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Effect of mechanical activation on TiC synthesis reaction in Al-Ti-C powder mixture①

MA Nai-heng(马乃恒), LIANG Gong-ying(梁工英), FANG Xiao-han(方小汉), SU Jun-yi(苏俊义)
(School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China)

[Abstract] After milling in a high-energy ball miller for various times, the synthesis reaction process of the Al-Ti-C powder mixture were investigated by difference thermal analysis (DTA) and X-ray diffractometry (XRD). According to the patterns of reaction peaks on the DTA curves, the activation energy of each reaction was calculated. The experimental results of DTA show that the synthesis reaction of Al-Ti-C powder mixture can be enhanced after high-energy milling. The longer the milling time, the lower the reaction temperature. The synthesis reaction of TiC is transformed from Ti+ C $\rightarrow$ TiC to Al_3Ti+ C $\rightarrow$ TiC+ 3Al with long period milling. Meanwhile, the activation energy of the reaction reduces with increasing milling time. The effect of milling time on reduced activation energy for low temperature region is more significant than that for high temperature region.

[Key words] Al-Ti-C powder mixture; mechanical activation; reactive synthesis; activation energy
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1 INTORDUCTION

Mechanical activation is a kind of pre-treatment technology in production of composites, especially particle reinforced metal matrix composites. It includes high temperature self-propagating synthesis[1], hot-pressing synthesis[2,3] and in-situ laser synthesis[4,5] etc.

During the in-situ laser cladding synthesis of surface composite, the synthesis reaction process is quite short. If pre-treatment process is insufficient, the synthesis reaction may hardly complete. In the previous work, in-situ laser cladding synthesis of TiC_p/Al composite layer on aluminum alloy was studied[6]. It was found that when the high energy ball-milling time of Al-Ti-C powder mixture was short, some Al_3Ti phases, which is an intermediate resultant in process of TiC synthesis, existed in the laser cladding composite layer. However, if the milling time was long enough, there was only TiC particles in the laser cladding composite layer.

Using mechanical activation method, the particle size can be reduced, the grain of each component will be refined, and the micro-strain and inner defect in the grains are all increased. These result in the high-energy state of powder mixture so that it may decrease the temperature of synthesis reaction and increase reactive rate[7,8]. Meanwhile, sufficient mechanical activation of powder mixture may also affect the synthesis reaction process.

In this paper, Al-Ti-C powders are milled using a high-energy ball miller for various milling times. The difference thermal analysis (DTA) and X-ray diffractometry were carried out to determine the feature of synthesis process and the activation energy.

2 EXPERIMENTAL

Commercial Al, Ti and active carbon powders with mean particle size of 75 μm and purity above 99.5% were used as reactants. Mixtures of 60% Al, 32% Ti and 8.0% C (mass fraction) were milled in a high-energy ball miller filled with argon gas for various time. During the ball milling, the mass ratio of ball to powder mixture was 30∶1.

Difference thermal analysis (DTA) was conducted on a TA2100 thermal analyzer. The temperature analysis region of DTA was 400~ 1350 ℃. The samples were heated in argon atmosphere at a rate of 20 ℃/s. X-ray diffraction analysis was carried out on Rigaku D/max-rA X-ray analyzer (CuK_α). Using a method of K value comparison[9], the quantitative content of each resultant of reaction such as Al_3Ti, TiC, Al and Ti in DTA samples was calculated.

3 RESULTS AND DISCUSSION

3.1 Chemical reaction during synthesis process

Fig. 1 shows X-ray diffraction patterns of powder mixture milled for various time. It can be seen that with increasing milling time, the diffraction peaks of Al and Ti get widen, which shows the grain size of Al and Ti reduces gradually. When the powder mixture is milled for 70 h, the diffraction peaks of Al and Ti disappear, and the Al-Ti-C powder mixture is transferred into amorphous structure. The fine Al, Ti

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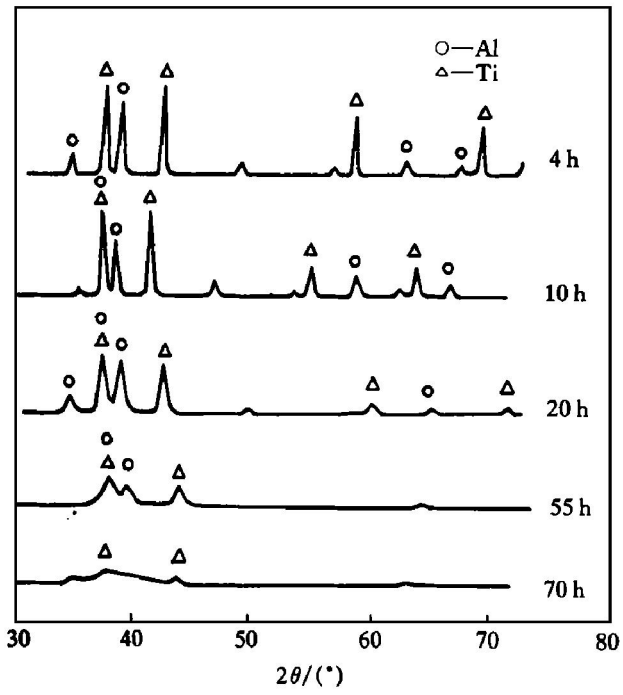

Fig. 1 X-ray diffraction patterns of powder mixture

powders suggest that the distances between elements become nearer and nearer. In the amorphous state, elements Al, Ti, C are in the random distribution. Therefore, with increasing milling time, the distribution of elements Al and Ti is more uniform. Although the active carbon is amorphous whose diffraction peak does not appear on the X-ray patterns, element C also gets fine and uniform with increase of milling time.

It is also found that there is no new compound forming in the process of the high-energy milling, such as Al_3Ti or TiC. That is to say that the chemical reaction among elements Al, Ti and C does not occur. This result is different from the phenomena reported in the Ref. [10]. This may be due to the fact that there is higher aluminum content (60%, mass fraction) in the selected Al-Ti-C powder mixture, which makes the exotherm of synthesis TiC disperse and it difficult to keep synthesis reaction of TiC continuing. Meanwhile, the high aluminum content may also postpone the synthesis reaction of TiC in the DTA test.

Fig. 2 shows the DTA curve of Al-Ti-C powder mixture milled for 10 h. In the low temperature region (< 800 ℃), there are two exothermal peaks and an endothermal peak. In the high temperature region (> 800 ℃), there are two exothermal peak and tail peak. It can be seen that the endothermal peak is formed by aluminum melting. In fact, the exothermal peaks in the low temperature region are caused by the chemical reaction according to X-ray analysis. Because of the endothermal effect of aluminum melting, the exothermal peak in the low temperature region is divided into two exothermal peaks.

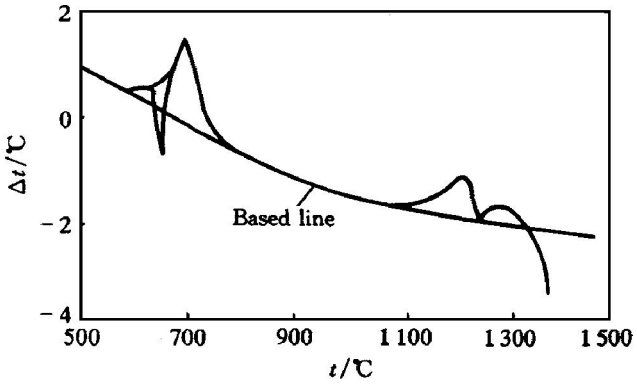

Fig. 2 DTA curve of Al-Ti-C powder mixture milled for 10 h

With increasing milling time, the temperatures of initial reaction of exothermal peaks decrease and the area of endothermal peak is reduced, which implies that the reactivity of the powder mixture increases. As milling time is increased up to 55 h, the reaction process of Al-Ti-C powder mixture is changed. Fig. 3 shows the DTA curve of Al-Ti-C powder mixture milled for 55 h. It can be seen that the reaction procedure of Al-Ti-C powder mixture is different from that of the powder milled for 10 h. Endothermal peak disappears and the exothermal peaks in the low temperature region are combined into one exothermal peak. The initial reaction temperature is decreased to 200 ℃. Reaction temperature in the high temperature region is also decreased.

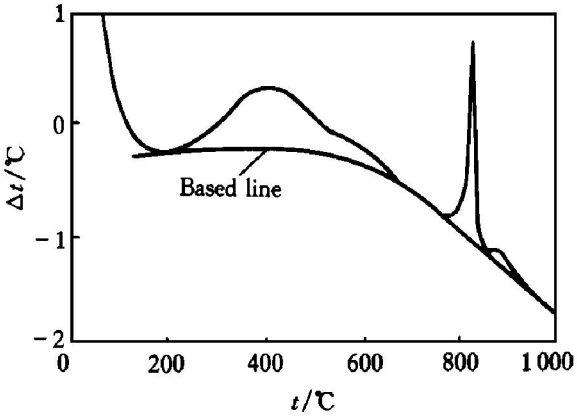

Fig. 3 DTA curve of Al-Ti-C powder mixture milled for 55 h

Table 1 shows some quantitative analysis results of DTA resultants of Al-Ti-C powder mixture in various temperatures. It can be seen that with increasing milling time, the content of Al_3Ti is increased, which is because that the synthesis reaction temperature of Al_3Ti reduces. However, the content of TiC is basically not changed, which relies mainly on the composition of powder mixture.

It is also seen that in the low temperature region (< 800 ℃), the synthesis reaction is

Table 1 Quantitative analysis of DTA resultants of Al-Ti-C powder mixture

Milling time/h	Temperature /℃	w/%			
		Al_3Ti	TiC	Ti	Al
10	630	10.54		27.20	54.84
	800	41.29		15.54	35.08
	1300	32.68	23.68		40.48
20	630	11.64		26.88	54.25
	800	43.32		14.60	34.80
	1300	35.94	21.54		39.44
55	760	80.60			11.38
	1050	33.76	21.80		40.78

$$3Al + Ti \longrightarrow Al_3Ti \quad (1)$$

The synthesis reaction of TiC results from

$$Ti + C \longrightarrow TiC \quad (2)$$

or

$$Al_3Ti + C \longrightarrow TiC + Al \quad (3)$$

The standard free energy of Eqns. (2) and (3), ΔG_1^0 and ΔG_2^0, are respectively given by[11]

$$\Delta G_1^0/(J\cdot mol^{-1}) = -1.8874\times10^5 + 15.4399T \quad (4)$$

$$\Delta G_2^0/(J\cdot mol^{-1}) = -5.5251\times10^3 - 48.8375T \quad (5)$$

ΔG_1^0 is much smaller than ΔG_2^0. In the experimental temperature region, the Eqn. (2) reaction will firstly occur if there are some free element Ti in the powder.

In the Fig. 2, the exothermal peaks in the high temperature region are caused by the reactions of Eqn. (2) and Eqn. (3), respectively. However, in the Fig. 3, the exothermal peak in the high temperature region is caused by the reaction of Eqn. (3) because element Ti is completely transformed to Al_3Ti before TiC synthesis reaction.

These results indicate that mechanical activation with high-energy miller can efficiently promote synthesis reaction of forming Al_3Ti in advance. At last, it will make TiC synthesis reaction process change.

3.2 Reaction activation energy of synthesis procedure

Using a method introduced in the Ref. [12], the reaction activation energy can be calculated by the configuration of exothermal peak on the DTA curve. According to the Arrhenius formula and mass action law, the relationship between resultant synthesis rate and reaction activation energy (E) is as follows.

$$\frac{d\alpha}{dt} = A\exp(-\frac{E}{RT})f(\alpha) \quad (6)$$

where α is resultant degree, A is constant.

Suppose the exothermal rates is in direct proportion to resultant synthesis rate. So we can define

$$\alpha = \frac{S_1}{S} = \frac{S - S_2}{S} \quad (7)$$

where S_1 is the exothermal area in the certain time, S is the total exothermal area, $S_2 = S - S_1$.

According to Eqns. (6) and (7), we can deduce

$$\ln\Delta T = C + n\ln S_2 - \frac{E}{RT} \quad (8)$$

where T is temperature (K), n is resultant synthesis rate factor. When the reaction equation is defined, both n and C are constants.

Take a difference quotient for the Eqn. (8), we can get

$$\frac{\Delta\ln\Delta T}{\Delta\ln S_2} = -\frac{E}{R}\frac{\Delta(1/T)}{\Delta\ln S_2} + n \quad (9)$$

In the each reaction peak, more than 5 different region and temperature were selected to calculate relevant $\Delta\ln\Delta T$ and $\Delta\ln S_2$. Through regression analysis, the reaction activation energy can be calculated from the slope.

In the calculation of reaction activation energy, the disturbance of aluminum melting to the area of Al_3Ti exothermal peak is modified:

$$\Delta H = K\frac{S}{m} \quad (10)$$

where ΔH is reaction enthalpy ($J\cdot mol^{-1}$), K is equipment constant, S is the area of exothermal peak and m is mass of resultant. The equipment constant K is obtained by DTA of standard Al sample. K_{Al} is 0.1118 J/K^2.

Fig. 4 shows a modified draft of Al_3Ti synthesis reaction on the DTA curve. In the Fig. 4, the endothermal area of residual aluminum melting is equal to $A_2 + A_4$. Only area A_4 makes the total exothermal peak reduce. Therefore, the modified area in the exothermal peak should be equal to A_4.

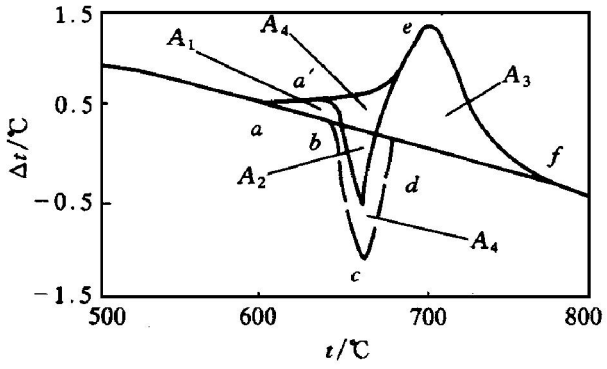

Fig. 4 Modified draft of Al_3Ti synthesis on DTA curve

The content of Al_3Ti formed by the modified area of exothermal peaks using enthalpy method is consistent well with that of the results of XRD quantitative analysis. Table 2 shows the contents of Al_3Ti that are detected respectively by the enthalpy method and XRD quantitative analysis in Fig. 2.

Table 3 shows some calculated results of reaction activation energy of Al-Ti-C powder mixtures milled for various time. It is seen that with increasing milling time, the reaction activation energies of

Table 2 Contents of Al_3Ti obtained by enthalpy method and XRD analysis (mass fraction, %)

Temperature / ℃	Enthalpy method result	XRD analysis result
600~ 650	5.0	
650~ 681	11.56	
681~ 769	24.77	
600~ 769	41.33	
780		41.29

Table 3 Calculated results of reaction activation energy ($kJ \cdot mol^{-1}$)

Chemical reaction	Milling time/ h		
	10	20	55
$3Al + Ti \longrightarrow Al_3Ti$	440	83.5	53.5
$Ti + C \longrightarrow TiC$	279.3	255.8	
$Al_3Ti + C \longrightarrow TiC + 3Al$			87.1

Eqn. (1) and Eqn. (2) are all reduced. The influence of milling time on reaction activation energy is more significant in the reaction at low temperature region. At high temperature region of reaction, the influence of milling time on reaction activation energy is not so important.

During the milling process, fracture, cold welding and distortion of solid Al-Ti-C powder mixture make grains refine and inner stress increase, which results in the increase of intrinsic energy greatly so that the reaction activation energy is reduced. With increasing temperature, a part of intrinsic energy will release so that the effect of milling at high temperature region is smaller than that at low temperature region.

4 CONCLUSIONS

1) The synthesis reaction temperature of Al-Ti-C powder mixture can be reduced after high-energy milling. The longer the milling time, the lower the reaction temperature.

2) With increasing milling time, the synthesis reaction form of TiC is transformed from $Ti + C \longrightarrow TiC$ to $Al_3Ti + C \longrightarrow TiC + 3Al$.

3) With increasing milling time, the reaction activation energies of $3Al + Ti \longrightarrow Al_3Ti$ and $Ti + C \longrightarrow TiC$ are reduced. The longer the milling time, the lower the reaction activation energies.

4) The effect of milling time on reducing reaction activation energy at low temperature region is more significant than that at high temperature region.

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