

PECULIARITIES OF THE TITANIUM AND NICKEL ALUMINIDES AUTO-SYNTHESIS

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Due to their unique intrinsic properties, intermetallic compounds such as titanium and nickel aluminides are of particular interest for high-end sectors, most notably the aerospace industry, which serves as the primary consumer of these materials. This paper presents a thermodynamic analysis of the main reactions involved in synthesizing these two metal aluminides, demonstrating that the synthesis processes are exergonic and highly exothermic across a wide temperature range. Furthermore, experiments focusing on direct synthesis from elemental aluminum, nickel and titanium revealed that these reactions progress via self-propagation and exhibit an explosive character.

Keywords: nickel and titanium aluminides, auto synthesis, thermo-dynamics of synthesis reactions, reactive synthesis, self-propagation, explosive character.

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1. Introduction

The transition metals, titanium and nickel, generate in the presence of aluminum, under strictly determined thermodynamic conditions, intermetallic compounds (IMCs) – called aluminides. The aluminides of the two transition metals are part of the category of intermetallic compounds of particular interest for a series of structural applications and mainly for the aerospace industry. The Al-Ni and Al-Ti binary phase diagrams (BPD), respectively, as shown in Figure 1 [1] and Figure 2 [2], highlight the presence of intermetallic compounds of the NiAl, NiAl₃, TiAl, TiAl₃ type, as well as other compounds, giving information related to the mode of formation and stability domains.

Nickel and titanium aluminides are characterized by low density values, for example 5.86 kg/m³ for NiAl, 7.5 kg/m³ for Ni₃Al, 3.9 kg/m³ for TiAl, 4.2 kg/m³ for Ti₃Al, high melting temperature values, 1395 °C for Ni₃Al, 1638 °C for

NiAl, 1460 °C for TiAl, 1340 °C for TiAl₃, 1600 °C for Ti₃Al, high oxidation and corrosion resistance values (in the case of TiAl aluminide in the temperature range 600–800 °C a thin oxide film is formed that grows rapidly with increasing temperature up to 1150 °C, also showing a tendency to exfoliate by detachment of successive layers) [3].

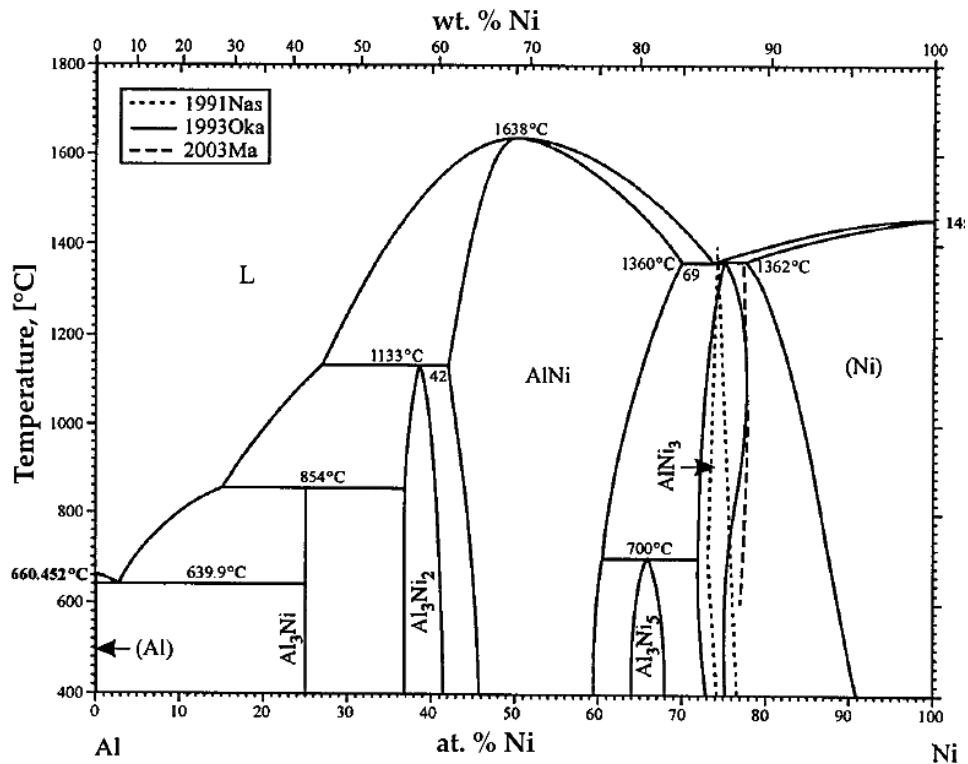


Figure 1. Al-Ni binary phase diagram [1].

In the case of TiAl₃, the oxide film remains on the surface of the compound but does not protect it from further interaction with oxygen, as shown by Samsonov and Vinitskii [4]. Titanium aluminide (TiAl) is of greatest interest among titanium aluminides, being a possible replacement for traditional components made of Ni-based superalloys, used in turbine aircraft engine components. Nickel aluminide (NiAl) has excellent resistance to oxidation and corrosion but a lower ductile-brittle transition temperature compared to other IMCs; in contrast, nickel aluminide (Ni₃Al) is brittle at ambient and elevated temperatures due to the inability of dislocations to move in an ordered manner, a disadvantage that can be limited by introducing small amounts of boron, which provides a strong increase in ductility [5].

The methods for obtaining titanium and nickel aluminides are extremely diverse. Due to the exceptionally high thermal effect of the reactions occurring under specific conditions, direct contact between titanium and aluminum particles—or between nickel and aluminum particles—enables the combustion synthesis (self-synthesis) of these IMCs at high temperatures. These reactions self-propagate simultaneously throughout the entire volume of the powder mixtures upon uniform and controlled heating. Such a synthesis variant is known due to the mode of propagation, as being by thermo-explosion [6]. In conclusion, the auto-synthesis process initiates spontaneously throughout the entire volume, is self-sustaining and has an explosive character [7].

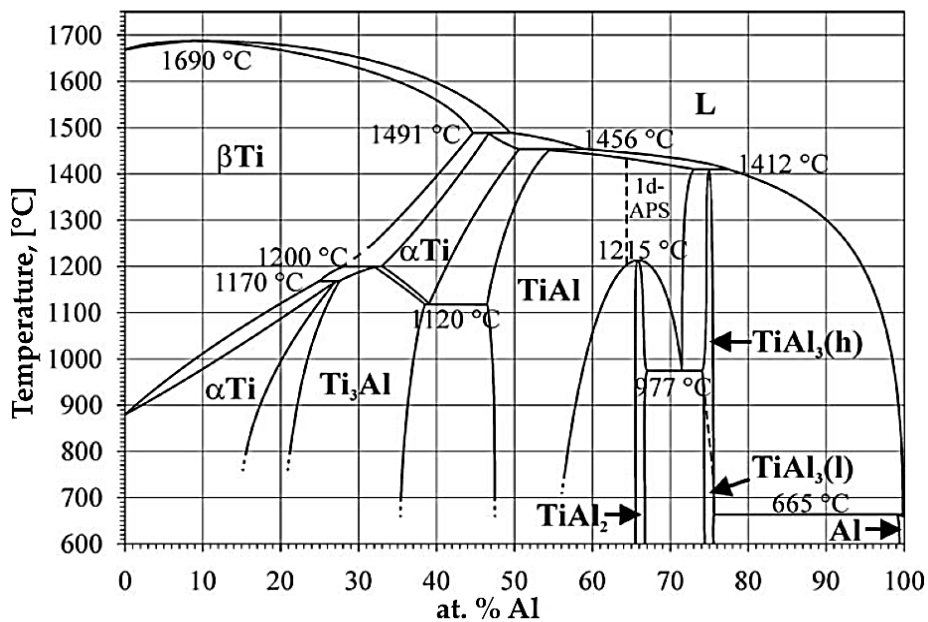


Figure 2. Al-Ti binary phase diagrams [2].

To determine the concrete conditions under which it becomes possible to initiate the auto-synthesis reaction of IMCs formed between Al and the transition metals Ni and Ti, the information provided by the BPDs (Al-Ni and Al-Ti) is necessary, with reference to the lowest temperatures at which the liquid phase still exists. The analysis highlights a eutectic reaction in the Al-Ni system at 639.9 °C and a peritectic reaction in the Al-Ti system at 665 °C, both occurring in the vicinity of the aluminum melting point (approx. 660 °C). Consequently, these specific phase transformation temperatures must be taken into account when determining the heating threshold required to initiate the auto-synthesis of intermetallic compounds from elemental Al, Ti, and Ni powder mixtures.

Moreover, differential thermal analysis (DTA) performed on stoichiometric Al-Ni powder mixtures reveals distinct ignition behaviors: a maximum reaction initiation temperature of 681 °C is recorded for the synthesis of the NiAluminide, whereas a maximum value of 879 °C is observed for the NiAl₃ aluminide. These results, however, have an indicative value determined by a multitude of factors, such as the real value of the contact between the particles and implicitly the thermal conductivity of the mixture (in the differential thermal analysis the powder mixture was found in a freely flowing state), the heating rate etc.

2. Materials and Methods

Elemental powders with the following characteristics were used:

- Al powder (99.2% pure) obtained by air spraying, manufactured at AMPELUM SA Zlatna, Romania; particle size fractions within the limits of 12.5–70 μm were used, with apparent densities ranging from 0.8 to 1.0 g/cm³ (measured using a funnel with an orifice diameter of $\Phi = 2.5$ mm) and tapped densities ranging from 1.1 to 1.3 g/cm³.

- Ni powder (99.9% pure) produced by hydrometallurgical process (Sheritt method), manufactured at Alfa Aesar (currently Thermo Fisher Scientific), Germany; particle size fractions within the limits of 10–90 μm were used, with apparent densities within the limits of 3.4–3.8 g/cm³ (measured using a funnel with an orifice diameter of $\Phi=2.5$ mm), fluidity of approximately 18–19 s/50g.

- Ti powders (99% pure) obtained by the Kroll process, manufactured at Alfa Aesar (currently Thermo Fisher Scientific), Germany; max. particle size: 40 μm.

The equipment used for experimental research:

- double-cone blenders for homogenizing the powder mixtures, operated at approximately 150–200 rpm;

- tungsten carbide ball mills with a capacity of 2.5 l;

- hydraulic press;

- chamber furnace (manufactured by UTTIS Industries SRL) with automatic control of the heating regime and with an atmosphere with controlled chemical composition.

Scanning electron microscopy (SEM) and determination of chemical composition on microvolumes by energy dispersive X-ray spectrometry (EDS) were performed on a Philips microscope model XL30 ESEM TMP.

X-ray diffraction was performed on a Bruker AXS D8 ADVANCE diffractometer, equipped with a Cu-K α radiation source (1.54 nm).

3. Results and Discussion

The thermodynamic analysis of the direct synthesis reactions of Ti and Ni aluminides, as presented in Figure 3 [8], highlights that all these reactions are strongly exergonic ($\Delta G < 0$) and at the same time exothermic ($\Delta H < 0$). It is also found that at temperatures above 600° C (in the vicinity of the Al melting point or the initiation of the eutectic transformation at the contact of Al and Ni particles, the effect of "contact fusion") the thermal effect of the IMCs synthesis reactions in the systems taken into analysis is considerably intensified [9, 10].

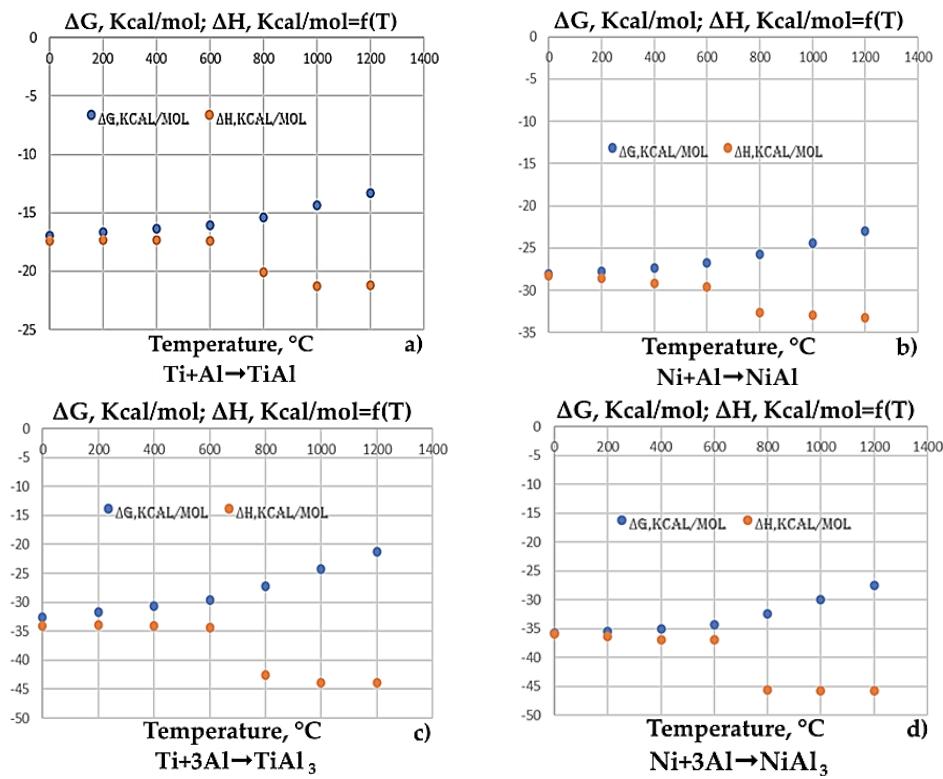


Figure 3. Thermodynamic parameters (ΔG) and (ΔH) for intermetallic compounds (IMCs) synthesis reactions in Ti-Al and Ni-Al systems [8]: a) TiAl; b) NiAl; c) TiAl₃; d) NiAl₃.

Figure 4 shows in the left side aluminum powder produced via air atomization (ALCOA process) and nickel powder – right side – obtained by the hydrometallurgical process from aqueous solutions by hydrogen reduction (Sherritt-Gordon process). Subsequently, an equal-mass mixture of both powders was prepared. The mixture was thoroughly homogenized with stearic acid in a free-flowing state inside ceramic containers. These containers were sealed with

steel lids and clay latches, and then placed in a double-cone blender for processing. They were maintained for 20 hours at a temperature of 650 °C, (below the aluminum melting temperature), but above the eutectic transformation temperature in the Al-Ni system (temperature range in which the synthesis reactions of nickel aluminides are likely exergonic reactions, with considerable thermal effect) in furnaces equipped with automatic temperature control.

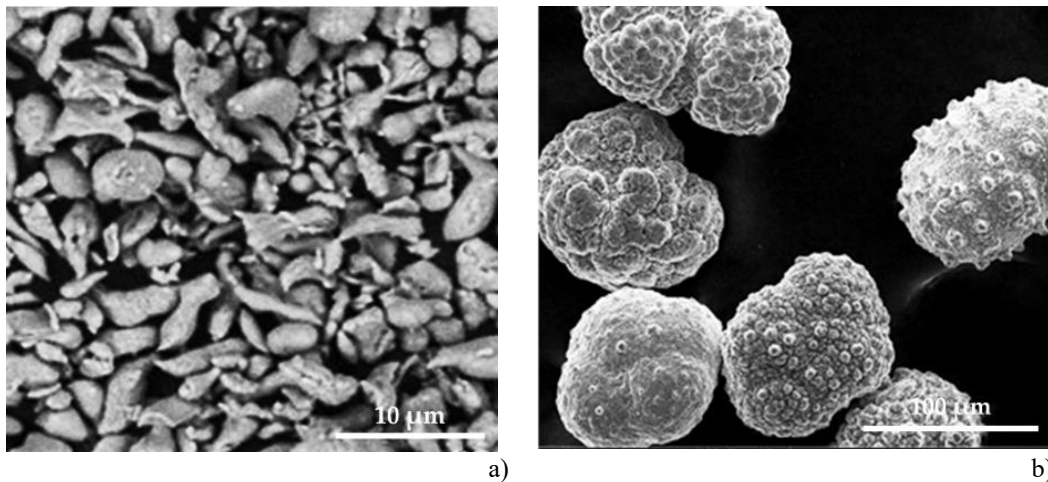
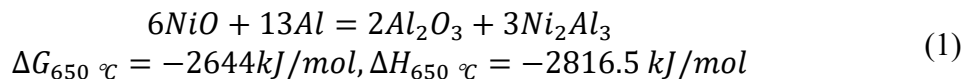


Figure 4. Morphology of the powders used in this research: a) SEM image of aluminum powder; b) SEM image of nickel powder

Under these conditions (limited contacts between particles and a reduced amount of liquid phase with eutectic composition, very rich in Al - about 94%), X-ray diffraction investigations have highlighted, in addition to the aluminides of great interest, NiAl and NiAl₃ (formed by solid-state diffusion of Al in the Ni matrix during heating until reaching the processing temperature) and other types of nickel aluminides, such as Ni₂Al₃ and Ni₃Al, unreacted Al and Al₂O₃, as shown in Figure 5 [11].

The presence of Al₂O₃ in the sintered product—despite being protected from furnace air by a steel lid and clay seal—is highly likely caused by pre-existing oxide films on the nickel particles. According to equation (1) [12], this presence is further driven by the highly exothermic chemical interaction with the aluminum powder, as well as the initial oxide content present from the start.



Such chemical interaction also results in the formation of Ni_2Al_3 aluminide, which can also occur because of a peritectic reaction carried out at 1133°C , according to the reaction: $\text{NiAl} + \text{L} \rightarrow \text{Ni}_2\text{Al}_3$ [1, 13].

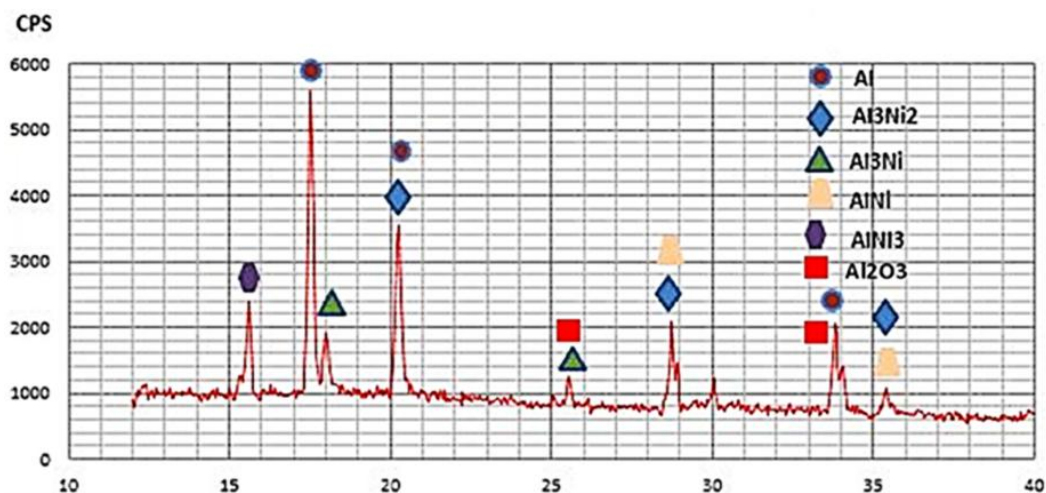


Figure 5. XRD pattern of the product obtained from the thermal treatment of an equal-mass mixture of Al and Ni powders at 650°C for 20 hours [11].

Increasing the contact surface between the particles of the powder mixture by pressing it, prior to heating to initiate the auto-synthesis process by combustion and self-propagation in volume, obviously amplifies the synthesis kinetics and increases the conversion rate into aluminides. Thus, in the case of Al-Ti powder mixtures, advanced homogenized in ball mills (useful volume 2.5 l and a ratio of the grinding bodies mass/ powder mass mixture of 11:1), for 2 hours, and subsequently compressed at a pressure value of 730 MPa, a high conversion rate of the two elements into their aluminides is recorded, according to Figures 6 and 7 [14].

The medium used in the furnace for thermal processing was urban fuel gas, which was not chosen randomly, considering that among the resulting reaction products could be carbon activated. Thus, it was assumed that, if part of the activated carbon resulting from the decomposition of methane or carbon monoxide interacts with the components of the pressed semi-finished product in the process of auto-synthesis by combustion with self-propagation in volume, the results of these interactions will represent hardening phases of the sintered product consisting of aluminides.

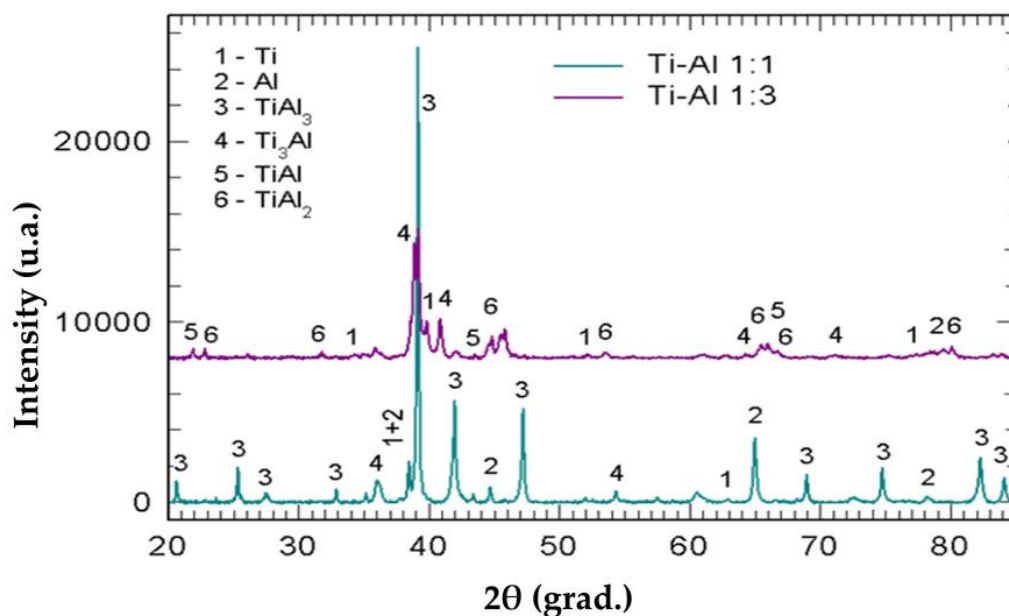


Figure 6. X-ray diffraction patterns of the sintered product from Al and Ti powder mixtures (Ti/Al=1:1 and Ti/Al=1:3), with an average particle diameter of 40 μm , pressed at 730 MPa, in urban fuel gas (84%CH₄; 10%H₂; 3%N₂; 2%CO; rest O₂+CO₂), at 650 °C for 0.5h and then at 900 °C for 1.5 h.

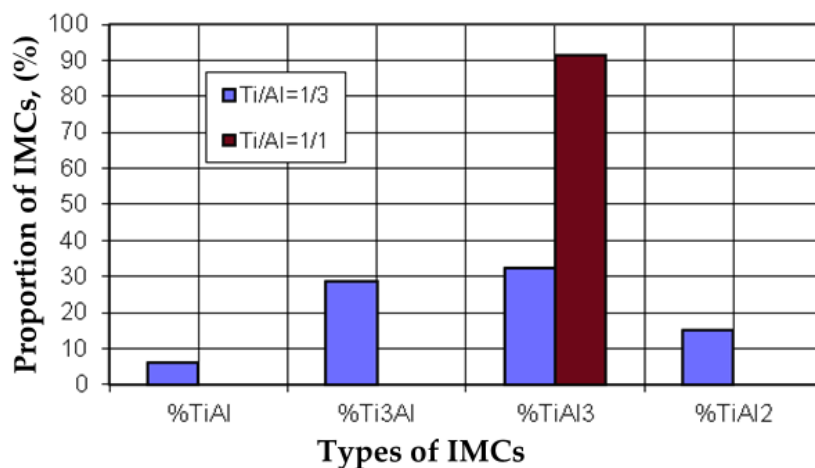
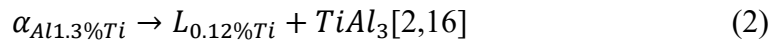


Figure 7. Effects of varying the atomic proportions of Ti and Al in powder mixtures pressed at 730 MPa and subsequently thermally processed at 650 °C for 0.5 h and then at 900 °C for 1.5 h, in urban fuel gas (average particle diameter below 40 μm).

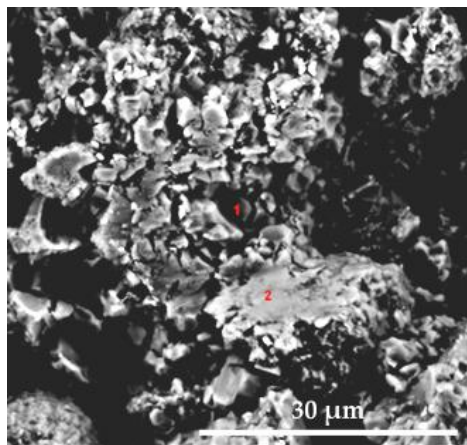
The mechanism of structure formation strongly depends on the composition of the initial reaction mixture. The diffusion of Al atoms in the Ti

particle network leads to nucleation in the diffusion zone of the IMC TiAl_3 [15]. Depending on the amount of Al in the mixture and the size of the contacts between the particles (dependence on the degree of densification) in the final structure, only TiAl_3 aluminide can be found, or a wide range of aluminides characterized by different concentrations of Al.

The explanations are related to the phenomena that occur during the formation of aluminides, in strict correlation with the Al content of the mixture. Thus, during the formation of IMCs, internal compressive and tensile stresses appear that can lead to the destruction of the IMC formed in the early stages of TiAl_3 saturation. The layer formed in the early stages of synthesis limits the movement of Al atoms in the Ti matrix. At the same time, the TiAl_3 layer grows, which theoretically leads to a decrease in the Al content and the initiation of the TiAl aluminide nucleation process. However, by exceeding the Al melting point and redistributing the melt through the channels of the porous semi-finished product, the peritectic transformation reaction (665 °C) is initiated with an immediate effect on the increasing proportion of TiAl_3 aluminide (equation 2):



Note: The formation of the solid solution of Ti in Al was achieved by the diffusion of Ti into Al in the temperature range below the peritectic transformation temperature.



a)

Elem.	Zone 1		Zone 2	
	Wt. %	At. %	Wt. %	At. %
C	9.78	18.47	15.41	24.75
O	21.00	29.78	34.62	41.76
Al	51.62	43.41	42.75	30.58
Ti	17.61	8.34	7.22	2.91

b)

Figure 8. Electron micrograph of powder mixture processed at a 1:1 Ti/Al ratio with determination of chemical composition of selected areas: a) SEM image; b) EDS results.

It is found that the maximum conversion efficiency is recorded in the case of equal proportions of the two elemental components of the Al-Ti powder mixture, the product having a very homogeneous composition, with over 90%

TiAl₃ type aluminide, as it is shown in Figure 7. When the Al proportion in the powder mixture increases, the phase composition of the product diversifies, registering almost the entire range of aluminides, from those rich in the Al of the TiAl₃ type to those rich in titanium of the Ti₃Al type.

As the process advances into deeper and deeper areas of the Ti particles, the Al content continues to decrease, a phenomenon that determines the nucleation of the IMC, Ti₃Al [17]. Scanning electron microscopy (SEM) investigations and Energy-dispersive X-ray spectroscopy (EDS) performed on the Al-Ti powder mixtures processed in this way also highlight the presence of C, as shown in Figure 8, bound in a Ti carbide of the TiC_{0.1} type.

In the SEM images, the spongy appearance of the products obtained (by holding them in the second stage of the synthesis, at high temperatures of 900 °C) is also observed, an aspect caused by the volume expansion due to solid state phase transformations.

4. Conclusions

The results of the synthesis are strictly dependent on the ratio of the mass proportions of the two interacting elemental components and on the state in which their mixture is found prior to the initiation of the synthesis reaction, freely flowing or compressed state, therefore on the size of the contacts between the particles of the two components.

For free-flowing equal-mass Al-Ni powder mixtures subjected to synthesis at temperatures triggering a sharp increase in the reaction's thermal effect, the resulting product retains a large amount of unreacted Al. This occurs due to the relatively low number of contacts between Ni particles, which allows the Al melt — precisely, an Al melt with approximately 6% Ni formed via a eutectic reaction at 640 °C — to segregate. This segregation induces a local Al deficit at the surface of the Ni particles, consequently generating the entire spectrum of nickel aluminides (NiAl₃, Ni₂Al₃, and Ni₃Al) alongside aluminum oxide (Al₂O₃).

In the case of powder mixtures in a pressed state subjected to synthesis, its results in terms of the phase composition of the final product depend on the proportion ratio of the two components (Al and Ti respectively considered in the analysis) and on the thermal regime of the auto-synthesis, as follows:

- for an equal-mass ratio of the two components, the synthesized product predominantly consists of the TiAl₃ aluminide (following a single-stage heating at 900 °C), exhibiting a spongy appearance driven by volume expansion during synthesis;
- for a ratio of the powder mixture Ti/Al=1/3, the phase composition of the final product will be heterogeneous, covering the entire range of Ti aluminides, from those poor in Al to those rich one.

The use of urban fuel gas, a supplier of active carbon, favors the finding of this element in the final product, most likely in the form of Ti carbides – $\text{TiC}_{0.1}$.

Supplementary Materials

This article contains no supplementary material.

Author Contributions

Conceptualization: M.O.C., M.B., S.C.; methodology: M.O.C., M.B., S.C.; validation: M.O.C., M.B., S.C., A.B., C.B. and R.E.D.; investigation, A.B. and C.B.; writing—original draft preparation, M.B. and R.E.D.; writing—review and editing, R.E.D.; supervision, M.O.C. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

The data are available from the corresponding author upon reasonable request.

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Conflicts of Interest

The authors declare no conflict of interest.

Artificial Intelligence Disclosure

No artificial intelligence-based or generative tools were used in the preparation of this manuscript

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REFERENCES

- [1] Okamoto, H. Al-Ni (Aluminum-Nickel), *J. Phase Equilibria Diffus.*, **2004**, 25, 394, <https://doi.org/10.1361/15477030420232>
- [2] Schuster, J.C.; Palm, M. Reassessment of the Binary Aluminum-Titanium Phase Diagram, *J. Phase Equilibria Diffus.*, **2006**, 27, pp. 255-277, <https://doi.org/10.1361/154770306X109809>
- [3] Froes, F.H.; Suryanarayana, C.; Eliezer, D. Synthesis, properties and application of titanium aluminides. *J. Mater. Sci.*, **1992**, 27, pp. 5113-5140, <https://doi.org/10.1007/BF02403806>

- [4] Samsonov, G.V.; Vinitiskii, I.M. *Tugoplavkie soedineniya [Refractory Compounds]*, 2nd ed., Metallurgiya, Moscow, USSR, 1976, pp. 43-67
- [5] Dey, G.K. Physical Metallurgy of Nickel Aluminides, *Sadhana*, **2003**, 28, pp. 247–262, <https://doi.org/10.1007/BF02717135>
- [6] Bertolino, N.; Monagheddu, M.; Tacca, A.; Giuliani, P.; Zanotti, C.; Tamburini, U.A. Ignition mechanism in combustion synthesis of Ti-Al and Ti-Ni systems, *Intermetallics*, **2003**, 11, pp. 41-49, [https://doi.org/10.1016/S0966-9795\(02\)00128-0](https://doi.org/10.1016/S0966-9795(02)00128-0)
- [7] Kattner, U.R.; Lin, J.C.; Chang, Y.A. Thermodynamic Assessment and Calculation of Ti-Al System, *Metall. Mater. Trans. A*, **1992**, 23, pp. 2081-2090, <https://doi.org/10.1007/BF02646001>
- [8] Outotec Research Oy, *HSC Chemistry Software*, version 6.12, Pori, Finland, 2007
- [9] Lucaci, M. *Sinteza compusilor intermetalici cu baza nichel (Synthesis of Ni-based intermetallic compounds)*, PhD Thesis, University POLITEHNICA of Bucharest, Romania, 2001
- [10] Sina, H.; Iyengar, S. Reactive synthesis and characterization of titanium aluminides produced from elemental powder mixtures, *J. Therm. Anal. Calorim.*, **2015**, 122, pp 689–698, <https://doi.org/10.1007/s10973-015-4815-6>
- [11] Tudose, F. *Sinteza aluminidelor nichelului prin metode specifice metalurgiei pulberilor (Synthesis of Nickel aluminides by specific powder metallurgy methods)* PhD Thesis, University POLITEHNICA of Bucharest, Romania, 2018.
- [12] Chrifi-Alaoui, F.Z.; Nassik, M.; Mahdouk, K.; Gachon, J.C. Enthalpies of formation of the Al-Ni intermetallic compounds, *J. Alloys Compd.*, **2004**, 364, pp. 121–126, [https://doi.org/10.1016/S0925-8388\(03\)00493-6](https://doi.org/10.1016/S0925-8388(03)00493-6)
- [13] Ansara, I.; Dupin, N.; Lukas, H.L.; Sundman, B. Thermodynamic assessment of the Al-Ni system, *J. Alloys Compd.*, **1997**, 247, pp. 20-30, [https://doi.org/10.1016/S0925-8388\(96\)02652-7](https://doi.org/10.1016/S0925-8388(96)02652-7).
- [14] Cojocaru, M.O.; Brânzei, M.; Druga, L.N.; Tudose, F.; Andrei, E.I.; Rosoiu, S. Direct Synthesis of Titanium Aluminides by Specific Methods of Powder Metallurgy, *UPB Sci. Bull. Ser. B*, **2020**, 82, pp. 153-162
- [15] Van Loo, F.J.J. *Diffusion in the Titanium-Aluminum System*, Ph.D. Thesis, Technische Hogeschool Eindhoven, the Netherlands, 1971, <https://doi.org/10.6100/IR36207>
- [16] Sereda, B.P.; Zherebtsov, A.A. Examination of structure formation of titanium aluminides in their producing by SHS method, *Metallurgy*, **2008**, 18, pp 66–71.
- [17] Wu, H.; Fan, G.-H.; Geng, L.; Cui, X.P.; Huang, M. Nanoscale origins of the oriented precipitation of Ti₃Al in Ti-Al systems. *Scr. Mater.*, **2016**, 125, 34-38, <https://doi.org/10.1016/j.scriptamat.2016.07.037>