Mechanical Alloys in The Al-rich Part of the Al-Ti Binary System

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Abstract. Aluminum is commonly used as fuel additive for propellants, incendiaries, and explosives. The main limitation to its use lies in comparatively slow ignition and oxidation/combustion kinetics. Performance can be significantly improved if pure aluminum is substituted by thermodynamically less stable alloys. In this context, mechanical alloys in the aluminum-rich section of the Al-Ti binary system were synthesized and evaluated. Powders with compositions in the range Al₀.₉₅Ti₀.₀₅ to Al₀.₇₅Ti₀.₂₅ were ball-milled under argon in a shaker mill. Alloying products were characterized by XRD, SEM/EDX, and DSC. In as-milled alloys, only the fcc Al phase was observed. Crystallite sizes decreased with increasing Ti concentration. Compositional inhomogeneities resolvable by SEM were only present in alloys with 25 at-% Ti. On controlled heating, a number of exothermic transitions were observed below the onset of eutectic melting. In addition to recrystallized fcc Al, two different tetragonal modifications of Al₃Ti were distinguished by XRD in samples recovered from below the eutectic. The high-temperature stable modification of Al₃Ti was found in alloys with 5% Ti, its low-temperature form in alloys with 20% Ti and higher; the two modifications coexisted in intermediate alloy compositions. An additional exothermic transition above the eutectic, attributed to Al₃ Ti precipitation, was observed. At still higher temperatures (900 °C), an irreversible endothermic transition observed for alloys with 20 at-% or less of Ti, suggests delayed melting of Al. The mechanical alloys were found to be metastable with respect to the reference elements, a maximum energetic destabilization was observed for 10-15 at-% Ti.

Introduction

Metals with high combustion enthalpies are of interest as high energy density materials. Aluminum in particular and aluminum-based alloys have been investigated as additives in various fuel formulations for propellants, explosives, incendiaries or pyrotechnics [1-3]. Practical applications are limited, however, since chiefly kinetic obstacles such as long ignition delays and slow burning rates prevent the theoretical combustion enthalpies from being fully exploited. Based on recent research [4] linking phase transformations to macroscopic events during combustion of metal particles, interest in metastable intermetallic materials developed. The present paper discusses mechanical alloys in the Al-Ti binary system with Ti concentrations of less than 25 at-%. Ti is of particular interest as a component to increase the density of metallic fuel additives, and thus the specific impulse of the respective propellants. Recent observations suggest that ignition and combustion of aerosols of Al-Ti mechanical alloys are enhanced compared to equilibrium alloys or blends of elemental powders [5].

A detailed characterization of phase relations and the degree of metastability in metastable Al-Ti alloys is needed to attempt performance optimization of these materials as advanced energetics. This information is also necessary to model processes of combustion of metallic fuel particles, specifically to quantitatively predict ignition behavior as a function of heating rate and of the particles’ environment [6]. The purpose of the present research is to characterize mechanical alloys in the system Al-Ti with the specific goal to optimize materials for combustion applications and to address issues arising for large-scale production.

A number of experimental and theoretical studies on mechanical alloying of Al₃Ti have been published. Less information is available about Al-Al₃Ti composites with compositions close to pure
Equilibrium phases in this region of the system include the \( \alpha \)-Al phase with fcc structure and low- and high-temperature modifications of Al\(_3\)Ti (D0\(_{23}\) below 735 °C, and D0\(_{22}\) above) [7]. In addition, a metastable phase with L1\(_2\) structure as been reported for Al\(_3\)Ti [7]. References disagree however about whether the D0\(_{23}\) phase is a stable phase in the system. Lattice dynamic calculations give the energy differences indicating relative stability of the Al\(_3\)Ti phases as D0\(_{22}\) < D0\(_{23}\) < L1\(_2\), showing therefore the D0\(_{22}\) phase as the most stable even at low temperatures [8]. Experimentally, it was found that the D0\(_{22}\) phase, when mechanically milled at ambient conditions deteriorates, and transforms first to the D0\(_{23}\) phase and eventually to the L1\(_2\) phase, supporting the sequence of relative stability [9]. The same study concluded that the D0\(_{23}\) and L1\(_2\) structures form via the formation of antiphase boundaries, causing a loss of long range order, and that the energetic differences are compensated by the arising configurational entropy in the increasingly disordered phases.

Mechanical alloying of Al and Ti powders with Al\(_3\)Ti bulk composition leads to the formation of a fcc phase with lattice dimensions close to the L1\(_2\) structure [10]. Re-equilibration of this material was shown by thermal analysis to result in the formation of the L1\(_2\) (at 365 °C), D0\(_{23}\) (at 454 °C) and D0\(_{22}\) (at 637 °C) phases [10]. A preliminary study investigating mechanical alloys in the Al-Al\(_3\)Ti compositional range and limited to temperatures below 600 °C, essentially confirmed this transformation sequence for all compositions [11].

In order to relate the re-equilibration processes in mechanical alloys to ignition and combustion behavior, their total energetic destabilization must be characterized, and the relaxation process must be described until equilibrium is achieved. Dependence of the equilibration processes on bulk composition need to be known in order to design mechanically alloyed powders for specific energetic requirements.

**Experimental**

The mechanical alloys were prepared in a SPEX 8000 shaker mill. Starting materials were elemental powders of Al (Alfa Aesar, 99.8 %, –40+325 mesh) and Ti (Alfa Aesar, 99 %, –325 mesh). Optimum milling parameters required to achieve a stationary state in a minimum amount of time were determined in a series of separate experiments before actual sample preparation was begun. For synthesis, 5 g of initially unmixed metal powder were milled in zirconia vials under Ar atmosphere with 2 wt-% of stearic acid (Fluka, 99 %) added as PCA. Zirconia balls of 10 mm diameter and a total mass of 50 g were used as milling medium, giving a ball-to-powder weight ratio (BPR) of 10. Samples were milled for a total time of 15 hours each, the time after which the mechanical alloy with Al\(_{0.75}\)Ti\(_{0.25}\) composition showed no further structural or compositional changes. The sample temperature rose up to 50-60 °C during milling. Moderate sample caking posed a problem for milling effectiveness; milling for extended periods also limits the useful lifetime of the mill. Therefore, milling was carried out in intervals of 180 min, after which the mill was allowed to cool to room temperature, and caked samples, if present, were manually broken apart in a glove box under protective Ar atmosphere.

Morphology and compositional homogeneity of the mechanical alloys were examined on a LEO 1530 Field Emission SEM, equipped with an energy dispersive x-ray spectrometer that allows standardless compositional analysis with a maximum spatial resolution of approximately 0.1 µm. Structure and phase makeup was determined for each mechanical alloy by x-ray powder diffraction (XRD) on a Phillips X’pert MRD diffractometer operated at 45 kV and 40 mA, using Cu-K\(\alpha\) radiation (\(\lambda = 1.5438 \text{ Å}\)).

Temperature dependent structural transformations were observed by differential scanning calorimetry (DSC) using a Netzsch STA409-PC. Samples were contained in alumina sample pans. The furnace of the STA409-PC was evacuated to approximately 0.3 bar and back-filled with Ar (Matheson, ultrahigh purity) three times before each measurement. During measurements, the furnace was continuously flushed with Ar at approximately 10 ml/min. DSC traces were recorded at a heating
rate of 15 K/min. Low-temperature scans (< 600 °C) were baseline corrected using a repeat heating of the equilibrated sample.

The back-transformation of the mechanical alloys to thermodynamically stable phase assemblages occurred over a wide temperature range. To relate events observed by DSC to structural transitions, DSC runs were interrupted at intermediate temperatures, and XRD patterns of these partially relaxed mechanical alloys were collected. The effective quench rates achieved in these experiments were relatively low – about 20-30 K/min. No strict temperature control at the end of a heating cycle in the used DSC apparatus is possible, therefore the targeted temperatures were likely to be overshot by as much as 10-20 °C. Nevertheless, the samples thus recovered prove instructive identifying intermediate transition products.

Results

SEM analysis of polished sections of the as-milled mechanical alloys showed them to be chemically homogeneous within the resolution limit of the instrument, ~10 nm. Only the bulk composition could be measured by EDX. XRD patterns showed only peaks consistent with an fcc phase with lattice dimensions similar to α-Al. Diffraction peaks became wider and weaker with increasing Ti concentration. The apparent lattice parameter vs. Ti concentration is shown in Fig. 1. The lattice parameter gradually decreases from the value for pure α-Al (4.049 Å [12]) with increasing Ti concentration up to 15 at-% Ti. The mechanical alloys with 20 and 25 at-% Ti deviate more strongly from pure α-Al with a lattice parameter closer to that of the L1_2 phase of Al_3Ti (3.972 Å [7]).

Figure 2 shows the DSC traces of all mechanical alloys up to a maximum temperature of 1500 °C. A number of exothermic peaks are observed below 600 °C. Eutectic melting of Al is observed at 660 °C except for Al_{0.80}Ti_{0.20} and Al_{0.75}Ti_{0.25}. At high temperatures (1200-1400 °C), endothermic peaks correspond to the liquidus of each respective bulk composition. An exothermic peak near 750 °C is present in Al_{0.95}Ti_{0.15} and decreases in intensity with increasing Ti concentration. A further endothermic peak near 900 °C is observed for all compositions except Al_{0.75}Ti_{0.25}.

To elucidate the nature of the endothermic peak near 900 °C, the Al_{0.85}Ti_{0.15} mechanical alloy was heated repeatedly between 600 °C and 950 °C at 15 K/min. Between heatings, the sample was cooled at the fastest rate possible (~ 40-50 K/min). The result is shown in Fig. 3. It is observed that while the enthalpy of the eutectic melting peak increases on each subsequent heating cy-

![Figure 1: Lattice parameter of the fcc phase observed in as-milled mechanical alloys.](image1)

![Figure 2: DSC traces of Al-Ti mechanical alloys (15 K/min; T_{max}=1500 °C).](image2)

![Figure 3: Repeated heating at 15 K/min of the same sample of Al_{0.85}Ti_{0.15} mechanical alloy.](image3)
dle, the enthalpy of the second endothermic peak, as well as its peak temperature, decrease. A sample held at 950 °C for 5 hours after initial heating at 15 K/min showed no endothermic peak at near 900 °C on repeated heating.

The temperatures of the observed transitions are shown in Fig. 4. The subsolidus peaks are broad and overlap strongly. The temperatures of the eutectic melting peak and of the endothermic peak near 900 °C decrease slightly with increasing Ti concentration, while the temperature of the exothermic peak near 750 °C increases. Temperatures of the liquidus peaks are not shown in Fig. 4, as they were found to conform to the equilibrium phase diagram [13].

XRD patterns were collected from samples recovered from intermediate temperatures, determined for each composition according to the peak temperatures shown in Fig. 4. The maximum temperatures from which powder samples could be recovered was limited to 900-1000 °C by increasing melt formation. The set of patterns for Al$_{0.85}$Ti$_{0.15}$ mechanical alloy is shown in Fig. 5. The fresh mechanical alloy only shows peaks corresponding to an fcc phase. At 360 °C, in addition to peaks of α-Al, diffraction peaks consistent with the L1$_2$ phase of Al$_3$Ti were observed. At 600 °C, the peaks of α-Al are sharper. The L1$_2$ phase has disappeared and the D0$_{22}$ and D0$_{23}$ phases are observed instead. At 850 and 920 °C, only peaks of the D0$_{22}$ phase are observed in addition to α-Al. The only observable difference between 850 and 920 °C is an increase in intensity of α-Al peaks compared to the D0$_{22}$ peaks. Recovery temperatures and observed phases for all compositions are listed in Table 1. The D0$_{22}$ phase is observed for all compositions at the respective highest temperatures from which powders were recovered. The temperature range over which the D0$_{23}$ phase is observed increases with increasing Ti concentration. While The D0$_{23}$ phase is not observed for Al$_{0.95}$Ti$_{0.05}$, it is observed to coexist with D0$_{22}$ at 600 °C for 10, 15, and 20 at-% Ti. It is the only phase detected at 600 °C for the Al$_3$Ti composition, and it persists to at least 800 °C and 850 °C for 20 and 25 at-% Ti, respectively.
X-ray diffraction peaks of the as-milled mechanical alloys become broader and weaker with increasing bulk Ti concentration. In addition, peak positions shift to higher values. From the deviation of the lattice parameter from pure $\alpha$-Al, the Ti concentration in the $fcc$ phase is estimated to be 1.6 at-% (2.8 w-%) at 15 at-% bulk Ti concentration using a lattice parameter vs. composition relation obtained from rapidly solidified Al-Ti alloys [14]. The remaining Ti is contained in x-ray amorphous phases, or in extended grain boundaries. The maximum observable solubility of any solute in the supersaturated $fcc$ phase depends on the mechanical alloying process parameters [15]. The present result is in agreement with 2.46 wt-% Ti previously found for an Al-20 w-% Ti mechanical alloy [16]. A different maximum solubility of Ti in the $fcc$ phase has been reported as 6.7 wt-% Ti [10]. That result corresponded to different milling conditions, and was obtained from the mechanical alloying of an elemental blend with Al$_3$Ti composition for 10 hours. The assignment of the exothermic transitions observed for Al$_{0.75}$Ti$_{0.25}$ to the formation of the L1$_2$, D0$_{23}$, and D0$_{22}$ phases, respectively, agrees with the interpretation suggested in Ref. [10]. Using the pure elements as reference state, the only exothermic transitions expected are
due to the formation of the equilibrium phase of Al₃Ti. Considering the observed phase transformations of Al₃Ti (Table 1, Fig. 5), it appears reasonable to compare the integral exothermic transitions to the enthalpy calculated for Al₃Ti formation from the reference elements (ΔfHₐl₃Ti = 47 kJ/mol [17]). Figure 6A shows a summary of the observed exothermic enthalpies. The sum of all exothermic transitions exceeds the exothermic heat effect calculated for Al₃Ti formation from the elements up to a Ti concentration of 15 at-%. This suggests that the mechanical alloys are energetically destabilized with respect to the component elements. At 20 and 25 at-% Ti the sum of exothermic enthalpies drops, consistent with the observed drop in lattice parameter (Fig. 1) and the assumption that the L₁₂ phase forms at least partially during milling.

Under equilibrium conditions, the only endothermic transitions expected are eutectic melting and melting at the liquidus. An endothermic transition at this temperature has been reported previously in an Al₀.₇₅Ti₀.₂₅ mechanical alloy, although no interpretation has been offered [10]. Enthalpies of the endothermic transitions are shown in Fig. 6B. Due to the wide temperature range over which melting along the liquidus occurs, the DSC features are difficult to integrate reliably and have therefore been omitted from Fig. 6B. The decrease of the enthalpy of the endothermic transition near 900 °C on repeated heating (see Fig. 3), accompanied by the increased eutectic melting peak suggests that both transitions are caused by Al melting. This is further supported by the relative increase in the intensities of α-Al peaks in the diffraction pattern of the sample recovered from 920 °C (Fig. 5). Figure 6B shows that for all compositions, the observed enthalpy of eutectic melting is less than that estimated for the system in equilibrium (ΔmHₐl = 10.79 kJ/mol [18]). This is a further indication that only a fraction of the Al component melts at this temperature. Part of the nominally free Al in the system must be stabilized, possibly by Ti supersaturation or morphological effects.

Conclusions

A series of mechanical alloys in the Al-rich part of the Al-Ti binary system was produced with identical process parameters. The mechanical alloys are chemically homogeneous on a scale of ~10 nm. The maximum Ti concentration in α-Al under these milling conditions was found to be 1.6 at-%. The as-milled alloys are increasingly metastable with respect to the component elements; a maximum degree of metastability is observed at 15 at-% Ti. The L₁₂ phase of Al₃Ti, energetically less stable than the D₀₂₃ or D₀₂₂ phases, is likely to be present in mechanical alloys with 20 and 25 at-% Ti based on the observed XRD patterns and trends in enthalpies of exothermic transitions. No such Al₃Ti precursor phases are present in mechanical alloys with compositions up to 15 at-%. Endothermic transitions absent from the equilibrium system were systematically observed near 900 °C. These were interpreted as delayed melting of superheated Al component.

In the context of energetic materials, the observed metastability is expected to result in a maximum increase in combustion rates and decrease in ignition temperatures for Al-Ti mechanical alloys with Ti concentrations in the range of 10-15 at-%.
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