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# Mechanically activated effect of friction stir processing in Al-Ti reaction

# Q. Zhang, B.L. Xiao, Z.Y. Ma\*

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

#### HIGHLIGHTS

- ► Al-Ti reaction kinetics during friction stir processing (FSP) was studied.
- ▶ The Al-Ti reaction during FSP was interfacial-reaction controlled.
- ▶ The reaction rate constant during FSP was much higher than that during annealing.
- ► The decrease in activation energy caused by FSP increased the rate constant.
- ▶ The effective temperature can show the mechanically activated effect of FSP.

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#### 1. Introduction

# Mechanical activation has been examined over the past few years as a method of making unusual or metastable materials such as amorphous alloys, superconducting alloys, or intermetallic compounds [1–3]. High energy milling (HEM) is the most common method of mechanical activation. It is thought that the repeated cold welding and fracturing of powder particles take place during ball–powder–ball and ball–powder–container collisions. Atom activation accompanied by enhanced diffusion would significantly enhance the reaction during HEM or subsequent thermal exposure [4].

Welham [5] reported that the onset temperature of an  $Al-TiO_2$  reaction decreased from 1050 to 560 °C after 10 h milling and attributed this decrease to the reduction in crystallite size and enhanced diffusion. Lü and Lai [6] suggested that the decrease in activation energy played an important role during HEM and was equivalent to an increase in the reactive temperature. Xu et al. [7]

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# ABSTRACT

The kinetics of the Al–Ti reaction during isothermal annealing and friction stir processing (FSP) was studied. The Al–Ti reaction was diffusion controlled during annealing at 525–550 °C and interfacial-reaction controlled at 575–650 °C, whereas the reaction during FSP with tool rotation rates of 1000 and 2000 rpm was interfacial-reaction controlled. The reaction rate constant *k* during FSP is substantially enhanced compared with that during annealing. This is attributed to the decrease in activation energy caused by severe deformation during FSP. The effective temperature was proposed to show the contribution of the mechanically activated effect of FSP, and was calculated to be 710 and 716 °C for FSP with rotation rates of 1000 and 2000 rpm.

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studied the phase transformation during HEM of Fe and Cu powder mixtures using the effective temperature ( $T_{\rm eff}$ ) model, which was originally proposed for radiation-enhanced diffusion [8], and suggested that the  $T_{\rm eff}$  for crystalline phases during milling can be much higher than their melting points, causing the formation of highly supersaturated solution in immiscible alloy systems.

The high  $T_{\text{eff}}$  during HEM is caused by deformation-induced diffusion, which can take place even at the cryogenic temperature where the thermal diffusion is almost frozen [9]. Decreasing the intensity of ball milling, which is equivalent to decreasing the  $T_{\text{eff}}$ , would cause the decomposition of the supersaturated solution [7].

Friction stir processing (FSP), originally developed as a solidstate processing technique for microstructural modification of metallic materials [10], has found several applications in the fabrication and synthesis of intermetallic compounds [11] and metal matrix composites [12–14]. During FSP, the material in the processed zone undergoes intense plastic deformation, mixing, and thermal exposure, inducing the in situ reaction in several seconds. To date, FSP studies in material synthesis have mainly focused on the relationship between FSP parameters and microstructures or mechanical properties, and researchers have usually attributed the rapid reaction during FSP to enhanced solid state diffusion and





<sup>\*</sup> Corresponding author. Tel./fax: +86 24 83978908. *E-mail address:* zyma@imr.ac.cn (Z.Y. Ma).

thermal exposure [12–14]. Little quantitative study of the reaction during FSP has been reported. The difficulty of distinguishing the contributions of deformation and heat to the reaction makes this problem more intractable.

In this work, the Al–Ti reaction during isothermal annealing at different temperatures and multiple-pass FSP at different rotation rates was studied. The aim is (1) to deduce a kinetic equation to describe the Al–Ti reaction during annealing and FSP, (2) to compare the Al–Ti reaction rate during annealing and FSP quantitatively, and (3) to elucidate the contribution of plastic deformation of FSP to the Al–Ti reaction.

# 2. Experimental procedure

The starting materials used in the present study were Al powder (99.9% purity, 13  $\mu$ m) and Ti powder (99% purity, 45  $\mu$ m). The Al and Ti powders with a nominal composition of Al–10%Ti (atom percent) were mixed in a bi-axis rotary mixer homogeneously and then cold compacted into billets. The cold compacted billets were hot pressed at 500 °C in a vacuum furnace. In order to improve the billet strength for easier handling in the subsequent FSP, the hot pressed billets were forged into pancakes at 480 °C.

Multiple-pass FSP with 100% overlapping was conducted on the forged billets at a traverse speed of 0.42 mm s<sup>-1</sup>. The tool rotation rates were 1000 and 2000 rpm, respectively. The schematic illustration of FSP is shown in Fig. 1. Multiple-FSP passes were run along the same line with the same processing direction. The plates were cooled to room temperature in air between successive passes. A steel tool with a concave shoulder 20 mm in diameter, a threaded conical pin 8 mm in root diameter, 5.5 mm in tip diameter, and 5.8 mm in length was used for FSP. Annealing experiments were carried out at 525, 550, 575, 600, 625 and 650 °C with the time varying from 180 to 86,400 s.

The microstructures of annealed and FSP samples were examined by scanning electron microscopy (SEM, Quanta 600) using backscattered electron imaging (BEI) pattern. The FSP samples were cut transverse to the FSP direction. The volume fractions of unreacted Ti particles in various samples were analyzed by the image analysis software (Image-Pro Plus 6.0) from at least 5 SEM images. 4-pass FSP sample with tool rotation rate of 2000 rpm was examined by transmission electron microscopy (TEM TECNAI20). Thin foil for TEM was prepared by the ion-milling technique.

# 3. Results and discussion

Fig. 2 shows SEM/BEI images of forged sample and annealed samples at 550 °C for different times. The Al–Ti reaction almost did



Fig. 1. Schematic of friction stir processing (FSP).

not take place in the forged sample (Fig. 2(a)), confirming the findings of our previous study [13]. After annealing at 550 °C for 10,800 s, the Al–Ti reaction took place at the interface of Al and Ti particles (white arrows in Fig. 2(b)). The reaction layers were thickened by the increase in annealing time (Fig. 2(c)-(e)). The other annealed samples at different temperatures show the similar characteristics with that annealed at 550 °C.

Fig. 3 shows SEM/BEI images of FSP samples with tool rotation rate of 1000 rpm. In the one-pass FSP sample, the Ti particles were severely deformed and some fine Ti particles were observed (Fig. 3(a)). With the increase of FSP pass, the size and volume fraction of Ti particles decreased (Fig. 3(b)-(d)). The evolution of Ti particles in the FSP samples with tool rotation rate of 2000 rpm is similar with that processed at tool rotation rate of 1000 rpm (Fig. 4).

The variation in the volume fractions of Ti particles with reaction time for various samples is summarized in Fig. 5. For the annealed samples, the annealing time is referred to as the reaction time. The reaction time for the FSP samples is considered to be the time during which the materials are affected by the rotating pin during FSP and is calculated based on the following formula [15]:

$$t = N(r/v) \tag{1}$$

where *t* is the reaction time of FSP, *r* and *v* are the root diameter of the pin and the traverse speed, and *N* is the number of FSP passes. As shown in Fig. 5, the volume fraction of Ti particles in the annealed and FSP samples decreased as the reaction time increased. Furthermore, increasing the tool rotation rate from 1000 to 2000 rpm caused the volume fraction of Ti particles to decrease slightly. For example, the volume fraction of Ti particles in the 4-pass FSP samples was determined to be 5.1% and 4.0%, respectively, for 1000 rpm and 2000 rpm.

Our previous study [13] indicated that the decrease in the volume fraction of Ti particles was due to the Al–Ti reaction during annealing and FSP, and Al<sub>3</sub>Ti is the only product of the Al–Ti reaction. Fig. 6(a) shows the morphology of Al<sub>3</sub>Ti in the FSP sample. The Al–Ti reaction formula during annealing and FSP is as follows:

$$3Al + Ti \rightarrow Al_3Ti$$
 (2)

Based on Eq. (2), the volume fractions of Al<sub>3</sub>Ti in various samples are calculated and summarized in Fig. 5.

The variation in the volume fraction of Al<sub>3</sub>Ti with reaction time can be fitted using an empirical formula:

$$V_{\rm Al_3Ti} = kt^n \tag{3}$$

where *k* is the reaction rate constant, *t* is the reaction time, and *n* is the kinetic exponent. The values of *k* and *n* for the annealed and FSP samples are listed in Table 1. At 525 and 550 °C, the kinetic exponent *n* is close to 0.5, indicating that the reaction is controlled by Al–Ti interdiffusion [16]. However, the kinetic exponent *n* at 575–650 °C is much larger than 0.5, indicating that the reaction is controlled by the interface reaction [17,18]. Similar results were observed by Xu et al. [18] in multi-laminated Ti/Al diffusion couples.

The Al–Ti reaction during annealing consists of two steps: (a) interdiffusion between Al and Ti particles, and (b) nucleation of Al<sub>3</sub>Ti particles at the Al/Ti interface [18]. The process of Al–Ti interdiffusion is still controversial. Some investigators suggested that Al is the only diffusing species below the melting point of Al (660 °C), however, the results of Xu et al. [18] and Nonaka et al. [19] indicated that both Al and Ti are diffusing species in Ti/Al diffusion couples at temperatures of 600–650 °C and lattice diffusion was dominant at this temperature range. Nevertheless, at lower temperatures, such as 525 and 550 °C, the diffusivity is low and the



Fig. 2. SEM/BEI images of forged and annealed samples: (a) forged, (b)-(e) annealed at 550 °C for 10,800, 18,000, 25,200, and 32,400 s, respectively.

interdiffusion between Al and Ti particles would be the controlling factor of Al—Ti reaction [18]. As the annealing temperature increases, Al—Ti interdiffusion is significantly enhanced, and a transition to the interface-reaction-controlled mechanism would occur. The kinetic exponent *n* of the FSP samples is close to that of the samples annealed at temperatures above 550 °C, suggesting that the main controlling factor of the reaction during these processes is similar, that is the interface-reaction controlled. This can be attributed to the following factors.

Firstly, although the peak temperature in the regions adjacent to the stir zone (SZ) during FSP was measured to be in the range of 450-500 °C [20,21], the actual temperature in the SZ is still unknown and the temperature distribution is considered nonhomogeneous [21]. Nevertheless, the maximum temperature in the SZ during FSP should be higher than the temperature recorded by thermocouples [22], and may be above 550 °C in the present study, considering that the Al–Ti reaction is exothermic. Secondly, during FSP, the rotating pin induced severe plastic deformation in the SZ with a strain rate of  $10^0-10^2$  s<sup>-1</sup> and a strain of up to ~40 [23], resulting in the breakup of the oxide film surrounding Al. In

this case, atomically clean surfaces of Al and Ti were brought into very close contact, facilitating diffusion between them. Thirdly, high density of dislocations was introduced in Al and Ti particles by severe plastic deformation during FSP. Fig. 7(a) shows the abundant tangled dislocation structures in severely deformed Ti particles. The diffusion would be substantially enhanced due to the occurrence of pipe diffusion. As a result of these factors, the Al–Ti reaction during FSP was interface-reaction controlled rather than diffusion controlled. Fig. 6(b) gives the morphology of Al–Ti interfacial reactive product, and the line scan of composition indicated that the interfacial reactive product is  $Al_3Ti$  (Fig. 6(c) and (d)).

Furthermore, the values of *n* of FSP samples is slightly lower than those of samples annealed at 575–650 °C, indicating that although the main controlling factor of Al–Ti reaction during FSP was interfacial-reaction controlled, there are still some other subsidiary controlling factors, such as Al–Ti interdiffusion, for the reaction during FSP. In fact, many factors would also cause variation in the kinetic exponent, for example, oxide film on Ti and Al, the morphologies and purity of Ti and Al, and so on [17].



Fig. 3. SEM/BEI images of FSP samples with tool rotation rate of 1000 rpm: (a) 1 pass, (b) 2 pass, (c) 3 pass, and (d) 4 pass.



Fig. 4. SEM/BEI images of FSP samples with tool rotation rate of 2000 rpm: (a) 1 pass, (b) 2 pass, (c) 3 pass, and (d) 4 pass.



Fig. 5. Variation of volume fractions of Ti and Al<sub>3</sub>Ti with reactive time during annealing at (a) 525 °C, (b) 550 °C, (c) 575 °C, (d) 600 °C, (e) 625 °C, (f) 650 °C, and during FSP with (g) 1000 rpm and (h) 2000 rpm.

In order to compare the reactive rate constant k and calculate the activation energy during annealing at 575–650 °C and FSP, the kinetic exponent n was normalized to the same value 0.9. Similar normalization had been reported by Xu et al. [18]. In their results, the values of n were 0.83, 1.08 and 1.06, respectively, during the annealing at 600, 630 and 650 °C, and the values of n were normalized to be 1.0. In the present study, for samples annealed at 575–650 °C, the values of n were close to 0.9, and for FSP samples, although n was slightly lower than 0.9, it is reasonable and convenient to normalize the values of n to be 0.9, considering that the main controlling factor is similar.

The variations in the volume fraction of Al<sub>3</sub>Ti with reaction time for samples annealed at 575–650 °C and FSP samples are re-fitted using Eq. (3) in which the values of n are 0.9. The rate constant kwas re-obtained and referred to normalized rate constant k. It is noted that the normalized k increased almost exponentially as the annealing temperature increased from 575 to 650 °C. And the normalized rate constant k is more than six times higher during FSP than during annealing at 650 °C, and it increased slightly when the rotation rate was increased from 1000 to 2000 rpm.

The activation energy of the reaction during annealing at temperatures above 550 °C can be obtained from the normalized rate constant k based on an apparent Arrhenius-type relation:

$$k = A \exp\left(-\frac{E_{a}}{RT}\right) \tag{4}$$

where *A* is the pre-exponential factor,  $E_a$  is the apparent activation energy, *R* is the gas constant, and *T* is the absolute temperature. Eq. (4) can also be written in the following form:



Fig. 6. TEM images of 4-pass FSP sample with 2000 rpm showing (a) Al<sub>3</sub>Ti particles distributed in Al matrix, (b) morphology of interfacial reaction product, (c) and (d) line scans of the compositions of interfacial reaction product.

$$\ln k = \ln A - \frac{E_{\rm a}}{RT} \tag{5}$$

The activation energy can be obtained from plot of ln *k* versus the reciprocal of temperature. Such plot is given in Fig. 8, yielding activation energy of 224.9 kJ mol<sup>-1</sup> for the Al–Ti interfacial reaction during annealing above 550 °C. The activation energy includes two parts: the activation energy of Al<sub>3</sub>Ti nucleation and activation energy of Al<sub>3</sub>Ti growth [17,24]. The activation energy of Al–Ti reaction in the present study is comparable with that obtained by vanLoo et al. [17] in Al–Ti diffusion couples (179.5 kJ mol<sup>-1</sup>), where the kinetic exponent was also determined to be 0.9.

It is known that the temperature in the SZ does not usually exceed the melting point of the processed metal (the melting point of Al is 660 °C) during FSP due to the self-limiting nature of the process [25]. However, the rate constant *k* during FSP is still more than six times higher than that during annealing at 650 °C. Based on Eq. (4), it can be deduced that the activation energy of the reaction during FSP is much lower than that during annealing. The lower activation energy of the reaction during FSP can be attributed to the following factors.

Firstly, the Ti particles were significantly refined during FSP, and more green interfaces of the Ti particles would be formed. Furthermore, the reaction product would be removed from the reaction interface during FSP. Thus the reaction interface would be significantly increased, resulting in the increase of the surface energy of the reactive system. Fig. 7(b) shows the clean interface between Al and Ti particles in the FSP sample. Secondly, it has been confirmed that the atoms of the reactants could be activated by severe deformation during HEM [6]. Similar activation would take place during FSP, which, like HEM, also introduced severe plastic deformation of the material [26].

Table 1		
Calculated values of k and n defined in Eq. (	(3)	

Because the actual temperature in the SZ is unknown and the temperature distribution is non-homogeneous, it is difficult to calculate the actual activation energy of the reaction during FSP in the present study. However, Eq. (4) indicates that for a constant k, the decrease in activation energy is equivalent to the increase in effective temperature ( $T_{\text{eff}}$ ). If we assume the activation energy of the reaction during FSP is the same as that during annealing above 550 °C, the  $T_{\text{eff}}$  can be calculated to show the contribution of the mechanically activated effect of FSP.

From the straight line fitted by Eq. (5) in Fig. 8, when the normalized rate constant *k* is 0.587 and 0.679, the corresponding absolute temperature is determined to be 983 K and 989 K, respectively. Thus the values of  $T_{\rm eff}$  for FSP with rotation rates of 1000 and 2000 rpm are calculated to be 710 °C and 716 °C. It can be seen that the  $T_{\rm eff}$  during FSP is much higher than the annealing temperature. This results in a higher rate constant *k* during FSP. However,  $T_{\rm eff}$  increased by only 6 °C when the rotation rate increase from 1000 to 2000 rpm, indicating that the increase in rotation rate caused only a small increase in the mechanically activated effect of FSP.

As discussed above, the decrease in activation energy results from the refinement of Ti particles and the activation of reactant atoms caused by the severe deformation introduced by FSP. Firstly, increasing the rotation rate from 1000 to 2000 rpm only caused slight further refinement of Ti particles (Figs. 3 and 4). This may be associated with the improved matrix flowability at the higher rotation rate [23] and the good ductility of Ti particles. Secondly, Welham [5] found that there was a limit for mechanical activation beyond which intensified deformation exerted little effect on the reaction during HEM. For mechanical activation during FSP, such a limit may also exist, and FSP with a rotation rate of 1000 rpm may

	525 °C	550 °C	575 °C	600 °C	625 °C	650 °C	FSP 1000 rpm	FSP 2000 rpm
n	0.48	0.52	0.82	0.91	0.89	0.91	0.74	0.79
k	0.097	0.120	0.013	0.020	0.042	0.091	1.066	1.081
Normalized n	-	-	0.9	0.9	0.9	0.9	0.9	0.9
Normalized k	-	-	0.006	0.022	0.039	0.098	0.587	0.679



Fig. 7. TEM images of 4-pass FSP sample with 2000 rpm showing (a) tangled dislocation structures in severely deformed Ti particles, and (b) clean interface between Al and Ti particles.



Fig. 8. Plot of rate constant *k* against reactive temperature.

be close to this limit. The mechanism accounting for this issue still needs further researches.

On the basis of the above results and discussion, the process of mechanically activated Al–Ti reaction during FSP can be considered as two stages. At the first stage, the coarse Ti particles are severely deformed and broken up (Figs. 3 and 4). A high density of dislocations was introduced both in Al matrix and Ti particles (Fig. 7(a)), and more green Al–Ti interfaces were formed (Fig. 7(b)). The second stage includes both chemical and mechanical processes. Firstly, mechanically activated effect of FSP reduced the activation energy of Al–Ti interfacial reaction and then increased the  $T_{\rm eff}$  of the reactive system (Fig. 8), thus the reactive rate was significantly enhanced. Secondly, the mechanical effect of FSP removed the interfacial reaction product and distributed it into matrix (Fig. 6(a)).

### 4. Conclusions

In this work, mechanically activated effect of friction stir processing in the Al–Ti reaction was studied quantitatively and the following conclusions can be reached:

(1) The Al–Ti reaction during isothermal annealing and FSP can be described by an empirical relationship:  $V_{Al_3Ti} = kt^n$ . The reaction was diffusion-controlled at 525 and 550 °C, and interfacial-reaction-controlled at 575–650 °C.

- (2) The Al–Ti reaction during FSP with rotation rates of 1000 and 2000 rpm was interfacial-reaction-controlled. The reaction rate constant *k* during FSP was substantially enhanced compared to that during annealing, which can be attributed to the decrease in activation energy caused by severe deformation during FSP.
- (3) The effective temperature was proposed to show the contribution of the mechanically activated effect of FSP, and was calculated to be 710 and 716 °C for FSP with rotation rates of 1000 and 2000 rpm.

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