Study on the adiabatic temperature of Al-Ti-C grain refiner synthesized by SHS technique

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***Abstract*—SHS technique and conventional melting and casting technology were combined and used for the preparation of Al-Ti-C grain refiner alloy. Experimental results show that when SHS reaction occurs to the Al, Ti and C powder reactant in Al melt and the composition proportion factor, n , is between 4 and 10, the effect of composition on the initial temperature of SHS reaction is small and its initial temperature ranges from 810 to 815℃. However, the highest temperature of the melt increases with increasing n values and increases gradually from 845 to 1370℃. In the meantime, when the composition proportion factor for Al, Ti and C powder reactant, n, is greater than 5.95, its adiabatic temperature T_d＞1800K which conforms to the empirical criterion proposed by Merzhanov et al. The SHS reaction of reactant can accomplish by self-maintenance.**

Keywords- SHS technique; Al-Ti-C grain refiner; composition proportion factor; adiabatic temperature

I. INTRODUCTION

SHS (Self-propagating High-temperature Synthesis) through which carbides, nitrides, borides, intermetallics and composites are made is an innovative method for preparating metallic ceramics or intermetallics developed in recent two decades. Its fundamental priciple is that necessary energy provided by the outside is utilized to induce high efficient local chemicaL reaction (ignition), form chemical reaction frontier (combustion wave), then keep the chemical reaction to proceed under self heat release, make the combustion wave to spread over entire system, and finally synthesize required materials (powder materials or products). SHS method posesses following characteristics: First, reaction process consumes less external energy, is able to utilize the chemical energy to the maximum extent and hence saves energy sources. Second, simple process and short reaction time. The reaction can be accomplished generally within several seconds to scores of seconds. Third, high purity products can be obtained under vacuum or controlled atomosphere. Fourth, the synthesis and sintering of materials are finished simultaneously. Fifth, less pollution of synthesiszed products and their microstructures and properties can be controlled.

Although this method has many advantages, one obvious shortcoming lies that the prepared materials are mostly in loosen and crackking state. Thus the SHS densification all-in-one technique is a developing direction of this technique. SHS-casting method and SHS-hot pressing sintering process are hotspots for the preparation of densification materials by SHS method. At present, SHS technique has been used in the preparation of metallic base TiC, TiB_2 reinforced composites et al[1-8].

In this work, SHS technique and conventional melting and casting technology were combined and used for the preparation of Al-Ti-C grain refiner alloy. First, Al, Ti and C powders are mixed in a certain proportion to make SHS reactants. Then the reactants are put into Al melt at definite temperature. Under the temperature of Al melt, the SHS reaction occurs to the reactants, $TiAl_3$ and TiC particles are formed. After stirring, the melt passes pouring and casting or continuous casting and extruding (CASTEX) and ingots or wires of Al-Ti-C grain refiner alloy are prepared[9]. As this process puts Ti and C into the Al melt to induce SHS reaction, it needs not complex equipment as compared with conventional SHS reaction and is relatively simple in preparation process and low in production cost. In addition, Al-Ti-C grain refiner alloys in different microstructure morphologies can be made by adjusting the composition of Ti and C. Therefore, it is necessary to conduct experimental study on relevant adiabatic temperature and thermodynamics parameters of Al-Ti-C grain refiner alloys prepared by SHS reaction. This investigation is favorable for the analysis of the SHS synthesis reaction mechanism of Al-Ti-C grain refiner alloys and the establishment of reasonable technical scheme.

II. EXPERIMENTAL

A. Experimental raw materials and set-up

The chemical compositions of target alloys were AlTi5C0.25 and Al3Ti0.15C (mass percentage). Experimental materials were commercial pure aluminum and Al, Ti and C powders. SHS reactants were made of mixed Al, Ti and C powders in a certain proportion. Relevant properties of above materials are shown in Tables 1 and 2.

Table 1 Main set-up used for the experiment included: (a) a 0.5kw SiC bar electric resistance furnace. Its maximum heating temperature was 1400℃. It was used for the activation of C powder, the heating of Al melt and the addition of reactant to the Al melt inside the furnace to initiate SHS reaction; (b) a 1000rpm stirrer used in the stirring and uniform mixing of Al, Ti and C powders. The mixture passed special treatment and became SHS reactant;

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(c) an infrared thermograph used in recording the variation in melt temperature with reaction time during SHS reaction process.

TABLE I. PHYSICAL AND CHEMICAL PROPERTIES FOR XPERIMENTAL MATERIALS

Experimental material	*Purity, wt.%*	*Particle size, ≤um,*	*Particle shape*
Pure Al ingot	98.5		
Al powder	98.0	80	Irregular lumpy
Ti powder	98.5	50	Granular
C powder	93.0	20	Amorphous

TABLE II. CHEMICAL COMPOSITION FOR REACTANT

Sample No.	*Target alloy*	*Composition of SHS reactant,wt.%*		
1	Al5Ti0.25C	Ti：5×n	C：0.3×n	Al balanced
2	Al3Ti0.15C	Ti：3×n	C：0.2×n	Al balanced

Note: n was the proportion factor of Ti and C composition of SHS reactant. Since the ratio of Ti to C in Al5Ti0.25C and Al3Ti0.15C was the same, only Al5Ti0.25C was investigated in this experiment.

B. Experimental procedure

Fig.1 shows the experimental flow chart. Raw powders passed activation and melting-aid treatment and were mixed homogeneously to fabricate SHS reactant. SHS reactant was added to the Al melt at a certain temperature under Ar atomosphere to initiate SHS reaction. Thermograph was used for recording the variation in Al melt temperature during SHS reaction process. Target alloy ingots were obtained in metallic mould and hence Al-Ti-C grain refiner alloys whose nominal composition is shown in Table 2 were obtained. TGA/SDTA851e differential thermal analyzer was used for the investigation of thermal transformation of SHS reactant. Under the protection of Ar atomosphere, the sample was heated at a rate of 5℃/ min to 1200℃.

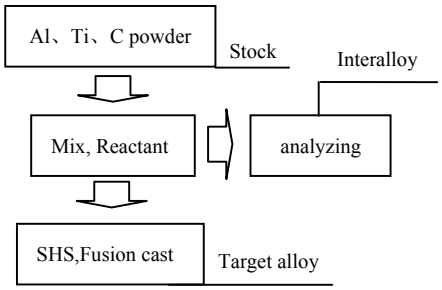

Figure 1. Experimental procedure

III. RESULTS AND DISCUSSION

A. Variation in melt temperature during SHS reaction

Fig.2 shows the variation curve in Al melt temperature with addition time when Al, Ti and C reactant (composition proportion factor n=8) is added to Al melt to initiate SHS.

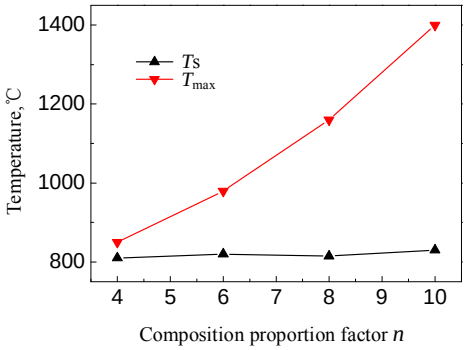

Figure 2. Variation in melt temperature during SHS reaction

As the initial temperature of reactant is lower than that of the melt, Al in the reactant melts when subjected to the heating and hence the platform appears in the temperature rise curve of the Al melt. Then with the severe rise of the Al melt temperature untill the maximum temperature, the Al melt temperature smooths out and descends. Reaction initial temperature T_s measured by the curve, the temperature at the point of intersection between the tangent of curve platform section and the tangent of severe rise section, is about 830℃. The maximum temperature of reaction T_{max} is about 1150℃. Temperature rise rate of reaction process is equal to $(T_{max}-T_s)/\triangle t$ whose value is adjacent to 75℃/s. Faster temperature rise rate shows that severe exothermic reaction occurs in the reactant in Al melt.

Fig.3 shows the vvariation curve in T_s and T_{max} with composition proportion factor n of Al, Ti and C reactant during SHS reaction.

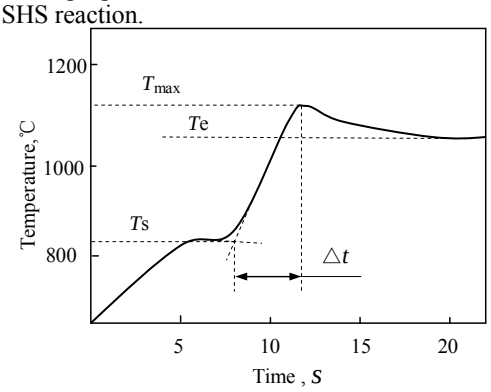

Figure 3. Variation in T_S and T_{max} with composition proportion factor during SHS reaction

When n value of composition proportion factor increases from 4 to 10, the initial reaction temperature Ts of the Al melt hardly varies and undulates in the small temperature range from 810℃ to 815℃. However, the maximum temperature T_{max} becomes larger with increasing n value and increases gradually from 845℃ to 1370℃. n increase means that the contents of Ti and C in the reactant increase. When target alloy composition is AlTi5C0.25，if n value is equal to 4，the contents of Ti and C in the reactant are 20,wt.%

and 1,wt.%, respectively, whereas if n value is equal to 10，the contents of Ti and C in the reactant are 50,wt.%和2.5,wt.%, respectively. Thus, the larger the n value, the more the contents of Ti and C powder taking part in the reaction. At the same time as the reactions Ti(s)＋C(s)＝TiC(s), 4Al(l)＋3C(s)＝Al_4C_3(s) and 3Al(l)＋Ti(s)＝$TiAl_3$(s) in initial reaction stage and $TiAl_3$(s)＋C(s)＝TiC(s)＋3Al(l), Al_4C_3(s)＋3$TiAl_3$(s)＝3TiC(s)＋13Al(l) and Al_4C_3(s)＋3Ti(s)＝3TiC(s)＋4Al(l) in derivation reaction stage are all exothermic reaction, the more the contents of Ti and C powder taking part in the reaction, the greater the thermal output of above reactions, and the larger the temperature rise for euqal mass melt. Therefore, the curve takes on the temperature variation as shown in Fig.3.

B. Analysis of the adiabatic temperature during SHS reaction

If melt and reactant are approximately considered as a adiabatic system, the adiabatic temperature T_{d1} during the SHS reaction of reactant can be estimated according to melt equilibrium temperature Te (Fig.2).

$$\sum m_i(H^0_{f,298}-H^0_{f,T})_{reactant}+\Delta H^0_{298}+\sum n_i(H^0_{TS}-H^0_{298})_{resultant}=\sum v_i\int_{298}^{Te}\Delta Cp_{melt}dT \quad (1)$$

where，m_i, n_i and v_i are the mole weight of reactant, resultant and Al melt, respectively.

Based on the thermodynamics data relevent to Al-Ti-C system [10], the adiabatic temperature T_{d1} of reactant under different composition proportion factors was calculated according to formula (1) and is shwon in Table 3.

TABLE III. ADIABATIC TEMPERATURE T_{D1} FOR REACTANT

n	4	6	8	10
T_{d1}, ℃	990	1400	1990	2100

The maximum temperature, i.e., the adiabatic temperature, for the synthesis reaction of reactant can be estimated directly using this method. However, because of possible incomplete reaction transformation and the existence of definite heat transfer between Al melt and crucible and between Al melt and air during reaction, there exists a certain difference between the estimated adiabatic temperature and practical reaction temperature. It is, therefore, necessary to use the calculation formula relevent to the adiabatic temperature to conduct further calculation of the adiabatic temperature of reactant so as to validate the calculation results shown in Table 3. The analysis and calculation process are as follows:

Due to the diversity of reaction forms of Al-Ti-C system, it is difficult to determine which reaction is the practical reaction during SHS reaction and their respective mass percentage of going-on reactions. Thus, above possible reactions are simplified as representative Ti(s)＋C＝TiC reaction and 3Al(l)＋Ti(s)＝$TiAl_3$(s) reaction. These two reactions are combined and Al is regarded as the thinner (as T_d > Al melting point, the percentage of molten Al in reaction is 100%). Thus, the adiabatic temperature of reactant is analyzed and calculated as follows:

(a) Combination of reaction formula

The atom ratio of Ti to C is 5 to 1 for Al5Ti0.25C grain refiner alloy. The combined reaction formula is

$$12Al(l)+5Ti(s)+C(s)=4TiAl_3(s)+TiC \quad (2)$$

For reactant whose composition proportion factor is n, the content of thinner Al is (1－0.0525n), formula (2) is rewritten as:

$$[(100-5.25n)/26.9]Al(l)+5n/48Ti(s)+0.25n/12C(s)$$

$$=4n/48TiAl_3(s)+0.25n/12TiC+[(100-5.25n)/26.9-n/4] \quad (3)$$

(b) Analysis and calculation of adiabatic temperature of reactant

According to the calculation results shown in Table 3, presuming that when adiabatic temperature exceeds Al or $TiAl_3$ melting point, Al and $TiAl_3$ completely melt, i.e.

$$4n(\Delta H^0_{298(TiAl_3)}-\Delta H^0_{Ts(TiAl_3)})+n(\Delta H^0_{298(TiC)}-\Delta H^0_{Ts(TiC)})$$

$$=4n[\int_{298}^{Td2}C_{p(TiAl_3)}dT+\Delta H_{m(TiAl3)}]+n\int_{298}^{Td2}C_{p(TiC)}dT$$

$$+[(100-5.25n)/26.9-12](\int_{298(Al)}^{Td2}C_{p(Al)}dT+\Delta H_{m(Al)}) \quad (4)$$

TABLE IV. ADIABATIC TEMPERATURE T_{D2} REACTANT

n	4	6	8	10
T_{d2} ,℃	1110	1730	2010	2210

It is found by comparing the adiabatic temperatures in Tables 3 and 4 that when n is greater than 6，T_{d2} value is slightly higher than T_{d1}. There are two probable reasons: on account of the melt abstraction of heat during SHS reaction, the equilibrium temperature Te used in the calculation T_{d1} is lower than the true value. Thus T_{d1} is lower than the true value of adiabatic temperature; DuringT_{d2} calaulation, owing to the simplified treatment on reaction formula and neglecting some endothermic reactions, e.g., Al_4C_3(s)＋3$TiAl_3$(s)＝3TiC(s)＋13Al(l) is an endothermic reaction. Thus, T_{d2} value is higher than its true value; when n is less than 6，T_{d2} value is slightly lower than T_{d1}. That is because the curve in Fig.4 is plotted by measuring the temperatures during the temperature rise of the melt, the heat liberation is less due to system reaction when n is small, and hence there are relatively more

heat transferred to the melt during the temperature rise of the furnace. Based on aformentioned resons, there exits a certain deviation between T_{d2} or $T_{d1}$and theoretical reaction temperatures. However, which T_{d2} or T_{d1} is more adjacent to true value remains further experimental analysis and validation.

Fig.4 shows the variation in adiabatic temperature T_{d2} and T_{d1} of reactant with composition proportion factor n

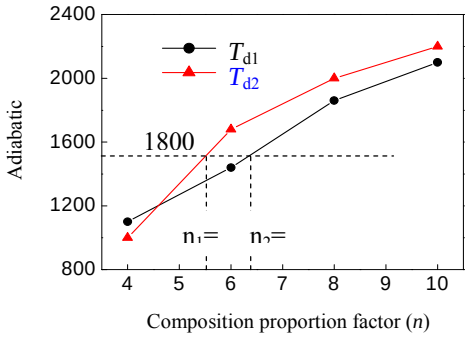

Figure 4. Effect of adiabatic temperature on *n*

It is shown in Fig.4 that the adiabatic temperatures of T_{d1} and T_{d2} all become larger with increasing n. It is believed through analysis that when n increases, the contents of Ti and C participation in the reaction increase and Al content becomes relatively small(however, even if when n＝10, Al content is still enough to react with Ti), the phenomenon that reaction heat liberation increases and endosthermic heat of resultant becomes less, thus the temperature rise in the system is larger. According to the empirical criterion proposed by Merzhanov et al[11], i.e., when T_d＞1800K，SHS reaction can be accomplish by self-maintenance. Thus, the composition proportion factors of reactant determined by Fig.4 are n1 =5.5 and n2 =6.4. In the meantime, in consideration of the analysis results of adiabatic temperature and true value in Table 3 and Table 4, the composition proportion factor of reactant is taken.

$$n = \frac{n_1 + n_2}{2} = 5.95 \quad (5)$$

When n=5.95, the chemical composition of Al, Ti and C corresponding to this value can be determined: Al-69,wt.%，Ti-29.5,wt.%，C-1.5,wt.%.

Through the analysis and calculation of the adiabatic temperature of Al, Ti and C powder reactant, we can determine theoretically the upper limit value of Al addition level. When Al addition level is lower than the upper limit value, system can self-maintain SHS reaction. However, it is note worthy that n is solved under the supposition of full reaction between C and Ti and between Ti and Al. Moreover, the heat elimination phenomena such as heat transfer and heat radiation existing in the reaction process certainly will lead to the result that the calculated adiabatic temperature is higher than practical reaction temperature. Whether or not practical reaction satisfies the thermodynamics condition of TiC synthesis reaction and how about the microstructure morphology, reaction process and mechanism of SHS reaction under different n values are remain further experimental investigation and theoretical analysis, which is significant to the optimization of the synthesis process of Al-Ti-C grain refiner alloy.

SUMMARY

When target alloys are AlTi5C0.25 and Al3Ti0.15C, the composition proportion factor of reactant that SHS can self-maintain and is determined by melt equilibrium temperature is 5.5； However, the composition proportion factor of reactant that SHS can self-maintain and is determined by theoretical calculation is 6.4； The chemical proportion of reactant determined according to above results is Al-69,wt.%，Ti-29.5,wt.%，C-1.5,wt.%.

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