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Mechanosynthesis of Ni-Al-Ti intermetallic compounds: influence of milling time and titanium content

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Abstract: The synthesis of intermetallic compounds in Ni-Al systems is of significant interest due to their potential applications in high-temperature materials. This study aims to investigate the effect of milling time and titanium addition on phase formation, particle size evolution, and microstructural development in Ni-Al and Ni-Al-Ti powder mixtures with different compositions. Mechanical alloying was carried out in a planetary ball mill for up to 6 hours, and the resulting powders were analyzed using X-ray diffraction and scanning electron microscopy. The results show that the particle size evolution follows a non-monotonic behavior, characterized by initial agglomeration during the early stage of milling, followed by fragmentation and subsequent stabilization. After 3 hours of processing, solid solutions based on nickel are formed due to the dissolution of aluminum and titanium in the crystal lattice. Further milling up to 6 hours leads to the formation of intermetallic phases with a disordered structure. The addition of titanium accelerates phase transformations and promotes structural refinement, with the most pronounced effect observed for compositions with higher titanium content. The findings demonstrate that mechanical alloying is an effective method for producing refined intermetallic structures, with optimal processing conditions in the range of 3 to 6 hours of milling.

Keywords: mechanosynthesis; intermetallic compounds; Ni-Al-Ti system; mechanical alloying; phase transformation; microstructure.

1. Introduction

Ni-Al intermetallic compounds are widely recognized as promising materials for high-temperature applications due to their combination of low density, high melting point, and excellent resistance to oxidation and thermal degradation. These properties make them suitable for use in aerospace, energy, and advanced engineering systems operating under severe conditions (Dey, 2003; Darolia, 1991). In particular, NiAl- and Ni_3Al-based alloys are of great interest because they retain mechanical strength at elevated temperatures while exhibiting good thermal stability. Despite these advantages, the practical application of Ni-Al intermetallics is limited by their intrinsic brittleness at room temperature. This behavior is primarily associated with a limited number of active slip systems and structural features such as grain boundary segregation (Liu, 1984). To address this limitation, various strategies have been proposed, including alloying with additional elements and the formation of complex or multiphase microstructures.

Among the alloying elements, titanium plays a particularly important role in modifying the properties of Ni-Al systems. The introduction of Ti promotes lattice distortion, enhances defect accumulation, and contributes to the stabilization of solid solutions and intermetallic phases such as $Ni_3(Al,Ti)$ (Gao et al., 2025; Li et al., 2023) . In addition, Ti-containing systems may exhibit improved microstructural homogeneity and enhanced mechanical performance. However, the influence of titanium strongly depends on its concentration, and excessive additions may lead to structural instability or defects (Riyadi, 2020).

In recent years, increasing attention has been given to the development of nanostructured intermetallic materials, as grain refinement is known to improve both strength and ductility. Mechanical alloying (mechanosynthesis) has emerged as an effective method for producing such materials. This process involves repeated cold welding, plastic deformation, and fracture of powder particles, leading to the formation of supersaturated solid solutions and refined microstructures (Suryanarayana, 2001). Compared to conventional melting and casting techniques, mechanical alloying provides better control over composition, structure, and phase distribution.

The phase evolution in Ni-Al-Ti systems during mechanical alloying is strongly influenced by processing parameters, particularly milling time and composition. Previous studies have shown that solid solutions may form at intermediate stages of processing, followed by the development of intermetallic phases with increasing milling duration. At the same time, titanium has been reported to accelerate diffusion processes and enhance the formation of homogeneous nanostructures (Chérif et al., 2017). However, the relationship between titanium content, milling duration, and the kinetics of phase formation remains insufficiently clarified.

Therefore, the aim of this study is to investigate the effect of composition and mechanical alloying time on the formation of intermetallic compounds in the Ni-Al-Ti system. Special attention is given to phase transformations, crystallite size evolution, and microstructural characteristics. The results provide new insights into the mechanisms of mechanosynthesis and contribute to the optimization of processing parameters for the development of nanostructured intermetallic materials.

2. Literature Review

Nickel-aluminum intermetallic compounds have been extensively studied due to their unique combination of high-temperature strength, low density, and excellent oxidation resistance. These properties make them promising candidates for applications in aerospace, energy, and high-temperature structural components (Dey, 2003; Darolia, 1991). However, a key limitation of Ni-Al-based intermetallics is their intrinsic brittleness at room temperature, which is associated with a limited number of active slip systems and grain boundary effects (Liu, 1984).

To overcome these limitations, various strategies have been proposed, including alloying and microstructural design. In particular, the addition of titanium to Ni-Al systems has been shown to significantly affect phase stability and mechanical properties. Titanium contributes to lattice distortion and promotes the formation of multicomponent solid solutions and intermetallic phases such as $Ni_3(Al,Ti)$, which can improve strength and structural stability (Gao et al., 2025; Li et al., 2023) . At the same time, excessive titanium content may lead to structural defects such as porosity or cracking, indicating the need for optimized compositions (Riyadi, 2020).

Another important approach to improving the properties of intermetallic compounds is the formation of multiphase microstructures. Systems containing both B2 and L12 phases have demonstrated enhanced mechanical performance due to the combined effect of high strength and improved ductility (Chanda et al., 2020; Gao et al., 2025). Such microstructures are often achieved near eutectic compositions, where fine lamellar structures can form and contribute to improved deformation behavior.

Mechanical alloying (mechanosynthesis) is widely used as an effective method for producing intermetallic compounds and nanostructured materials. This process involves repeated deformation, cold welding, and fracture of powder particles, leading to grain refinement and enhanced diffusion (Suryanarayana, 2001). As a result, supersaturated solid solutions and intermetallic phases can form directly during milling, without the need for high-temperature processing.

The evolution of phase composition during mechanical alloying strongly depends on processing parameters, particularly milling time. At early stages, cold welding dominates, resulting in particle agglomeration, whereas prolonged milling leads to fragmentation, homogenization, and refinement of the structure. However, excessive milling may cause contamination and does not necessarily lead to further improvements in phase formation (Samani et al., 2009; Enayati et al., 2008).

In Ni-Al-Ti systems, previous studies have shown that titanium accelerates the formation of solid solutions and enhances microstructural refinement. The presence of Ti reduces the tendency for cold welding and promotes more uniform particle size distribution during milling (Chérif et al., 2017). At the same time, the kinetics of phase transformation and the relationship between composition, milling time, and structural evolution remain insufficiently understood.

Thus, the present study contributes to the existing body of research by systematically analyzing the effect of titanium content and milling duration on phase formation, crystallite size, and microstructural evolution in the Ni-Al-Ti system. This approach allows for a better understanding of the mechanisms governing mechanosynthesis and the optimization of processing parameters for the production of nanostructured intermetallic materials.

3. Materials and Methods

Materials. Elemental powders of nickel (Ni), aluminum (Al), and titanium (Ti) were used as starting materials. The powders had the following characteristics: Ni (purity 99%, average particle size < 50 µm), Al (purity 99.5%, average particle size < 90 nm), and Ti (purity 99%, average particle size < 50 µm). Powder mixtures with nominal compositions $Ni_{68}Al_{25}Ti_7$, $Ni_{72}Al_{22}Ti_6$, $Ni_{70}Al_{21}Ti_9$, and $Ni_{75}Al_{25}$ (at.%) were prepared to investigate the effect of titanium addition and composition on phase formation and microstructural evolution.

Mechanosynthesis Procedure. Mechanical alloying (mechanosynthesis) was carried out using a planetary ball mill (Fritsch Pulverisette 7 classic line). Prior to milling, the powder mixtures were pre-mixed for 10 minutes at 200 rpm to ensure initial homogenization. The mechanosynthesis process was performed in two hardened steel vials with a volume of 45 mL. Steel balls with a diameter of 5 mm were used as the milling media. The ball-to-powder weight ratio was maintained at 10:1. Milling was conducted at a rotational speed of 600 rpm for different durations of 1, 3, and 6 hours. To prevent excessive heating inside the vials, the milling process was carried out in cycles consisting of 10 minutes of milling followed by a 5-minute pause. To minimize oxidation, all operations, including loading and unloading of powders, were performed in a vacuum glove box under an argon atmosphere. In addition, mechanical alloying was conducted in an argon-filled environment at a pressure of approximately 0.3 MPa. A process control agent (stearic acid) was added in an amount of 2 wt.% of the powder mass to reduce particle agglomeration during milling. During milling, the powder particles were subjected to repeated plastic deformation, cold welding, and fracture, leading to progressive refinement of the structure and activation of diffusion processes.

Characterization Techniques. The phase composition of the powders was analyzed by X-ray diffraction (XRD) using Cu Kα radiation in the 2θ range of 20–100°. The diffraction patterns were used to identify phase evolution, including the formation of solid solutions and intermetallic compounds during milling.

The morphology and microstructure of the powders were examined using scanning electron microscopy (SEM). This analysis provided information on particle shape, degree of agglomeration, and structural refinement as a function of milling time.

Particle size distribution was determined using laser diffraction analysis. This method was used to evaluate the average particle size and to monitor its evolution during mechanosynthesis.

Experimental Design and Reproducibility. For each composition and milling duration, powder samples were prepared and analyzed under identical conditions to ensure consistency. The experimental design allowed for a direct comparison between binary and ternary systems as well as between different milling times. All measurements were performed multiple times, and the results were verified for reproducibility. The applied methodology ensures that the observed trends in phase formation, particle size evolution, and microstructural changes are reliable and representative of the mechanosynthesis process.

4. Results and Discussion

The evolution of particle size during mechanosynthesis was analyzed using a laser particle size analyzer (Fritsch Analysette 22 NEXT), and the results are summarized in Figure 1. After initial mixing (10 min at 200 rpm), the average particle sizes differed depending on the composition. The smallest particles were observed for sample No. 1 ($Ni_{68}Al_{25}Ti_{7}$), with an average size of approximately 10 µm, whereas samples No. 2 ($Ni_{72}Al_{22}Ti_{6}$), No. 3 ($Ni_{70}Al_{21}Ti_{9}$), and No. 4 ($Ni_{75}Al_{25}$) exhibited larger particle sizes of 18.3, 17.2, and 18.6 µm, respectively. This behavior can be attributed to the presence of nanosized aluminum particles, which contribute to a more dispersed initial mixture.

After 1 hour of mechanical alloying, a noticeable increase in particle size was observed for all compositions. The average particle size increased to 31.1 µm (sample No. 1), 35.3 µm (sample No. 2), 23 µm (sample No. 3), and 40.5 µm (sample No. 4). This enlargement is associated with intensive cold welding and agglomeration of particles, which dominate at the early stage of milling. The SEM observations confirm the formation of large agglomerates with irregular morphology, indicating that plastic deformation prevails over fragmentation.

With further milling up to 3 hours, the dominant mechanism shifts from agglomeration to fragmentation. As a result, a significant reduction in particle size is observed. The average particle sizes decreased to 11.3 µm (sample No. 1), 6.04 µm (sample No. 2), 15.7 µm (sample No. 3), and 6.4 µm (sample No. 4). At this stage, the highest fraction of fine particles is achieved; however, a relatively wide particle size distribution is still present, indicating incomplete homogenization.

After 6 hours of milling, a more stable and uniform particle size distribution is established. The average particle sizes reached 7.6 µm (sample No. 1), 8.05 µm (sample No. 2), 9 µm (sample No. 3), and 9.8 µm (sample No. 4). The reduction in size variability and the decrease in the number of large agglomerates indicate that a quasi-stationary state is achieved, where the processes of cold welding and fragmentation are balanced.

A comparison of the compositions shows that the addition of titanium influences the particle refinement behavior. In particular, sample No. 3 ($Ni_{70}Al_{21}Ti_{9}$) demonstrates a more stable evolution of particle size, with less pronounced agglomeration at early stages and more controlled refinement during prolonged milling. This effect can be attributed to the role of titanium in reducing cold welding tendencies and promoting more uniform deformation and fracture processes.

Overall, the obtained results confirm that particle size evolution during mechanosynthesis follows a non-monotonic trend, governed by the competition between cold welding and fragmentation mechanisms. The optimal milling duration for obtaining a relatively uniform and refined powder structure under the given conditions is 6 hours.

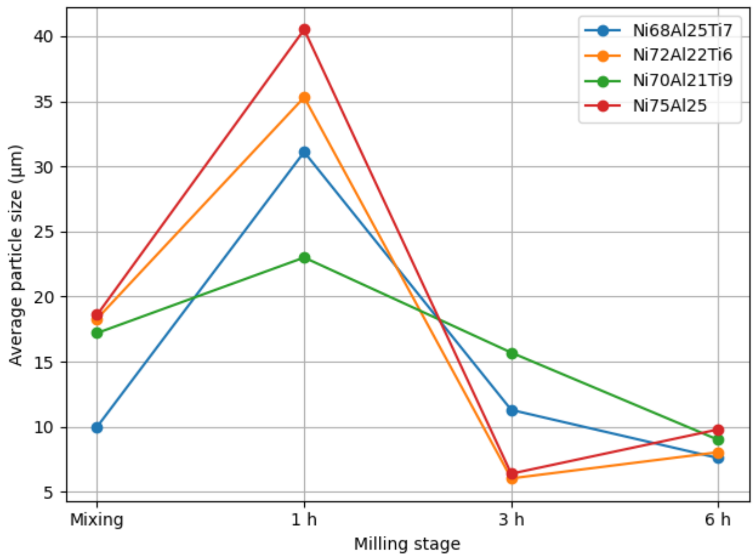

Figure 1. Evolution of average particle size during milling of powder mixtures.

The morphology of the powder mixtures at different stages of mechanosynthesis is presented in Figure 2, which combines 16 SEM micrographs corresponding to four compositions and four milling times (10 min, 1 h, 3 h, and 6 h). The rows represent different compositions ($Ni_{68}Al_{25}Ti_7$, $Ni_{72}Al_{22}Ti_6$, $Ni_{70}Al_{21}Ti_9$, and $Ni_{75}Al_{25}$), while the columns correspond to the milling duration.

The combined SEM dataset clearly demonstrates that the evolution of powder morphology during mechanosynthesis proceeds through three characteristic stages: initial agglomeration, subsequent fragmentation, and final stabilization.

At the initial stage (10 min), all compositions exhibit relatively loose and heterogeneous structures consisting of fine particles and small agglomerates. This is primarily associated with the presence of nanosized aluminum, which enhances the dispersion of the powder mixture.

After 1 hour of milling, a pronounced increase in particle size is observed across all compositions. The SEM images show the formation of large, dense agglomerates with irregular morphology. This behavior indicates that cold welding dominates over fracture at this stage, driven by severe plastic deformation and the high ductility of metallic components.

With further milling up to 3 hours, a transition to fragmentation becomes evident. The SEM micrographs reveal the breakdown of previously formed agglomerates and the appearance of finer and more dispersed particles. This stage corresponds to the most intensive refinement, where fracture mechanisms begin to prevail over cold welding.

After 6 hours of milling, the morphology becomes significantly more uniform. The images show relatively fine, equiaxed particles with a reduced number of large agglomerates, indicating that a dynamic equilibrium between cold welding and fragmentation has been established. As a result, the particle size distribution stabilizes.

A comparison of different compositions within the combined figure highlights the influence of titanium on the milling behavior. The $Ni_{75}Al_{25}$ composition (without Ti) shows the highest tendency toward agglomeration, particularly after 1 hour of milling. In contrast, Ti-containing compositions, especially $Ni_{68}Al_{25}Ti_7$, exhibit more efficient particle refinement and reduced agglomeration at later stages. This suggests that titanium plays a key role in suppressing cold welding and promoting more uniform deformation and fracture processes.

Furthermore, the combined visualization allows for direct comparison of structural evolution across all systems. It can be observed that compositions with higher Ti content demonstrate a more gradual and controlled transition from agglomeration to fragmentation, resulting in a more homogeneous microstructure at prolonged milling times.

Overall, the analysis of the combined SEM figure confirms that the most effective particle refinement occurs between 1 and 3 hours of milling, while further processing up to 6 hours leads primarily to structural stabilization. The unified representation of all compositions and milling stages provides a comprehensive understanding of the mechanosynthesis process and highlights the role of composition in controlling microstructural evolution.

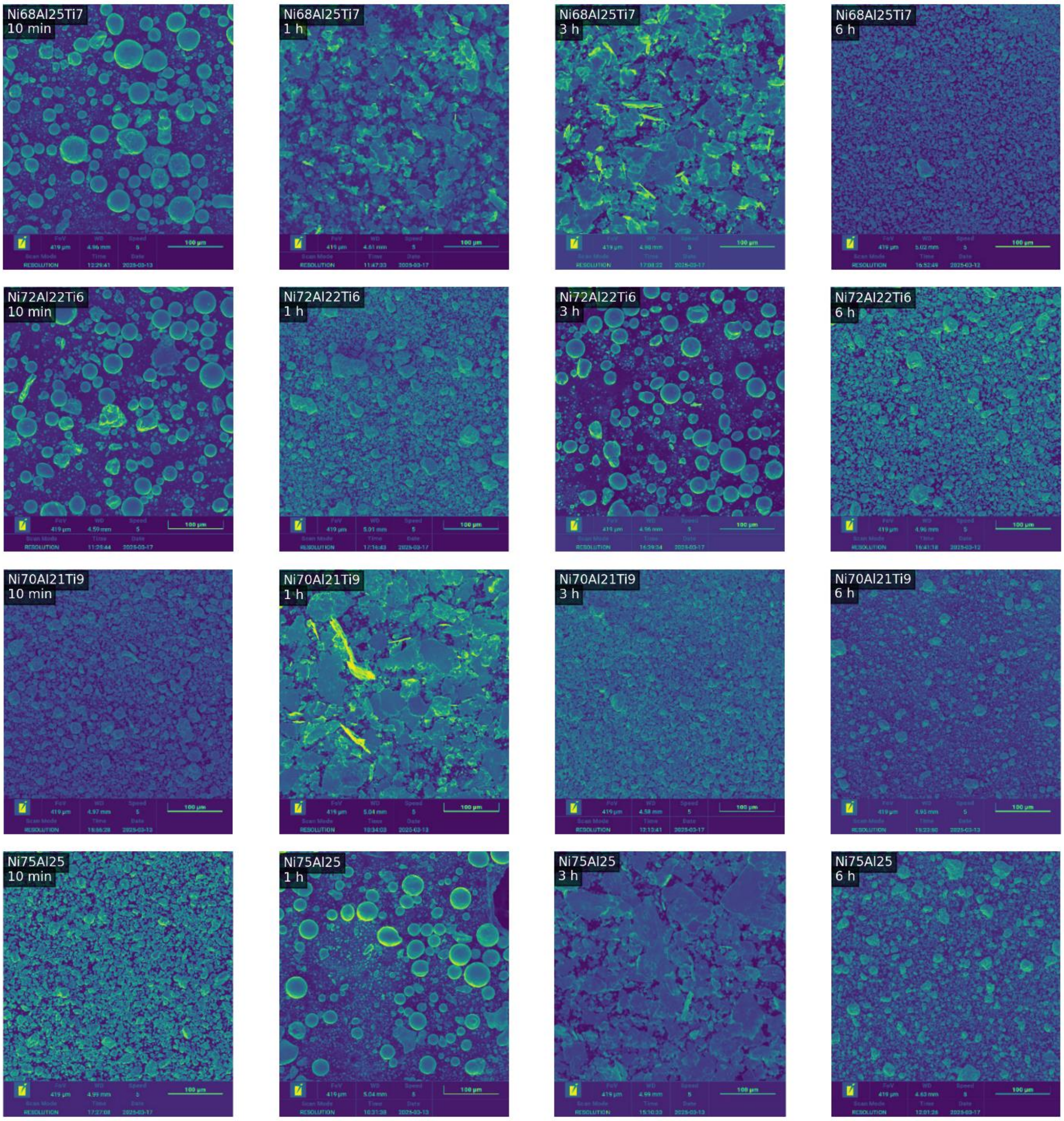

Figure 2. SEM micrographs of Ni-Al-Ti powder mixtures with different compositions at various milling stages. Rows correspond to compositions, and columns represent milling time (10 min, 1 h, 3 h, and 6 h).

Figure 2 presents the X-ray diffraction patterns of the Ni-Al and Ni-Al-Ti powder mixtures after different milling times. The diffraction data clearly show that mechanical alloying strongly affects the phase composition and structural state of the powders.

In the binary Ni-Al system, sharp and intense diffraction peaks corresponding to Ni and Al are observed at the initial stage and after 1 h of milling. This indicates that the initial components largely retain their crystalline structure during the early stage of processing. After 3 h of milling, the Al peaks disappear, while the Ni peaks shift slightly toward lower diffraction angles. This shift indicates lattice expansion caused by the dissolution of Al atoms in the Ni crystal lattice and the formation of a Ni(Al) solid solution.

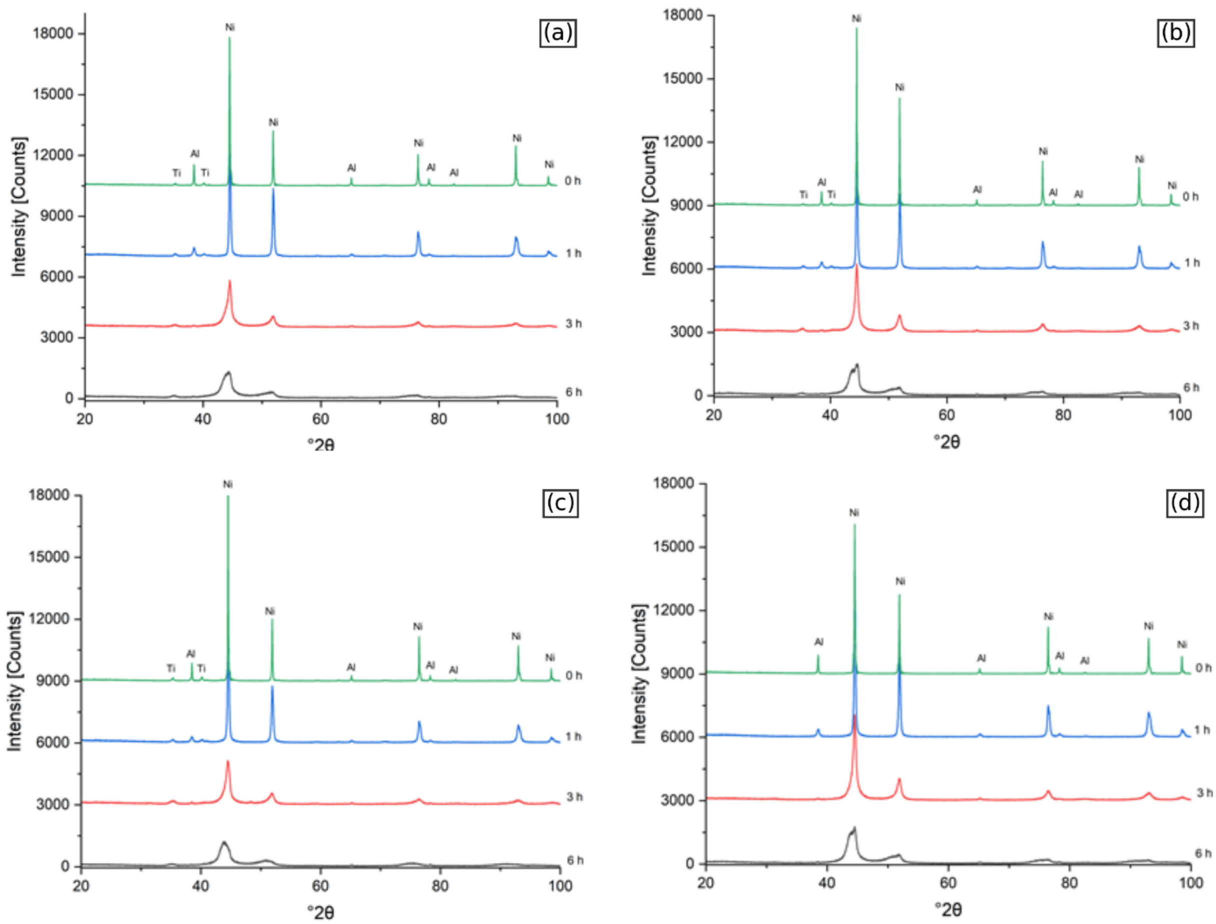

Figure 3. X-ray diffraction patterns of Ni-Al and Ni-Al-Ti powder mixtures at different milling times (0 h, 1 h, 3 h, and 6 h): (a) $Ni_{68}Al_{25}Ti_7$; (b) $Ni_{72}Al_{22}Ti_6$ (c) $Ni_{70}Al_{21}Ti_9$; (d) $Ni_{75}Al_{25}$.

After 6 h of milling, the diffraction peaks become broader and less intense, which is associated with crystallite refinement and the accumulation of lattice strain during severe plastic deformation. At this stage, the characteristic peaks of metallic Ni are significantly reduced, while reflections corresponding to the Ni_3Al intermetallic phase begin to appear. The absence of superstructure peaks suggests that the formed Ni_3Al phase has a disordered structure.

For the ternary Ni-Al-Ti compositions, a similar but more intensive transformation behavior is observed. With increasing milling time, the diffraction peaks gradually broaden and decrease in intensity, indicating grain refinement, defect accumulation, and increasing internal stresses. After 1 h of milling, the peaks of Ni, Al, and Ti can still be identified, showing that complete alloying has not yet occurred.

After 3 h of milling, the intensities of the Al and Ti peaks are significantly reduced, which indicates the gradual dissolution of these elements into the Ni lattice and the formation of a Ni(Al,Ti) solid solution. Further milling up to 6 h results in additional peak broadening and a slight shift of the main reflections toward lower 2θ angles. This behavior confirms the expansion of the Ni lattice due to the incorporation of larger Al and Ti atoms and the development of a supersaturated solid solution. The appearance of $Ni_3(Al,Ti)$ reflections after prolonged milling indicates the formation of an intermetallic phase in the ternary system. Similar to the binary system, the absence of superstructure reflections suggests that the formed $Ni_3(Al,Ti)$ phase is structurally disordered.

A comparison of the ternary compositions shows that increasing Ti content promotes stronger peak broadening and lower peak intensity. This indicates that titanium accelerates structural refinement, enhances lattice distortion, and promotes faster phase transformation. Among the investigated compositions, $Ni_{70}Al_{21}Ti_9$ demonstrates the most pronounced transformation behavior, suggesting that this composition provides the fastest formation of the $Ni_3(Al,Ti)$ phase.

Overall, the XRD results confirm that mechanical alloying induces a gradual sequence of phase transformations: from the initial elemental powders to solid solutions Ni(Al) and Ni(Al,Ti), followed by the formation of intermetallic phases Ni_3Al and $Ni_3(Al,Ti)$ after prolonged milling. These structural changes are consistent with the SEM and particle size results, which show particle refinement, reduced agglomeration, and stabilization of the powder structure after 6 h of milling.

5. Conclusion

Elemental powder mixtures of the Ni-Al-Ti system with different compositions were successfully processed by mechanical alloying using a planetary ball mill. The results demonstrate that the phase evolution during mechanosynthesis strongly depends on milling time and chemical composition.

After 3 hours of milling, the formation of solid solutions Ni(Al) in the binary system and Ni(Al,Ti) in the ternary systems was observed, indicating the dissolution of alloying elements into the Ni lattice. Further milling up to 6 hours led to the formation of intermetallic phases Ni_3Al and $Ni_3(Al,Ti)$ in the binary and ternary systems, respectively. The absence of superstructure reflections suggests that these intermetallic phases possess a disordered structure.

It was also established that increasing the titanium content from 6 to 9 at.% accelerates the formation of the $Ni_3(Al,Ti)$ phase, highlighting the significant role of Ti in enhancing diffusion processes and phase transformation kinetics during mechanical alloying.

Overall, the obtained results confirm that mechanosynthesis is an effective method for producing intermetallic compounds in the Ni-Al-Ti system. The optimal milling duration is in the range of 3-6 hours, which ensures the formation of refined and structurally homogeneous powders with controlled phase composition.

References

1. Aubakirova, D., Sagymbekova, E., Kozhakhmetov, Y., Kowalewski, P., Dauletkhanov, Y., Yerbolat, D., & Urkunbay, A. (2025). Structural and functional enhancement of Ni–Ti–Cu shape memory alloys via combined powder metallurgy techniques. Open Engineering, 15, 208–211. https://doi.org/10.1515/eng-2025-0208
2. Aubakirova, D., Sagymbekova, E., Kozhakhmetov, Y., Dauletkhanov, Y., Urkunbay, A., Yerbolat, D., Kowalewski, P., & Tabiyeva, Y. (2025). Evolution of the structural and phase composition of Ni–Ti–Cu alloy produced via spark plasma sintering after aging. Crystals, 15, 939. https://doi.org/10.3390/cryst15090939
3. Chanda, B., Potnis, G., Jana, P. P., & Das, J. (2020). A review on nano-/ultrafine advanced eutectic alloys. Journal of Alloys and Compounds, 827, 154226. https://doi.org/10.1016/j.jallcom.2020.154226
4. Chérif, A., Bachaga, T., Saurina, J. J., Khitouni, M., & Makhlouf, T. (2017). Morphology and structure effect of Ti addition on Ni–Al powders during mechanical alloying. The International Journal of Advanced Manufacturing Technology, 88, 1767–1776. https://doi.org/10.1007/s00170-016-8908-4

5.Darolia, R. (1991). NiAl alloys for high-temperature structural applications. JOM, 43(3), 44–49. https://doi.org/10.1007/BF03220103
6.Dey, G. K. (2003). Physical metallurgy of nickel aluminides. Sadhana, 28(1–2), 247–262. https://doi.org/10.1007/BF02717135
7.Enayati, M. H., Karimzadeh, F., & Anvari, S. (2008). Synthesis of nanocrystalline NiAl by mechanical alloying. Journal of Materials Processing Technology, 200(1–3), 312–315. https://doi.org/10.1016/j.jmatprotec.2007.08.034
8.Frommeyer, G., & Rablbauer, R. (2008). High temperature materials based on NiAl. Steel Research International, 79(7), 507–513. https://doi.org/10.2374/SRI08SP130
9.Gao, M., Wen, D., Huang, Z., Kong, F., Liu, J., Li, Q., Zhang, C., Liu, C. T., & Wang, A. (2025). Rational design of eutectic Ni–Al–Ti alloys. Materials & Design, 249, 113532. https://doi.org/10.1016/j.matdes.2024.113532
10.Grabke, H. J. (1999). Oxidation of NiAl and FeAl. Intermetallics, 7(10), 1153–1158. https://doi.org/10.1016/S0966-9795(99)00054-7
11.Li, L., Ding, Q., Zhang, Z., Li, Y., Wei, X., Zhang, Z., & Bei, H. (2023). Effect of Al and Ti on Ni_3(Al,Ti) alloys. Journal of Materials Research and Technology, 24, 4650–4660. https://doi.org/10.1016/j.jmrt.2023.04.089
12.Liu, C. T. (1984). Physical metallurgy and mechanical properties of ductile ordered alloys. International Metals Reviews, 29(1), 168–194. https://doi.org/10.1179/imtr.1984.29.1.168
13.Mardiha, P., Bahrami, A., & Mohammadnejad, A. (2019). Ni/Ni_3Al multilayer composite. Science of Sintering, 51(4), 401–412. https://doi.org/10.2298/SOS1904401M
14.Ozdemir, O., Zeytin, S., & Bindal, C. (2008). Tribological properties of NiAl intermetallics. Wear, 265(7–8), 979–985. https://doi.org/10.1016/j.wear.2008.01.010
15.Riyadi, T. W. B. (2020). Structure and properties of Ni–Al–Ti systems. Materials Science Forum, 991, 44–50. https://doi.org/10.4028/www.scientific.net/MSF.991.44
16.Samani, M. N., Shokuhfar, A., Kamali, A. R., & Hadi, M. (2009). Production of nanocrystalline Ni_3Al by mechanical alloying. Journal of Alloys and Compounds, 500(1), 30–33. https://doi.org/10.1016/j.jallcom.2009.03.030
17.Suryanarayana, C. (2001). Mechanical alloying and milling. Progress in Materials Science, 46(1–2), 1–184. https://doi.org/10.1016/S0079-6425(99)00010-9
18.Wu, L., Yao, J., Dong, H., He, Y., Xu, N., Zou, J., Huang, B., & Liu, C. T. (2011). Corrosion behavior of Ni_3Al intermetallics. Intermetallics, 19(11), 1759–1765. https://doi.org/10.1016/j.intermet.2011.06.010