

Combustion synthesis of Co–Al and Ni–Al systems under reduced gravity

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Abstract

Combustion synthesis of Ni–Al and Co–Al powder mixtures was investigated to determine the effect of gravity on the reaction process and the resultant microstructure and composition. Low gravity levels were found to play a significant role when liquid phases are present across the propagating reaction front. Experiments were conducted on binary systems, containing Al, that require the presence of the liquid phase for starting the propagating process. Temperature profile measurements were made by a two color pyrometer while qualitative observations of the whole phenomenon were extracted from video pictures obtained by a digital TV camera. The analysis and comparison (microgravity vs ground conditions) of the results indicate that the reaction temperatures are higher when operating under microgravity conditions and this change can be considered the main effect that yields improvement in the homogeneity of product microstructure.

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1. Introduction

The combustion synthesis (CS) process is based on the concept that an exothermic wave, propagating in a self-sustained manner through an heterogeneous medium, is used to synthesize different advanced materials [1]. The physico-chemical processes occurring during the thermal wave propagation in the pellet depend on powder mixture characteristics and operating conditions [2]: the synthesized product features can be modified by the choice of these parameters. The combustion wave characteristics, such as the reaction temperature and propagation rate, determine the product of the CS process. Once the powder mixture is selected (in term of stoichiometry, particle sizes of the reactants, dilution, sample density and thermal heating history) the structure formation mechanism can be controlled only by changing the external operating conditions. For that reason, experiments carried out under

microgravity conditions can give advances in understanding new aspects of the combustion and structure formation mechanisms.

Previous work, reporting experiments performed under microgravity conditions, indicated that the characteristics of thermal wave structure are different in comparison with tests carried out at terrestrial gravity [3–6] and in particular wave velocity, reaction temperature, and length of the reaction zone are modified. The reported results showed that microgravity conditions yield a better microstructure formation in the final product (more uniform and finer) [7,8] while the porosity is larger and with a more uniform distribution [9,10]. Several papers on this subject have been published [11] on different systems such as carbides, nitrides, oxides, borides, intermetallic compounds [12,13] (aluminides in particular) and composite materials. The mechanism of combustion of these materials was shown to include several steps such as melting of reactants and products, spreading of the melt, droplet coalescence, diffusion and convection in the molten phase, nucleation of the solid products, crystal growth, buoyancy of solid particles and bubbles in the melt. Many of the above steps involve the presence of liquid phases and are consequently affected by gravity [11].

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In this paper, the effect of gravity on the combustion synthesis of binary systems, containing aluminum, was studied during the ESA (European Space Agency) parabolic flight campaigns with A300 ZERO-g technique. Suitable procedures were required to carry out experiments during the parabolic flight in order to guarantee the capability to ignite, react and cool the sample within 20 s of microgravity conditions. The sample change and apparatus setting must be done within the 60 s of horizontal flight (see [14]). These conditions can be achieved if the experimental set up is designed so as to ignite the sample in less than 5 s and to assure that the reaction process and the product solidification can occur in the last 15 s of microgravity conditions. It has previously been shown that combustion synthesis experiments are affected by the relative orientation of the burning velocity and the acceleration of gravity [13] and that the position of the igniter can generate two limiting situations. When the burning velocity and gravity vectors have the same orientation during the combustion process, the reaction zone is compressed while, in the opposite case, it is expanded. This results in different burning behavior, as reported in [15], where it was shown that the combustion synthesis of the Al–HfB₂ system changed from slow and incomplete when ignited from the top to faster and completed combustion when ignited from the bottom. In order to verify the effect of the low gravity condition on the combustion synthesis, experiments were carried out adopting the configuration that gave the best results (ignition from the bottom) on the ground. This consideration is important for defining the experimental apparatus and in particular for the choice of the ignition procedure that was used on board.

The main objective of this work was to investigate the relationship between reaction temperatures, microstructure, and composition of the synthesized materials, focusing the attention on the effect played by the gravity on the CS process. To achieve this goal, the binary systems Ni–Al and Co–Al have been selected because (1) the atomic species show equivalent value of the atomic mass (Ni = 58.71 g and Co = 58.93 g), (2) the ignition and propagation characteristics of these systems are similar: from the ignition of the reaction and throughout the propagation, at least one of the reactant and possibly the product is present in liquid state, a favorable situation for the investigation of the influence of the gravity conditions (low or terrestrial level) on the combustion process. At this regard, preliminary experiments on the ignition of NiAl powder mixture, carried out at terrestrial gravity conditions [16–18], indicate that the reaction generally starts below the Al melting temperature (660 °C) and close to the Al-rich eutectic temperature (639.9 °C). Similarly, in the case of Co–Al system an ignition temperature of around 660 °C was measured; in this system the Al-rich eutectic temperature (657 °C) is very close to the Al melting point. It must be underlined that differences in the ignition temperature were detected when reactants with different particle size were used. Samples of

CoAl prepared with coarse Co particles (<150 μm) were observed to ignite at much a higher temperature (~900 °C). In the low gravity experiments only the finer reactant particle were therefore employed to limit the heating time.

2. Experimental apparatus and procedures

Elemental powders of the reactants (Table 1) were dry mixed in stoichiometric ratios corresponding to the following intermetallic phases: CoAl, Co₂Al₅, Co₂Al₉ (only for ground tests), NiAl, NiAl₃, NiAl₂, Ni₂Al₃, and Ni₃Al (only for ground tests). The powder mixtures were then cold-pressed to form cylindrical pellets with a diameter of 8 mm and a height of 12–14 mm having a green density that varied depending on the stoichiometry ratio (see Table 2). The experiments were carried out under a high purity argon atmosphere (99.998%) at the pressure of about 0.1 kPa.

A special sample holding system was designed in order to prevent any movement during pellet storage and fixing procedure and the adopted solution is illustrated in Fig. 1. The pellet placed in the sample box was kept in touch with the heating wire by a bolt screw which assured the best contact between them.

Temperature profiles of the reacting powder mixture were detected by a two colors pyrometer (Mikron fiber optic model M78) placed outside the reactor, 250 mm far from the sample, that can measure temperature in the range: 900–3000 °C. The ignition and combustion processes were recorded by a CANON digital video camera (mod. MV-20) that can be operated by the remote control placed on the control panel outside of the experimental box. The pellet, once placed in the sample box, must always be inserted in the reactor at the same position in order to maintain the right distance from the two colors pyrometer detector as this is the condition assuring the correct temperature measurement. The vacuum is obtained by a single stage rotary vane pump (Alcatel, 1012 A) connected with the outside atmosphere by the aircraft's vent line, so that the exhausted gases could be ejected. The power supply used for the sample ignition is made by a Variac providing the maximum current of 50 A to the tungsten wire. Data generated by the pyrometer, once the selected acquisition time is elapsed, are acquired by a PCMCIA analog input board and transferred to a PC notebook. All the process is managed by a software written for these tests that, at the end of the flight, converts

Table 1
Starting powders characteristics

Element	Supplier	Grain size (μm)	Purity
Co	Aldrich	<150	99.9%
Co	Aldrich	<2	99.9%
Ni	Aldrich	<45	99.8%
Al	Aldrich	<75	99.0%

Table 2
Ni–Al and Co–Al pellets characteristics

Powder mixture	Stoich. ratio	Density g/cm ³	Porosity %
Al–Ni	1:3	5.1–5.5	32–25
Al–Ni	1:1	3.8–4.0	35–30
Al–Ni	2:1	3.3–3.6	30–24
Al–Ni	3:1	3.0–3.4	28–20
Al–Ni	3:2	3.8–4.0	26–23
Al–Co	1:1	4.1–4.2	28–27
Al–Co	5:2	3.5–3.6	20–18

and stores the acquired data into temperature vs time files. In order to check the capability of the apparatus installed in the flight module to work properly and also to be able to compare results obtained under low gravity condition, Ni:Al and Co:Al systems, characterized by different densities, have been tested on ground, operating under the flight constraints to verify the possibility to carry out the experiments within 20 s. More details on the flight module design, apparatus configuration and working procedures can be found in [14].

The products obtained reacting the powder mixtures under microgravity and 1-g conditions were examined either by scanning electron microscopy (SEM) (Leica Stereoscan 430) and X-ray powder diffraction (XRPD) (Bruker, D8 Advance).

3. Results

The same experimental procedure was used for both the ground and low-gravity experiments to ensure similar

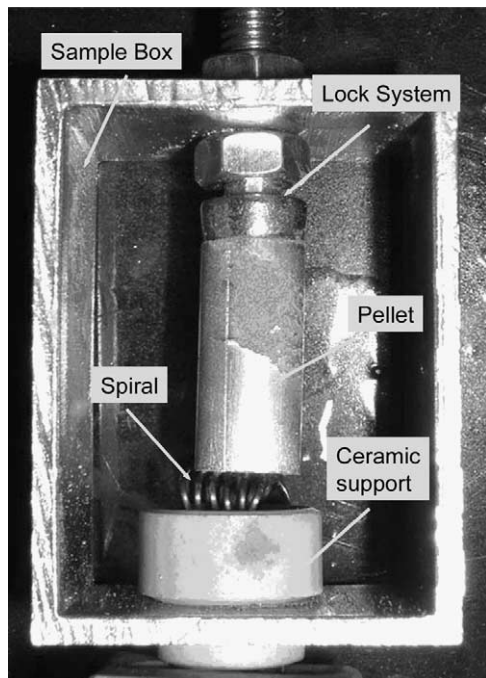


Fig. 1. Reaction box used in both ground and low gravity experiments.

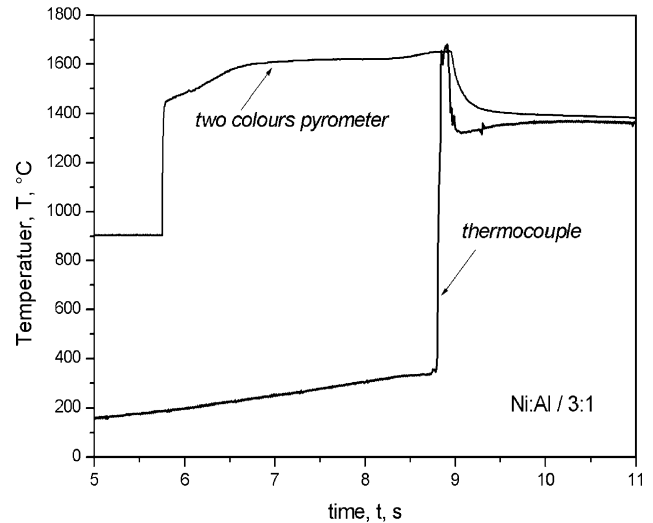


Fig. 2. Comparison of the reaction temperature measured by microthermocouple and two colors pyrometer.

heating transient and the same ignition temperature. In few ground experiments, home made microthermocouples (Pt-10%Rh, 50 or 100 μm bead size) were embedded in the sample during the powders cold pressing to enable a comparison between the maximum temperature values measured inside (microthermocouples) and on the external surface (pyrometer) of the reacting pellet. Temperatures measured by pyrometer, averaging the temperature value on a spot size of 2 mm, and microthermocouples were found to be in good agreement as shown in Fig. 2.

Typical temperature traces, measured by two colors pyrometer, during ground and low gravity tests on the Co:Al/1:1 system are reported in Fig. 3. The measured maximum reaction temperatures of all Ni–Al and Co–Al mixtures, for both ground and reduced gravity experiments, are shown in Figs. 4 and 5, together with the corresponding

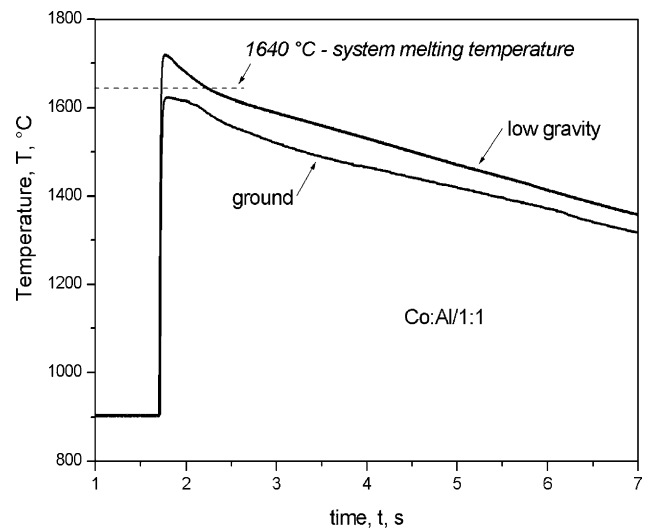


Fig. 3. Temperature profiles for the Co:Al = 1:1 mixture reacted in ground and low gravity conditions.

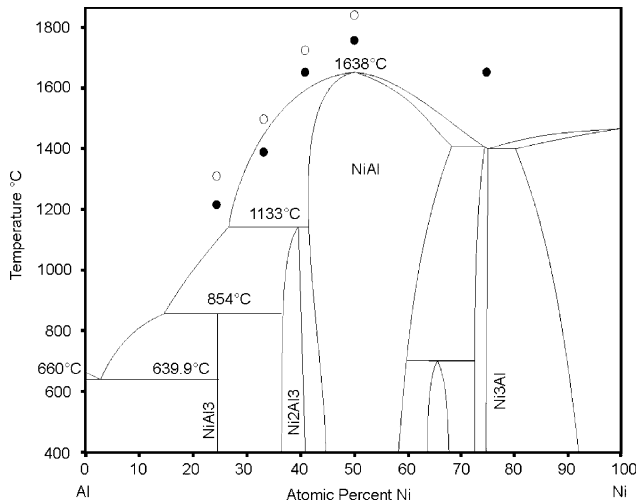


Fig. 4. Phase diagram and combustion temperatures measured for the Ni–Al mixtures in ground (black dots) and low gravity conditions (white dots).

phase diagram. For both systems, the higher reaction temperature has been measured when the test powder mixture had the stoichiometric ratio 1:1. Temperatures gradually decrease as the composition of the reacting mixture is changed. The measured temperatures are generally slightly higher than the corresponding adiabatic values (Ni:Al/1:1 T_{ad} = 1911 K; Ni:Al/1:3 T_{ad} = 1127 K; Co:Al/1:1 T_{ad} = 1901 K). This is likely due to the experimental set up employed in the present study: due to the fact that the reacting samples were kept in touch with the heating wire and the long heating times some preheating of the reacting mixture was unavoidable. In fact, as reported in [19] (Fig. 4) the adiabatic combustion temperature of the Ni:Al/1:2 mixture increases with the reactants initial temperature increase.

Numerical simulation of the sample heating transient, taking into account the dependence of the thermal diffusivity of the powder mixtures on porosity and

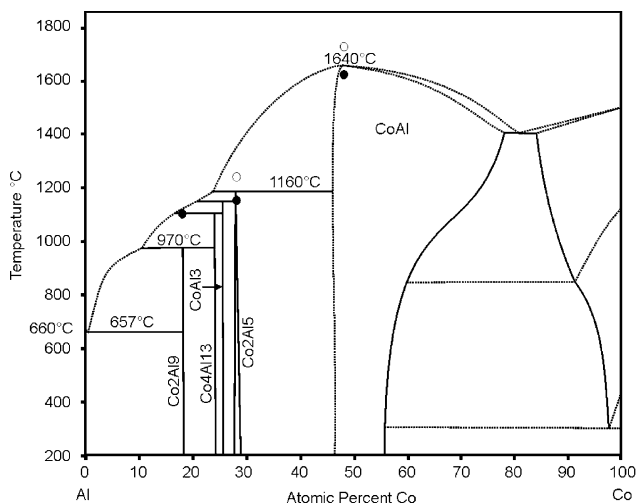


Fig. 5. Phase diagram and combustion temperatures measured for the Co–Al mixtures in ground (black dots) and low gravity conditions (white dots).

temperature [20], have been done to estimate the temperature of the cold sample side. It was found that this value, heating time of 5 s, after the reaches about 100 °C and that justify a measured temperature larger than the adiabatic one.

Comparison between ground and reduced gravity experiments shows that, for both systems, the reaction temperatures are approximately 100 °C higher when tests have been carried out at low gravity. In many cases, particularly for low-gravity tests, the reaction temperature is higher than the melting temperature of the product (in the case of 1:1 stoichiometries) or higher than the liquidus temperature corresponding to the starting mixture stoichiometry. In such cases, the large amount of liquid phases formed during the reaction causes a change in the pellet shape from cylindrical to spherical. Deformation is particularly evident in Al rich mixtures such as Ni:Al/1:2 and Ni:Al/1:3 or when the temperature is well above the product melting point as in the case of Ni:Al/1:1. Higher combustion temperature under microgravity conditions have been observed in other systems [11] when a liquid phase is formed ahead of the reaction front, as it occurs in the synthesis of aluminides. This temperature increase has been explained by a reduction of heat loss because the liquid phase is held by capillary forces and is not drawn away by gravity, creating improved reactant contact. Another possible cause for differences in reaction temperature is indeed related to the possibility of forming different products in different gravity conditions. XRPD results for samples reacted in low gravity conditions are shown in Figs. 6 and 7 for the Ni–Al and the Co–Al systems, respectively. Co:Al = 1:1, Ni:Al = 1:1, and Ni:Al = 2:3 gave a single phase product (CoAl, NiAl, and Ni₂Al₃ respectively) while Co:Al = 2:5, Ni:Al = 1:2, and Ni:Al = 1:3 mixtures gave products that contained more than one intermetallic compound together with small amounts unreacted elements, in agreement with previous literature reports [21]. The lack of completion of these reactions has

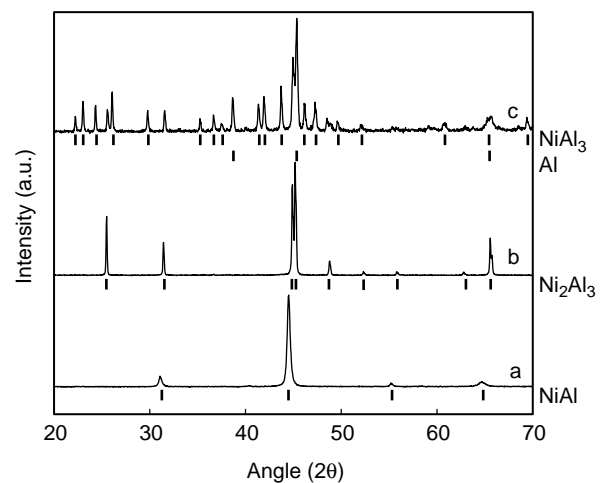


Fig. 6. X-ray diffraction patterns (Cu $K\alpha$) for the following starting mixtures: (a) Ni:Al = 1:1, (b) Ni:Al = 2:3, (c) Ni:Al = 1:3.

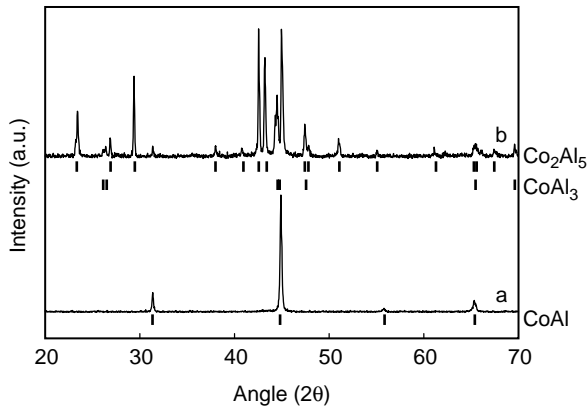


Fig. 7. X-ray diffraction patterns (Cu K α) for the following starting mixtures: (a) Co:Al = 1:1, (b) Co:Al = 2:5.

been addressed to the lower combustion temperature and to incongruent nature of the corresponding product phases (i.e. with the composition equal to the starting mixture), such as Co_2Al_5 and NiAl_3 , that must therefore be formed through peritectic reactions, generally considered too slow to be completed in the short times involved in SHS processes.

The products obtained in normal gravity conditions showed no significant difference. This result rules out the possibility that the differences in the combustion temperatures observed in different gravity conditions can be due to differences in the product compositions and consequently in the reaction enthalpy.

A comparison between the microstructure of the product obtained in normal and low gravity conditions is shown in Figs. 8–12. The microstructure of most of the samples are indicative of extensive melting, in agreement with the measured temperatures. This is particularly evident in the case of Ni:Al/1:1 (Fig. 8) whose reaction temperature was well above the melting point of the product. Particularly interesting are the cases where the reaction temperature is lower and the final products are porous. In the case of the Ni:Al/1:2 (Fig. 9) Ni:Al/1:2 (Fig. 10), the microstructure obtained in normal and low gravity conditions are quite

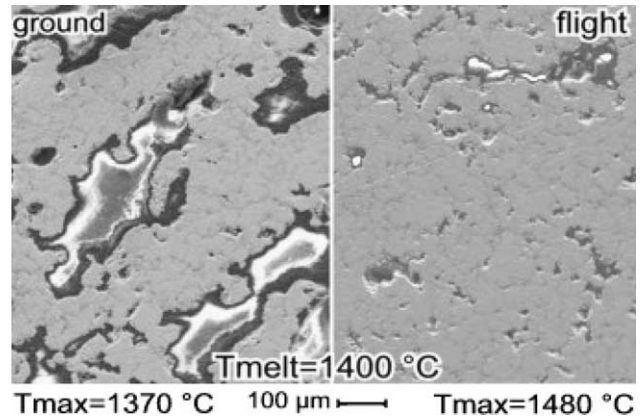


Fig. 9. SEM image of Ni:Al/1:2 products obtained at ground (left image) and low gravity (right image) conditions.

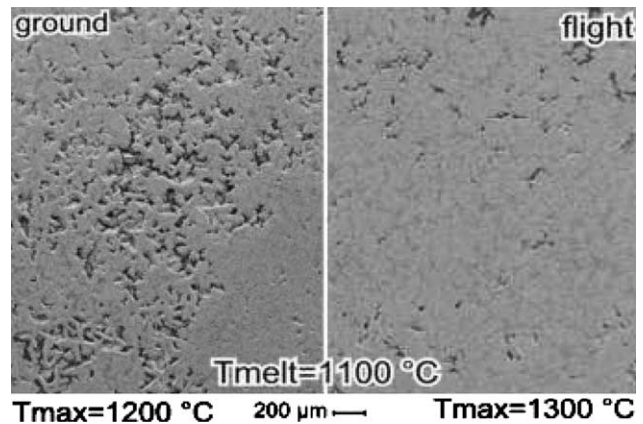


Fig. 10. SEM image of Ni:Al/1:3 products obtained at ground (left image) and low gravity (right image) conditions.

different; the low gravity samples are, in both cases, considerably less porous. Moreover, for the Ni:Al/1:2 composition, the large pores ($> 100 \mu\text{m}$) present at normal gravity conditions disappear in low gravity, where the residual porosity is much finer leading to a more homogeneous morphology of the sample. An increased

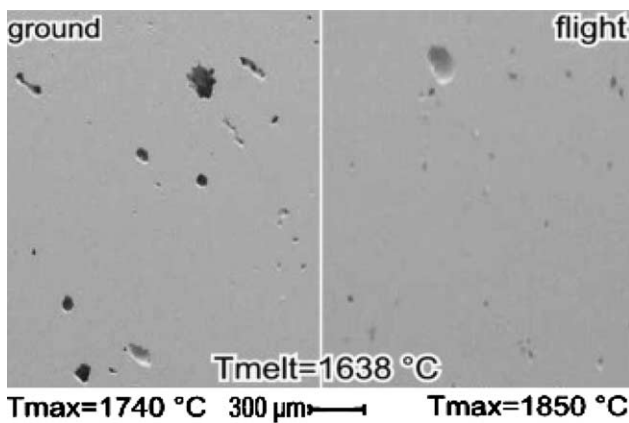


Fig. 8. SEM image of Ni:Al/1:1 products obtained at ground (left image) and low gravity (right image) conditions.

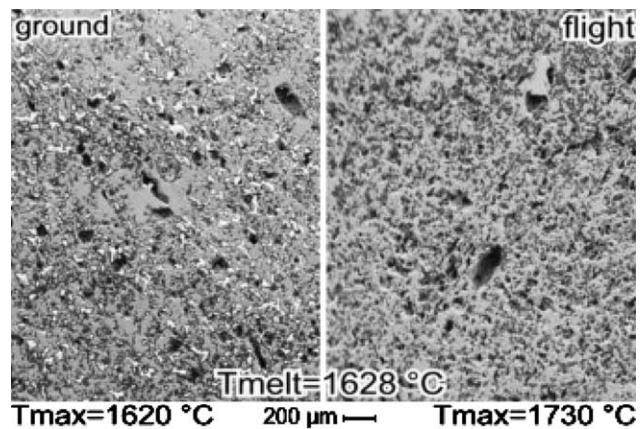


Fig. 11. SEM image of Co:Al/1:1 products obtained at ground (left image) and low gravity (right image) conditions.

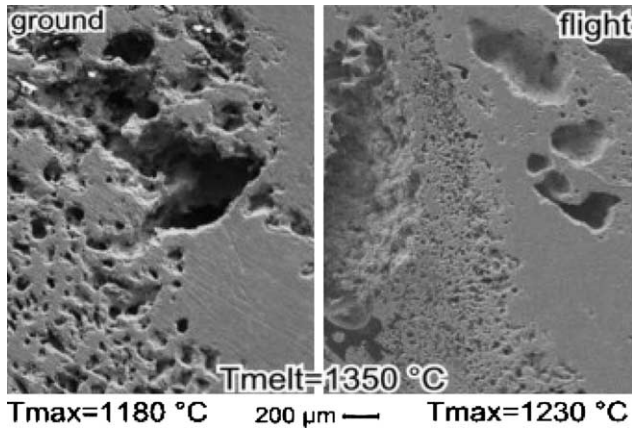


Fig. 12. SEM image of Co:Al/2:5 products obtained at ground (left image) and low gravity (right image) conditions.

uniformity of pore distribution in microgravity samples has been observed also on other systems [11]. The reduced porosity observed in our samples is apparently in contrast with the results recently obtained by Merzhanov [13]; the author found that the NiAl intermetallic compound produced under microgravity was more porous than that prepared at ground conditions. In this study, however, the reaction was conducted inside a quartz ampule initially half-filled with the reacting mixture, and the high porosity observed in the microgravity sample was due to the larger expansion of the sample that, at the end of the reaction, filled the ampule completely. In our experiments, on the contrary, expansion of the sample was prevented by the bolt screw and no direct comparison with the above results [13] can be made. Fig. 13 shows the spherical shape of the pellet (Ni:Al/2:3, initial sample density 3.86 g/cm^3) at the end of the reaction in low gravity conditions. From this picture it is possible to determine the volume of the sphere and then the density of the product. In this case the evaluated density is

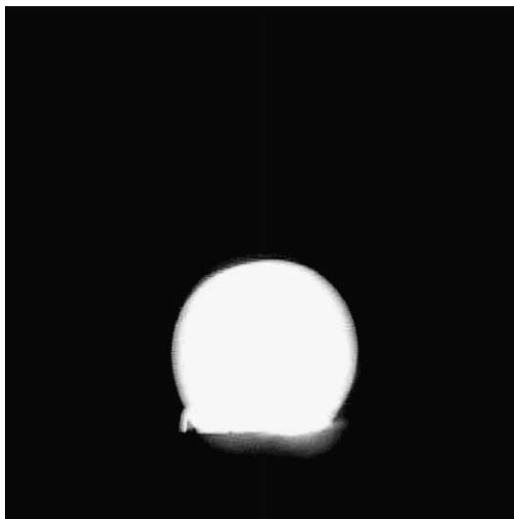


Fig. 13. Spherical shape of the pellet after reaction under low gravity.

higher than in the green mixture (4.17 g/cm^3) and a low porosity content is expected in the final product.

A quite different situation can be observed on the Co–Al system (Figs. 11 and 12) where the reaction product show a quite large porosity for both reaction conditions. In this system however, the observed temperatures are much closer to the melting point of the product phases and less extensive melting is expected to occur during the combustion process.

4. Conclusions

The effect of the gravity conditions on the final structure of the products obtained by the combustion synthesis of aluminide cylindrical samples was investigated. Experiments were conducted using powder mixtures of Ni–Al and Co–Al with different stoichiometries. The reaction temperature was detected by two colors pyrometer while a digital video camera recorded the whole test. The obtained results demonstrated that the flight module and the experimental apparatus are suitable for performing tests under microgravity conditions by parabolic flight technique. Analysis and comparison (microgravity vs ground conditions) of the data indicate that the reaction temperatures are always higher when operating at low gravity level. A more homogeneous microstructure was found in the low gravity samples for some Ni–Al reaction mixtures that under low gravity condition always reacts at temperature higher than the melting point (or liquidus temperature) of the corresponding product.

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