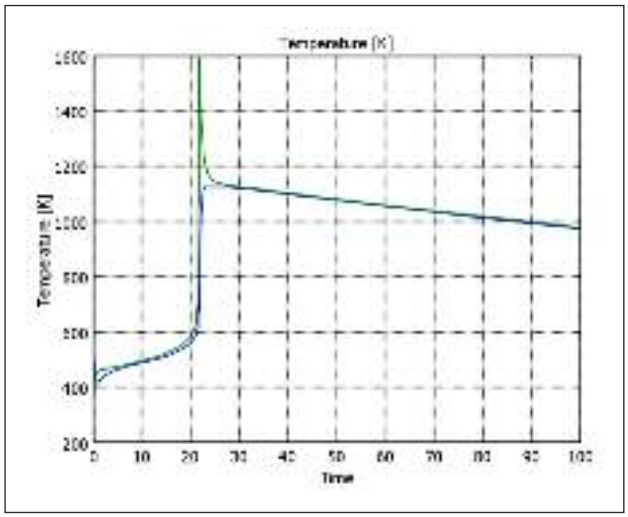


**FIG. 10** ***CS curve at 600 W.***

*Curva di CS con potenza emessa dal generatore di 600 W.*

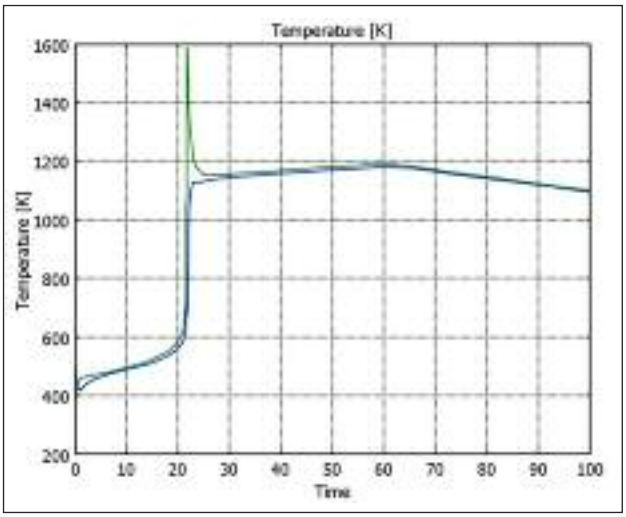


**FIG. 12** ***CS curve, microwaves stop at 60 s, 600 W.***

*Curva CS, microonde fermate a 60 s, con potenza emessa dal genratore di 600W.*

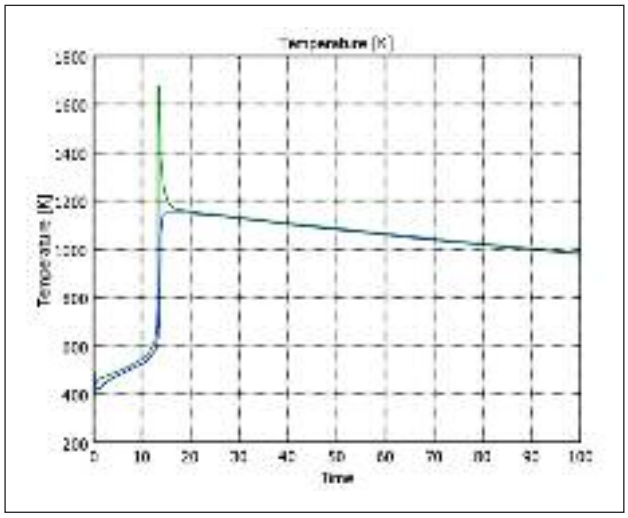


**FIG. 11** ***CS curve at 1200 W.***

*Curva CS potenza inviata 1200 W.*

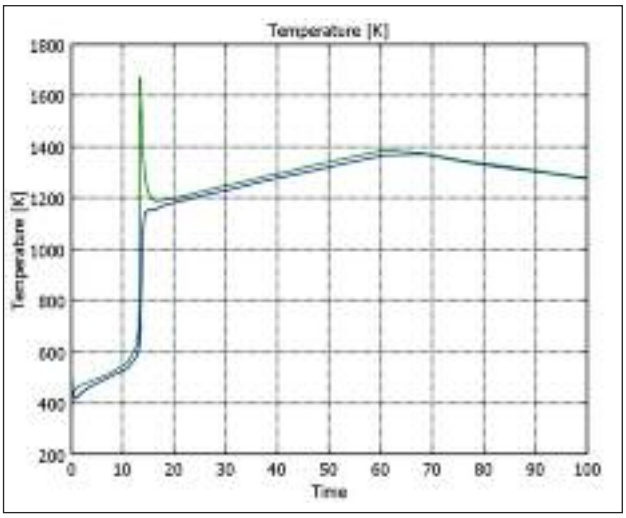


**FIG. 13** ***CS curve, microwaves stop at 60 s, 1200 W.***

*Curva CS, microonde fermate a 60 s, con potenza emessad al generatore di 1200 W.*

down the cooling. In the case of reactive support (titanium) a slow cooling leads to longer time of existing liquid phase, which involves to check interface thickness Ni-Al-Ti, just changing microwaves exposition time

The latter aspect is a distinctive feature of microwave heating, where volumetric heating generation in the sample allows to slow down, or even revert, the cooling (blue line Figures 10-13). In the case of reactive support (titanium) a slow cooling leads to longer time of existence of the liquid phase, which at its turn affects the intermediate interface thickness. Thus, by varying the microwave power applied during CS, the ternary layer thickness can be controlled directly during intermetallic synthesis.

## CONCLUSION

The study is based on simulation and effective synthesis of NiAl on titanium substrates, obtained by means of combustion synthesis activated by microwaves at 2.45 GHz. The multi-physics model developed to simulate the microwave assisted CS is simplified to allow to reduce simulation time and lack of reliable data of dielectric proprieties of powder mixture as a function of temperature. Despite the assumption of no shape change of reactants and no temperature dependence of their dielectric and magnetic properties, the model allowed to gather a deeper insight to the microwave assisted CS of Ni and Al powder compacts on titanium, showing that an intermediate ternary layer, belonging to the Ti-Ni-Al system, is formed, and whose thickness can be controllably altered by varying microwave emitted power. Further developments of the model will include temperature –dependent dielectric and magnetic properties, as well as its extension to other aluminide synthesis, both as thick coating or as freestanding materials.

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## Abstract

### Sintesi per combustione assistita da microonde di composti intermetallici. Simulazione numerica multifisica e validazione sperimentale

**Parole chiave:** simulazione numerica, metallurgia delle polveri, sinterizzazione

La sintesi per combustione (Combustion Synthesis, CS) sfrutta reazioni chimiche fortemente esotermiche che, una volta innescate, si autopropagano fino a completo esaurimento delle specie reagenti. Lo scopo del presente lavoro è lo studio della CS di β –NiAl da miscele di polveri di Ni ed Al (1:1 at. %), con ignizione mediante microonde (frequenza di 2.45 GHz), per la produzione di campioni massivi. Per ottenere informazioni altrimenti difficilmente misurabili sperimentalmente e sviluppare un modello predittivo della CS di polveri metalliche micrometriche innescata da microonde si è utilizzata la simulazione numerica. La simulazione ha riguardato l'accoppiamento sia di aspetti chimici, sia termici, sia elettromagnetici. In tal modo è stato ricavato un modello predittivo per lo studio della variazione composizionale, delle temperature caratteristiche del processo e della cinetica di reazione durante il procedere della CS, dimostrando come l'applicazione delle microonde durante e dopo la sintesi possa alterare significativamente la velocità di raffreddamento dei prodotti e, di conseguenza, la loro microstruttura. Questo è possibile grazie al riscaldamento a microonde, il quale è basato sul trasferimento di energia invece che sul trasporto di calore. Pertanto una volta innescata la reazione, mediante le microonde è possibile continuare a generare calore nei prodotti, riscaldandoli, nonostante l'avverso gradiente di temperatura che si instaura tra ambiente di reazione (più freddo) e materiale reagito (più caldo).
Lo studio si è basato sulla simulazione e realizzazione di un disco di NiAl ottenuto per attivazione della combustione attraverso microonde con frequenza 2.45 GHz. Il modello è stato implementato sia con geometria bidimensionale sia con geometria tridimensionale. Si è preferito considerare alcune semplificazioni al modello, quali l'invarianza di geometria tra il campione prima e dopo CS e l'indipendenza della permettività dalla temperatura, sia per riuscire a contenere i tempi di calcolo sia per la mancanza di dati affidabili relativi alle proprietà dielettriche equivalenti di miscele di polveri conduttive in funzione della temperatura. Tali difficoltà sono da imputare sia all'elevata velocità della reazione sia alle alte temperature che non permettono di avere valori sperimentali sempre attendibili da inserire all'interno del software utilizzato. Se da un lato la realizzazione effettiva della CS ai fini della validazione del modello ha permesso di verificare la variazione di microstruttura dell'intermetallico al variare della potenza e del tempo di applicazione delle microonde, dall'altro la simulazione ha permesso di ottenere curve in ottimo accordo con i dati riportati in letteratura e sperimentalmente misurati per questo tipo di processo.