



Effect of High-Energy Ball Milling on Structure and Properties of Some Intermetallic Alloys: A Mini Review

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Abstract

Currently, lightweight materials and structures are potentially required for economical aspects. A major preoccupation of engineers and materials scientists is to create and to develop existing materials to satisfy the rising needs of industries and population. It is well known that intermetallic compounds, such as aluminides, are used for a wide range of applications, due to their superior properties. These materials are generally produced through conventional manufacturing routes: melting, casting, powder grinding, and consolidation by hot pressing. However, these methods are inapplicable to the elaboration of some intermetallic alloys. The solid-state reaction of mechanical alloying makes it a processing way of choice for alloying elements that are difficult or impossible to combine by conventional melting methods. On the other hand, MA process seems to be a simple and cost-effective technique for improving structural and magnetic properties of intermetallic alloys. Within this context, this paper provides an overview of the experimental investigations performed on mechanical alloying/milling of γ -TiAl, τ -MnAl, and B2-RuAl intermetallic alloys.

Keywords Mechanical alloying · Mechanical milling · γ -TiAl · τ -MnAl · B2-RuAl

Introduction

One of the biggest challenges faced by industrial laboratories is the provision of new materials designed to have superior properties: stronger, lighter, smaller, faster, cheaper, and safer or to improve the performance and efficiency of current materials. Materials scientists have been continuously conducting fundamental and applied studies with the intention of bringing up the properties of the materials and their operation in various structural and energy generation utilizations. Substantial advances in physical, chemical, electrical, and optical characteristics have been successfully realized by alloying and through chemical alteration and by subjection the systems to a series of conventional thermal, mechanical, and chemical manufacturing processes [1, 2]. Currently, there are several techniques available for the modification of structural and microstructural characteristics of materials,

among them mechanical alloying (MA) or high-energy ball milling.

Mechanical alloying (MA) is a simple, dry powder processing technique, which involves repeated welding, fracturing, and rewelding of powder particles by highly energetic collisions of grinding media in a high-energy ball mill. The powder particles are trapped between the colliding spheres during the operation and undergo fracture, deformation, and/or phase development features [3]. However, despite this apparent simplicity, high-energy ball milling is a complicated, less understood technique and the required structures are mainly obtained in an empirical fashion by trial and error [4]. This uncertainty arises, generally due to the far from equilibrium processing conditions during high-energy ball milling, which makes it difficult to predict the thermodynamic and kinetic aspects of the phase transitions occurring during milling [4]. Actually, MA has been used to synthesize both equilibrium and non-equilibrium phases of commercially useful and scientifically interesting materials from metallic to ionic: supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructured materials, and amorphous alloys [5]. MA has been found to be very effective in producing powders with unique properties: (i) homogeneous material with highly dispersed components

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far away from thermal equilibrium state, (ii) a defected structure, grain boundaries, and (iii) ultrafine grain structure [5, 6].

In fact, mechanical alloying is the main term used to describe the mechanical processing of powders in high-energy ball mills [7]. Based on the classification proposed by Koch [8], ball milling can be divided into two classes that depend on the originating materials used. Ball milling of powders with different types of compositions, in which material transfer and solid-state interdiffusion take place, is named mechanical alloying (MA); however, ball milling of uniform composition, where the material transfer is not required, has been called mechanical milling (MM) [8, 9]. The most frequently used words that are used to describe the high-energy processing of powders are the following: mechanical disordering, mechanical grinding, reaction milling, cryo-milling, rod milling, mechanically activated annealing, and double mechanical alloying [10].

Beginning with Benjamin's successful synthesis of mechanically alloyed IN-853 in 1970, the attempts to improve the properties of aluminum by using mechanical alloying technique have received a great deal of attention [11]. Aluminum is widely used in pre-alloyed powders, to produce high-performance composite materials [12]. Aluminum is the third most abundant metallic element on earth, posing a combination of excellent physical (2.7 g/cm³, high thermal and electrical conductivity), chemical, and mechanical properties (excellent machinability and competitive cost) which made it a very popular cladding material [11, 13]. Aluminum is the second most employed metal in the world after steel. Due to low strength, its utility is limited, but dramatic improvements in mechanical properties can be achieved by the introduction of alloy additions of secondary elements [11]. The choice of aluminum alloys as structural engineering materials is dictated by the compelling need to have vehicles with low fuel consumption and reduced emissions for a sustainable future [14, 15].

Ordered intermetallics based on aluminides are another subclass of aluminum alloys. They have exhibited considerable attention due to their potential application possibility, especially at high temperatures [16]. Investigation on intermetallic alloys has been mainly driven by the needs of the aerospace industry for innovative materials with high specific strength and stiffness, as well as the ability to retain their strength and resist environmental degradation at elevated temperatures [17]. Aluminides of significant scientific and technological utility are from the following systems: Ni–Al, Fe–Al, and Ti–Al, which have been studied extensively [17–30].

Prior to World War II, less attention has been paid to the research on intermetallic alloys. They were considered as materials of little interest except to those individuals concerned with phase equilibria in polycomponent metallic

systems [31]. Later, interest in intermetallics, particularly those containing rare earths, has intensively increased. The number of scientific research projects that involve multiple disciplines, materials scientists, chemists, physicists, engineers, and production specialists, has increased, too [31]. A great deal of understanding on the intermetallics has been gained and significant progress has been defined repeatedly in some detail by Westbrook, one of the key people in the investigation and development of intermetallics in the second half of this century [32]. In the past two decades, significant fundamental and developmental research studies have been performed on intermetallic alloys [17], and excellent reviews and book chapters have been published [10, 32–39]. As a result, the structure–property relations of these materials are reasonably well understood, which has led to a road map for further study to develop high-performance materials for many engineering fields [17].

The formation of the intermetallic alloys by high-energy ball milling process has been previously summarized by Suryanarayana [10]. Mechanisms involved in the formation of ordered intermetallic alloys during mechanical treatment have not been exactly determined. It has been suggested that a phase will exist in either the ordered or disordered condition, depending upon the balance between atomic disordering introduced by MA and the thermally activated reordering [10]. The effects of high-energy ball milling on transition metal intermetallics, TM–Al (TM = Fe, Ni, Co) having a B2 structure, have been previously highlighted [40]. The current paper is intended to provide an overview of the major efforts made over the last years on MA/MM of γ -TiAl, τ -MnAl, and B2-RuAl intermetallic alloys.

Titanium and γ -TiAl Intermetallic Alloys

Titanium is the fourth most abundant metal, comprising about 0.63% of the earth's crust, and it is distributed widely throughout the world [41]. The presence of this element has been detected in meteorites, on the moon, and in the stars [41, 42]. Titanium (Ti), named after the Greek God Titan, was recognized as a new element by Reverend William Gregor in 1791 [41, 43]. Although it has been available more than two hundred years, it has only been produced industrially since the 1950s [44]. It has been reported that the first known investigation of titanium powder metallurgy was performed by Dr. Kroll [45, 46]. Titanium and its alloys are largely utilized in both aerospace and non-aerospace fields: gas turbine engines, airframes, pulp and paper, oil and gas, marine, biomedical, and consumer goods industries [47–50].

Titanium aluminides are part of a large family of intermetallic compounds, and they present exciting materials for use in high-temperature applications [32]. At the beginning of 1970s, γ -TiAl intermetallic compounds were developed

as the first intensive and successful structural materials with fundamental deformation studies [32, 51]. Actually, titanium aluminide-based intermetallic compounds have been considered of great importance. They offer excellent mechanical properties, with low values of density (4.506 g/cm^3 for pure titanium), high resistance to high temperatures, high electric and thermal conductivity, resistance to the oxidation, a tensile strength of 1000 MPa, and Young's modulus of 160 GPa [52]. Reason for development of TiAl alloys is to improve a class of materials whose properties are between those of nickel-based superalloys and elevated temperature ceramics [34].

Structural Properties

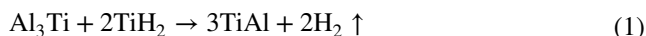
The Ti–Al binary phase diagram is complex, as shown in Fig. 1a [53]. Its alloys show different microstructures for different compositions near the 50:50 aluminum-to-titanium ratio [54–56]. Ti–Al alloys in the range of 40–50 at.% Al are named γ -TiAl-based alloys [57, 58]. γ -TiAl phase has a face-centered tetragonal (fcc) $L1_0$ structure (CuAu type) [59]. γ -TiAl-based alloys contained two phases (γ and α_2) and a little quantity of reinforcing precipitations of the third phase [58, 60]. The structure of γ -TiAl presents a layered arrangement of Ti and Al atoms on successive (002) planes (Fig. 1b). γ -TiAl has $a, c/a=1.02$ at $\text{Ti}_{50}\text{Al}_{50}$ [61]. The lattice parameters a and c show a linear variation with Al content and the tetragonal distortion increases with increasing Al concentration [64, 65]. The γ -TiAl phase can remain ordered up to its melting point of about 1450 °C [65].

MA γ -TiAl Intermetallic Alloys

As previously mentioned, TiAl alloys have remarkable properties that are regarded as promising candidates in aerospace and automobile industry [66–68]; however, low-temperature ductility and poor formability limit them extensive

application [66, 69, 70]. Actually, alloying elements can be added to improve the mechanical properties of γ -TiAl intermetallic alloys [71]. Moreover, it has been reported that powder metallurgy via mechanical alloying (MA) process can fabricate ultrafine-grained materials with controlled composition [18, 19, 24] and good homogeneity which the latter have the improved mechanical properties [20, 21]. It is important to note that TiAl alloys can be synthesized via different powder metallurgy methods: hot isostatic pressing, hot extrusion reaction synthesis, and spark plasma sintering [72].

The effect of milling parameters, on the formation of γ -TiAl phase, has been investigated by Hales and Vsquez [73]. Suryanarayana [61] has mentioned that there have been some reports on the possible synthesis of the disordered γ -TiAl (fcc) phase by MA process. However, a careful investigation conducted by XRD has revealed that the fcc phase interpreted as the disordered form of the γ -TiAl phase was the contaminant nitride TiN [61]. In another investigation, Suryanarayana et al. [74] have produced the equiatomic TiAl phase. These authors have synthesized the γ -TiAl phase by mixing titanium hydride and the Al_3Ti intermetallic powders in the proper proportion, according to the chemical reaction:



Other experimental works have studied the solid-state reactions from elemental powder mixtures to titanium aluminides [75–83]. The milling conditions used by these investigators as well as their main results are summarized in Table 1.

Other researchers have obtained nanostructured intermetallics in ternary and quaternary powder mixtures. Nargesi et al. [79] have conducted an investigation aiming to study the effect of Cr on TiAl formation. They have reported that the addition of 5% at. Cr to the TiAl samples shifted the γ -TiAl phase to nanostructured duplex phase ($\gamma + \alpha_2$). Kennedy et al. [84] have successfully prepared

Fig. 1 (a) Equilibrium phase diagram of Ti–Al [62]. Reprinted by permission from Springer Nature [62] and (b) crystal structure of γ -TiAl [63]. Reprinted from [63], with permission from Elsevier

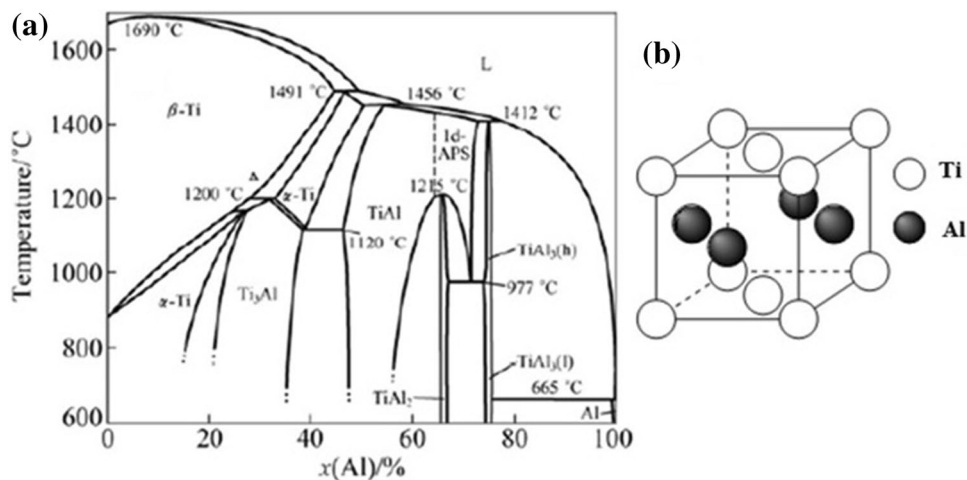


Table 1 Mechanically alloyed mixtures of elemental Al and Ti powders

Alloy/composition	Mill	BPR	Atmosphere	Time, h	Main results	References
Ti ₅₀ Al ₅₀ , Ti ₄₃ Al ₅₇ and Ti ₄₄ Al ₅₆	Centrifugal ball mill of the model AGO-2MI	20:1	Ar or He	2–3	Annealed products showed the formation of single γ -TiAl The activation energy of transformation: hcp phase \rightarrow tetragonal phase was close to 260 ± 43 kJ/mol	[75]
Ti ₅₀ Al ₅₀	Planetary ball mill P5	10:1	Ar	80	The structural phase transformations: Ti ₅₀ Al ₅₀ \rightarrow Ti(Al) \rightarrow amorphous \rightarrow hcp supersaturated Ti(Al) and the structural phase transformations during heating: amorphous \rightarrow metastable hcp \rightarrow disorder fcc TiAl \rightarrow TiAl (L1 ₀) <i>Heat treatment of powders resulted in the formation of TiAl intermetallic compound (50 nm, microhardness of 1190 HV).</i>	[76]
Ti ₅₀ Al ₅₀	Planetary ball mill P6	10:1	Ar	100	The structural phase transformations: Ti ₅₀ Al ₅₀ \rightarrow Ti(Al) \rightarrow amorphous \rightarrow hcp supersaturated Ti(Al) (with trace amounts of TiAl after 80 h of milling) Additional milling up to 100 h, gave rise to TiAl, Ti ₃ Al, and TiAl ₃ intermetallic compounds (200 nm)	[77]
Ti ₅₀ Al ₅₀	Planetary ball mill Retsch PM 100	20:1	Ar	100	The structural phase transformations: nanocrystalline Ti(Al) supersaturated solutions \rightarrow TiAl phase after 40 h of milling Subsequent heat treatment of 1. Powder milled for 80 h, exhibited the formation of a mixture of: mainly α_2 -Ti ₃ Al and γ -TiAl phases 2. Powder milled for 100 h, exhibited the formation of: a major γ -TiAl, α_2 -Ti ₃ Al and a little TiAl ₃ phases.	[78]
Ti ₅₀ Al ₅₀	Planetary mill FP4	15:1	Methanol + Ar	70	An amorphous phase was detected after 50 h of milling Heat treatment of MA powders led to the formation of nanocrystalline γ -TiAl phase	[79]
Ti ₅₀ Al ₅₀	Planetary ball mill P5	10:1	Ar	100	After 50 h of milling, homogeneous hcp supersaturated Ti(Al) solid solution was formed After 55 h, the material is partially amorphized (milling intensity of 5)	[80]

Table 1 (continued)

Alloy/composition	Mill	BPR	Atmosphere	Time, h	Main results	References
Ti ₅₃ Al ₄₇	SPEX 8000 Mill	8:1	Ar	8	The bulk nanostructured alloys consisted of TiAl and a small fraction of Ti ₃ Al phases The addition of a small fraction of powder particles such as Nb, Cr, B, and Ta led to the formation of alloys with small average particle sizes	[81]
Ti ₅₂ Al ₄₈	An INSMART high-energy ball mill	10:1	Stearic acid + Ar	50	An amorphous structure was produced after complete dissolution of Al in Ti Thermal stability of MA powders decreased with increasing milling time Prolonged milling time led to the formation of an amorphous alloy	[82]
TiAl	–	20:1	Ar	3	After a series of processing routes, the obtained TiAl alloy showed high density and refined grain sizes of ($\alpha_2 + \gamma$) lamella and γ The compressive yield strength of the sintered TiAl was 600 MPa at 800 °C	[83]

It should be noted that only the conditions of high-energy ball milling experiments are presented in the table

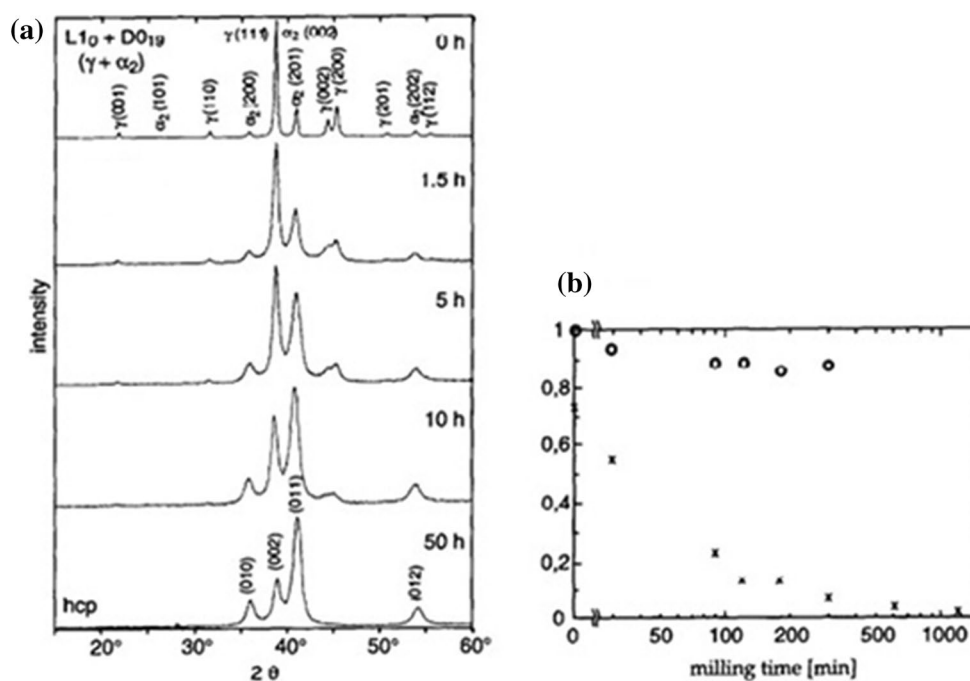
TiAl alloy with the addition of Nb, Cr, Mo, and B and consolidated by spark plasma sintering (SPS). They have reported that the addition of Nb increased the densification of TiAl intermetallic compound, which was also related to the effects of milling such as the decrease in particle size and the morphological changes. Another research group has synthesized TiAl-based alloy with nearly the same elements [85]. The composition was Ti–45Al–2Cr–2Nb–1B–0.5Ta–0.225Y (mole fraction, %). These powders have been subjected to double mechanical milling (DMA) and spark plasma sintering (SPS) processes. The results showed that the DMA powders have nanometer-scale structure. The authors of the study reported that the microstructure of SPSed samples showed TiAl and few phases of Ti₃Al, Ti₂Al and TiB₂. They have shown that with the increase in the SPS temperature, the microhardness and the bending strength decreased from HV658 to HV616 and 781–652 MPa, respectively [85]. Huang et al. [86] have studied the effects of milling and hot isostatic pressing processes on Ti–48Al–2Cr–2Nb powder mixtures. The results showed that the microstructure of powders milled for 8 h consisted of equiaxed γ -TiAl and α_2 -Ti₃Al phases; however, the annealed powder displayed a duplex microstructure of γ -TiAl matrix and lamellar ($\gamma + \alpha_2$) grains.

MM γ -TiAl Intermetallic Alloys

The systematic researches on MM TiAl alloys are reported in the literature. Oehring et al. [79] have indicated that milling γ -TiAl with L1₀ structure did not lead to a transformation into an fcc but into a fine-grained hcp solid solution. Powders of the intermetallic phase γ -TiAl were ball-milled by Klassen et al. [87]. It was found that the intermetallic phase was chemically partially disordered which transformed into a solid solution after prolonged milling time. This structural transformation was accompanied by a slight decrease in the long-range order parameter. Figure 2 shows the XRD patterns of MM γ -TiAl and the evolution of the long-range order parameter, as a function of milling time [87].

The structural and microstructural evolutions occurring to γ -TiAl-based alloy fabricated by cryo-milling of gas atomized powders followed by spark plasma sintering (SPS) have been investigated by Shanmugasundaram et al. [88]. The results indicated that the cryo-milled powder was fully densified at a temperature nearly 125 °C lower than that of un-milled powder. The microstructure of the sample heated at different temperatures consisted of fine grains of γ -TiAl and α_2 -Ti₃Al phases in different volume fractions. They have mentioned that cryo-milling reduced the temperature required for the densification.

Fig. 2 (a) XRD of $\text{Ti}_{51}\text{Al}_{49}$ powder as a function of milling time and (b) phase fraction (x) and relative long-range order parameters (circles) for γ -TiAl as a function of milling time [87]. Reprinted from [87], with permission from Elsevier



Manganese and τ -MnAl Intermetallic Alloys

Manganese is generally found to be combined with other elements. It is the twelfth most abundant element and constitutes about 0.085% of the earth's crust [89]. Although its concentration in particular rocks was given much earlier [90–92], it is present in only one part per billion in seawater due to the tendency of manganese to oxidize and form insoluble nodules in the ocean [93, 94]. Manganese was recognized as a chemical element in 1774 by Scheele [89]. Mn is an essential trace element in most tissues of all living organisms [95]. Most of its usage is in steelmaking with a much lesser amount going into the production of batteries. It should be noted that Mn and Fe shared similar chemical characteristics [96].

Al–Mn alloys have important technological applications due to their high mechanical properties and also for their interesting and attractive magnetic properties [97–100]. Mn–Al alloys are attractive candidates for rare earth-free permanent magnet, with potential magnetic properties superior to the well-known alnicos and hard ferrites [101, 102]. The Mn atom is known to exhibit a high magnetic moment, though its value depended on the distance from the neighboring atoms. The latter give rise to different magnetic behaviors: ferromagnetic, antiferromagnetic, paramagnetic, or ferrimagnetic [103].

The τ -phase of MnAl is a well-known RE-free permanent magnetic material [97–99, 104, 105], due to its high maximum magnetic energy density product per unit mass, low cost, low density (5.3 g/cm^3), good machinability, high

specific strength and modulus of elasticity, and remarkable corrosion resistance [105–107].

Structural Properties

The binary Al–Mn system has attracted much attention because of the wide variety of equilibrium and metastable phases it contains: solid solutions, 9 intermetallic phases, quasicrystalline phases, and amorphous alloys [108]. Figure 3a shows the phase diagram of binary Al–Mn alloys. This system is of great importance for magnetic applications in the composition range of 50–60 at.%Al (~67–75 wt.%). In this range, there is a metastable, ferromagnetic τ -phase, which makes Mn–Al alloys a potential candidate for permanent magnet applications. First reported by Kono [97] and Koch et al. [98], τ -MnAl is the only ferromagnetic phase in the Mn–Al binary system. It has been reported that τ -MnAl formed only within a very narrow window of composition, with a maximum probability for the composition $\text{Mn}_{54}\text{Al}_{46}$. Hence, the τ -phase tends to decompose or transform into non-magnetic phases [109]. It has been reported that τ -MnAl coexisted with γ_2 and β phases, depending on the preparation technique and annealing temperature or time [109, 110]. It is well known that τ -phase can be obtained by quenching the high-temperature ϵ -phase followed by isothermal annealing from 673 to 973 K. Prolonged annealing resulted in its decomposition to the equilibrium γ_2 and β phases [111]. τ -MnAl phase is an ordered structure and displays the following properties: a Curie temperature close to 635 K,

a magnetic moment of $1.94 \mu\text{B}$, and a high uniaxial magnetocrystalline anisotropy value of $93 \times 10^4 \text{ J/m}^3$ which is quite unusual for RE-free permanent magnets [111–114].

Figure 3b (top) presents the crystal structure of τ -phase. The face-centered cell can also be described using a primitive tetragonal unit cell shown with dashed lines. The primitive lattice parameters are: $a = 2.77 \text{ \AA}$ and $c = 3.54 \text{ \AA}$, which are the axes of easy magnetization. The tetragonal cell itself can be considered as being a distorted cubic cell (Fig. 3b, bottom) [113, 115]. This ferromagnetic phase has body-centered tetragonal structure, in which the Mn atoms occupy the (0, 0, 0) sites and exchange ferromagnetically with each other, while the Al atoms and the Mn atoms in excess with the equiatomic composition take the (1/2, 1/2, 1/2) sites. Mn moments in these two sites exchange antiferromagnetically [116–119].

MA and MM τ -MnAl Intermetallic Alloys

The past few years have witnessed a rapid growth in the investigation and understanding of τ -MnAl intermetallic alloys prepared by high-energy ball milling. It has been mentioned that, in the equilibrium, the solid solubility of aluminum in α -Mn is 2 at.%; however, mechanical alloying markedly increased this value and induced important phase transitions [119]. The intermetallic phases and the transformations that can be attained in MA Al–Mn are not completely clear and depended on the milling conditions [100, 119, 120].

Some studies have not reported the formation of τ -MnAl intermetallic alloys. However, these studies have investigated the composition ranges of τ -MnAl phase. These works are summarized in Table 2.

The synthesis of τ -MnAl intermetallic alloys by MA has been successfully achieved by several researchers. Singh et al. [105] have obtained τ -MnAl phase in MA $\text{Mn}_{54}\text{Al}_{46}$

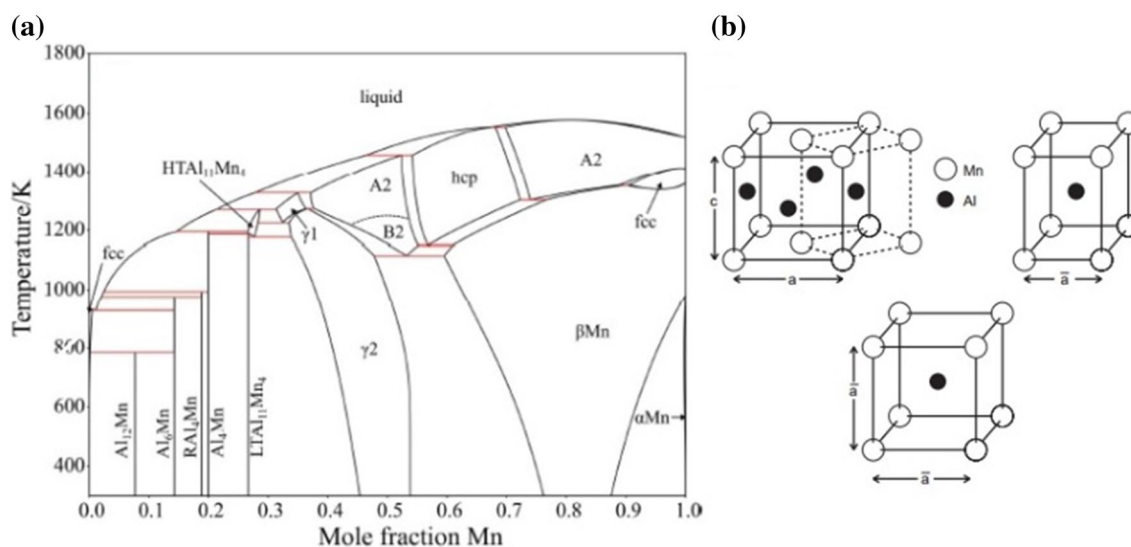


Fig. 3 (a) Calculated stable phase diagram of the Al–Mn system [115]. Reprinted from [115], with permission from Elsevier and (b) top: crystal structure of τ -MnAl. The dashed lines showed the

reduced tetragonal cell, and the tetragonal lattice parameter, bottom: idealized simple cubic structure of MnAl [113]. Reprinted from [113], with permission from Elsevier

Table 2 Mechanically alloyed mixtures of elemental Al and Mn powders

Alloy/composition	Mill	BPR	Atmosphere	Time, h	Type of investigation	References
$\text{Mn}_{42}\text{Al}_{58}$	SPEX 8000	11:1	N_2	50	Structural and magnetic properties	[100]
$\text{Mn}_{55}\text{Al}_{45}$	–	23:1	Ar	500	Structural and magnetic properties	[119]
$\text{Mn}_{56}\text{Al}_{44}$	Planetary ball mill	10:1	Toluene	25	Mechanical and magnetic properties of milled powders followed by spark plasma sintering	[121]
$\text{Mn}_{55}\text{Al}_{45}$	Planet ball milling machine QM-ISP	20:1	Ethanol	24	Relationship between temperature and phase formation Microwave absorbing properties	[122]
–	–	20:1	Hexane + Ar	26	Structural and magnetic properties	[123]

It should be noted that only the conditions of high-energy ball milling experiments are presented in the table

powders, by using three different materials processing routes: arc melting, mechanical alloying, and a combination of them. They have reported that the formation of τ -MnAl phase was always accompanied by other non-magnetic phases: β and γ . However, the relative fraction of these phases was found to be dependent on the materials processing route and consequently on the grain size of the parent phase. It was reported that the alloy prepared by MA showed the smallest grain size and the lowest fraction of the magnetic phase. The authors also reported that in addition to the magnetic τ -MnAl phase, the magnetic properties could be related to the density of structural defects induced by the processing route. MnAl flakes with different size were obtained using the surfactant-assisted ball milling method by Su et al. [124]. They have indicated that after annealing the textured flakes, high-purity τ -phase has been synthesized from milled powders. It has been reported that the magnetic properties depended on the fraction of the τ -phase and ball milling time. The main results of this study were: a coercivity of about 234.9 kA/m and a saturation magnetization close to 0.47 T. A high coercivity up to 5.3 kOe and a saturation magnetization of ~ 62 emu/g have been reported by Lu et al. [117]. These investigators have shown that the coercivity firstly increased and then decreased, leading to the formation of knee point coercivity, while the saturation magnetization decreased simultaneously. The authors have stated that the chemical disordering and internal strain of τ -MnAl were greatly enhanced with increasing milling time (Fig. 4).

Other research studies have investigated mechanically alloyed ternary systems with carbon addition. The first investigated in the late 1950s and early 1960s, and the discovery

that the addition of carbon to MnAl not only stabilized the τ -phase, but also allowed the processing of anisotropic permanent magnets with good machinability [125, 126] has attracted a great deal of attention [127–129], with focus on the effect of milling and annealing conditions [130]. A correlation between the coercivity and internal strain has been established for as-milled τ -phase $\text{Mn}_{51}\text{Al}_{46}\text{C}_3$ flakes obtained by surfactant-assisted ball milling (SABM) [131]. These researchers reported that the high coercivity up to 266.2 kA/m was accompanied by a relatively large residual strain, due to the domain wall pinning effect of the defects and the associated strained areas. Another study has been conducted by Jian et al. [102]. The investigation revealed the formation of flake-shaped powders 2 h of milling. They have found that magnetization decreased and coercivity increased continuously with milling time due to the defects introduced by the milling. It has been seen that the magnetization increased significantly because of the recovered crystal structure of τ -phase. The relationships between magnetic properties and milling time of $\text{Mn}_{53.3}\text{Al}_{45}\text{C}_{1.7}$ powders are illustrated in Fig. 5.

Obi et al. [130] have shown that carbon addition highly affected the structural and magnetic properties of MA $\text{Mn}_{0.53}\text{Al}_{0.47-x}\text{C}_x$ ($x=0-0.015$), upon annealing. They have mentioned that M_s and M_r decreased, while H_c increased with the increase in carbon concentration which was attributed to the formation of Mn_3AlC phases and the reduction in grain size, respectively. The investigators reported that the magnetic properties such as M_s and M_r strongly depended on the quantity of the ferromagnetic τ -MnAl phase, while H_c depended on the volume fraction of the Mn_3AlC phase.

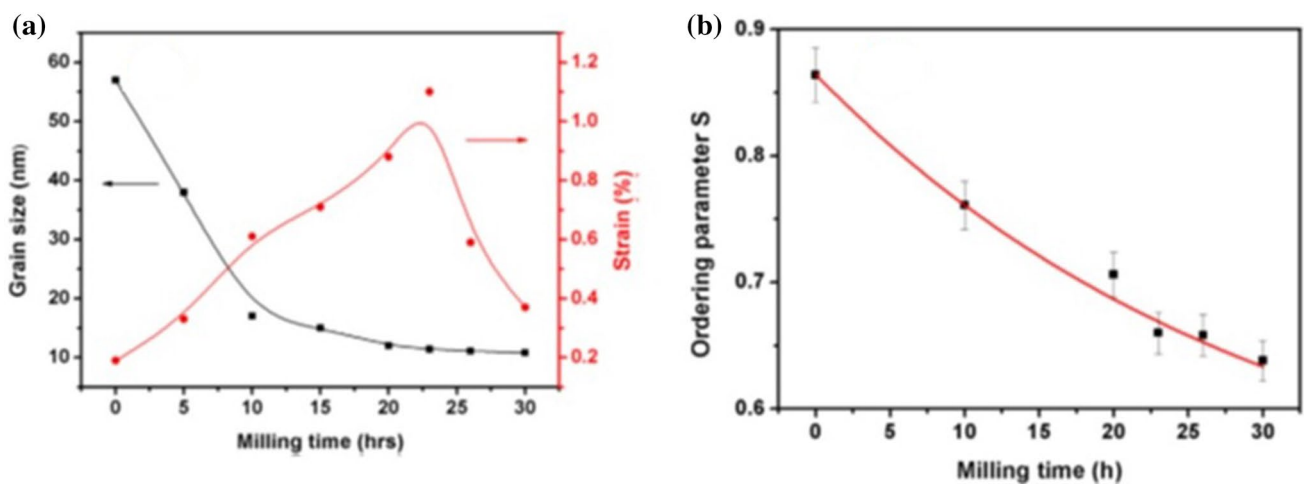


Fig. 4 (a) Dependence of grain size and internal strain on the MM time in τ -MnAl alloys and (b) relation between long-range order parameter S and mechanical milling time [117]. Reprinted from [117], with permission from Elsevier

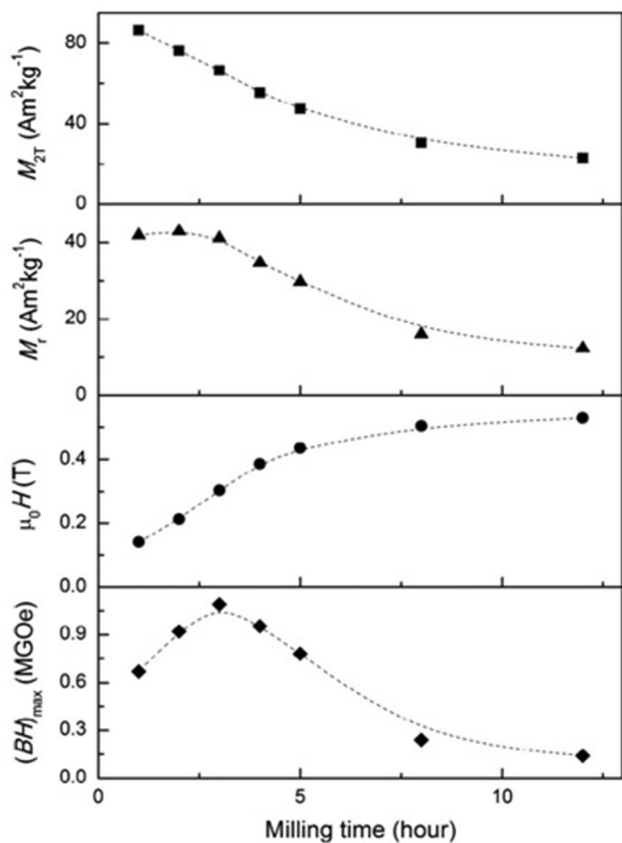


Fig. 5 Dependence of magnetic properties on the milling time of MM $\text{Mn}_{53.3}\text{Al}_{45}\text{C}_{1.7}$ powders [102]. Reprinted from [102], with permission from Elsevier

Ruthenium and B2-RuAl Intermetallic Alloys

Ruthenium is a very little chemical element. It is the 74th most abundant metal on earth. It was discovered in Kazan (Russian Federation) by Karl Karlovich Klaus in 1844 [132]. It has been reported that the first publications were printed in Russian journals which are difficult to get at present, but were published in Western Europe in 1845 [133–135] with a summary in English [133, 136]. Klaus called it ruthenium in honor of his native land (*Ruthenia*, Latin for Russia) [133]. Gottfried Wilhelm Osann identified what he thought was a new element in 1827 and named it ‘ruthenium,’ but his claim is generally discounted [133, 137, 138] though he still has some supporters [133, 139]. Ru is generally found in ores combined with other metals in the Ural Mountains and in America. Due to the remarkable characteristics of Ru, ruthenium-containing complexes are well suited for biological and pharmacological uses [123].

RuAl phase was first recorded in 1960 by Obrowski (Degussa Laboratories, Germany), who shortly described its structural properties [140]. Three years later, Obrowski investigated other alloys in Ru–Al system [141]. The work

that followed in the late 1970s by Wopershow and Raub [142] who have studied a wide range of properties of several binary intermetallic phases including RuAl [143]. An interesting overview on RuAl published by Wolff [144] gave a better description of structural properties of this intermetallic aluminide. Due to its elevated melting temperature (about 2323 K), high-temperature strength, oxidation and corrosion resistance, and good room-temperature toughness, B2-structured intermetallic compound RuAl has been considered as a good base material for elevated temperature utilizations in exceedingly aggressive environments, especially as a candidate material for spark plug electrode [144–146]. The B2-RuAl intermetallic compound displays strong thermodynamic stability along with good oxidation resistance at high temperatures due to the growth of a protective $\alpha\text{-Al}_2\text{O}_3$ scale [147–149]. The most important advantage of this compound over other aluminides arises on the coefficient of thermal expansion (CTE), which is substantially lower than that of B2 Al-X (X = Fe, Ni, Co) and nearer to that of the $\alpha\text{-Al}_2\text{O}_3$ [150]. Intermetallics based on RuAl have shown relatively good oxidation resistance up to 900 °C, [151–153]. RuAl has shown strong resistance to attack from aqueous solution such as nitric acid, aqua regia, HF, sulfuric acid, FeCl_3 , NaOH, and HCl, but the only solution reported to attack RuAl is NaOCl [144, 154]. RuAl alloys have received much attention in last years because of their high-room-temperature ductility, which was attributed to the existence of five independent slip systems in the RuAl phase [155].

Structural Properties

B2-RuAl with CsCl crystal structure type [88] is formed in the composition ranges from 49.9 to 53.4 at.% Al [149, 156]. As shown in the existing Ru–Al phase diagram (Fig. 6a), the ordered B2 structure is not stable for wide deviations from stoichiometry and the existence limits of the RuAl phase are still not exactly determined [157–161]. Thermodynamic information on the formation of RuAl was deduced both experimentally and theoretically. Calorimetric analysis at (1473 ± 2) K revealed a high negative value of enthalpy of the formation of RuAl ($\Delta H_f^\circ = -124.1 \pm 3.3$) kJ/mol, indicating a very huge chemical interaction between Ru and Al [110, 162]. The lattice parameter of RuAl has been defined by both experimental works and theoretical calculations. Villars and Clavert have found a value of 0.303 nm; however, Fleischer reported a value close to (0.29916 ± 0.00008) nm [163, 164].

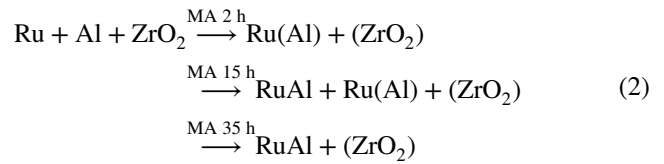
MA B2-RuAl Intermetallic Alloys

RuAl has become a candidate for future structural or coating materials for high-temperature applications. However, this is impeded by problems in the production of single-phase

RuAl, by conventional melting methods [166]. Ingot metallurgy is difficult because of the elevated melting point of RuAl and the large difference in melting temperatures between Al and Ru elements ($\Delta T_m = 1674$ K) [145, 166]. This alloy can be manufactured by powder processing techniques, especially by reactive powder processing [161, 167], or reactive hot isostatic processing [151, 161]. Many interesting papers have been published dealing with the structural characterization of the intermixing between Ru and Al elements (see Table 3).

Some research works have investigated mechanically alloyed Ru–Al–X ternary systems. Liu et al. [173] have obtained B2-structured single-phase (Ru, Ni)Al by an abrupt reaction during MA of the elemental powders of Ru, Al and Ni. Complete solubility between pseudo-binary RuAl–NiAl was achieved in a range between 10 and 25 at.% Ni, while the range for Al remained at 50 at.%. The research clearly showed that Ni was found to improve the sluggish reactivity

of Ru by promoting the abrupt reaction. Liu and Mucklich [146] reported the synthesis of RuAl/ZrO₂ nanocomposite, starting from stoichiometric Ru and Al powders mixture with 10 and 20 at.% of ZrO₂ particle additions. The overall structural evolutions during MA can be summarized as follows:



The investigators have reported that ZrO₂ was distributed uniformly in RuAl matrix after annealing, and the RuAl/ZrO₂ nanocomposite exhibited a strong thermal stability at high temperatures (Fig. 7).

Fig. 6 (a) Partial Al–Ru phase diagram [165]. Reprinted from [165], with permission from Elsevier and (b) B2 crystal structure of RuAl

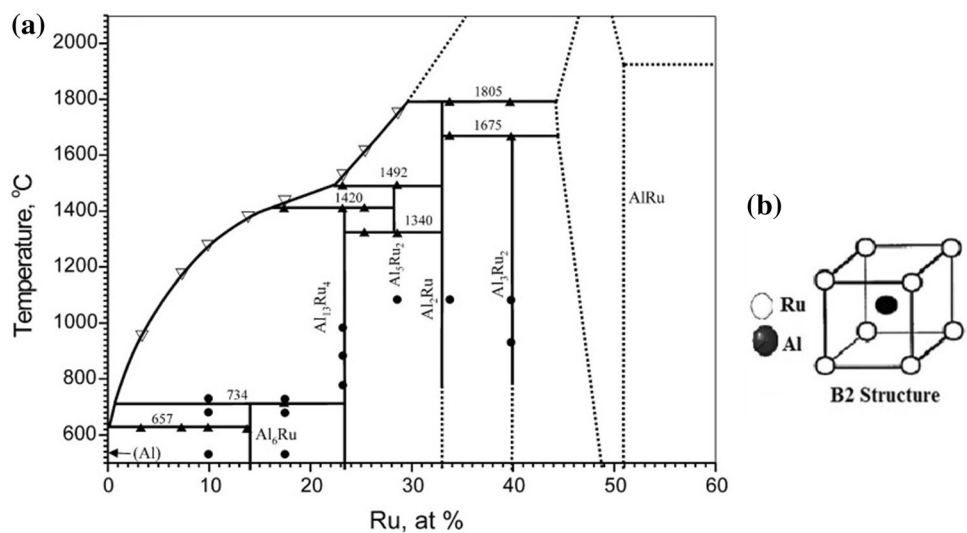


Table 3 Mechanically alloyed mixtures of elemental Al and Ru powders

Alloy/composition	Mill	BPR	Atmosphere	Time, h	Main results	References
Ru ₅₀ Al ₅₀	Turbula mixer	–	–	6	MA Ru–Al samples heated at 0.25 K/s, led to the formation of RuAl MA RuAl samples heated at 0.08 K/s, led to the formation of RuAl ₂ and RuAl	[168]
Ru ₅₀ Al ₅₀	Spex 8000 mill	10:1	Ar	50	Two stages of MA reaction before single RuAl formation are reported Heat treatment of RuAl exhibited reordering, strain relaxation and grain growth 15 at.% Fe existed in the form of solid solution in RuAl as substitutional element and as segregation in grain boundaries.	[169, 170]
Ru ₄₇ Al ₅₃	Attrition mill	10:1	Stearic acid + Ar	50	RuAl phase was formed after 7 h of milling Density close to 97% of the theoretical value was reported after cold compaction and sintering of milled powder	[171, 172]

It should be noted that only the conditions of high-energy ball milling experiments are presented in the table

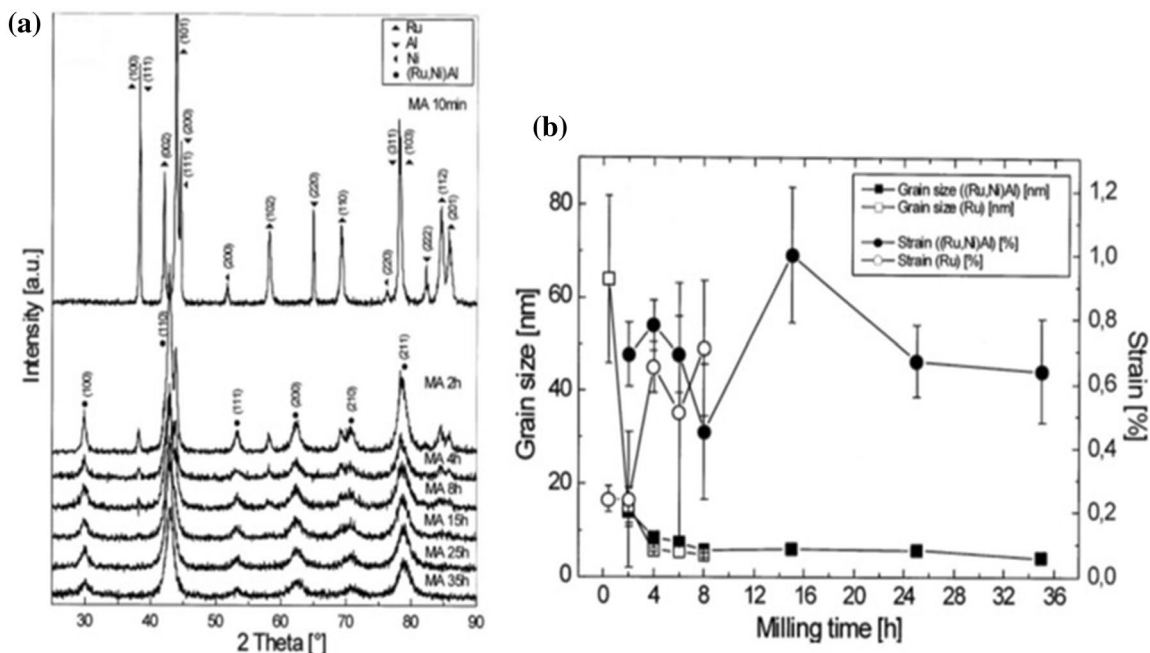


Fig. 7 (a) XRD patterns and (b) grain size and lattice strain of MA $\text{Ru}_{40}\text{Al}_{50}\text{Ni}_{10}$ powders as a function of milling time [173]. Reprinted from [173], with permission from Elsevier

MM B2-RuAl Intermetallics

Research on MM B2-RuAl intermetallics is quite limited. Hellstern et al. [174] studied structural and thermodynamic modifications occurring during ball milling AlRu intermetallics. They have found that the milling caused a decrease in the long-range order (LRO) parameter from 1.0 to 0.7. They have indicated that ball milling of AlRu compound did not lead to the formation of an amorphous alloy, but showed the development of a fine nanocrystalline structure with an average grain size close to 7 nm, accompanied with a lattice strain of about 3%.

Concluding Remarks

Over the past decade, the need of intermetallic alloys for structural, mechanical, and magnetic applications has intensively increased. These lightweight materials are mainly utilized in the aerospace and automobile industries. Numerous processing routes have been developed to produce these materials or to improve the existing structural and mechanical characteristics. Among these techniques is the mechanical alloying or high-energy ball milling.

In this article, the current state of knowledge on MA/MM of binary γ -TiAl, τ -MnAl, and B2-RuAl intermetallic alloys has been presented. The conclusions of the paper may be drawn as follows:

- The reported studies perfectly illustrated the effectiveness of high-energy ball milling process in obtaining nanostructured intermetallic alloys.
- High-energy ball milling process has been used jointly with other techniques in order to perform nanostructured intermetallic alloys.
- It was reported that even after having the mechanically alloyed state, a suitable heat treatment was necessary to obtain the perfect crystalline structure.
- The structural and magnetic properties of powders so obtained are different, even for the same composition, which clearly showed that the milling parameters played a vital role in achieving the desired structure/property.
- It was demonstrated that the structural imperfections such as disordering and defects played the most important role in the changes in the magnetic properties of milled intermetallic alloys.

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