

# Preparation of CoAl intermetallic compound by combustion synthesis in self-propagating mode

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## Abstract

The production of cobalt aluminide (CoAl) from elemental powder compacts was conducted by self-propagating high-temperature synthesis (SHS) in this study. Effects of the initial sample density, particle size of the reactants, and initial sample temperature on the combustion characteristics, as well as on the composition and morphology of final products were studied. Unlike most of the intermetallic reactions, the combustion on the CoAl powder compact is self-sustained upon initiation even without any preheating prior to ignition, implying that the reactions are highly exothermic. The combustion process was preceded by the fast propagation of the flame-front, followed by vigorous bulk combustion. The flame-front propagation velocity and combustion temperature were found to increase with increasing sample green density. The use of fine particles of Al (10  $\mu\text{m}$ ) also increased the flame-front velocity. In addition, the combustion products synthesized from the samples using fine Al particles were slightly shrunk or retained the original shape. However, when the coarse particles of Al (350 mesh) were used the sample exhibited a volume expansion after combustion, resulting in an increase in the sample porosity. According to the XRD analysis, combustion products obtained in this study were all made up of a single-phase composition of CoAl without the presence of any secondary phases or unreacted constituent elements. Based upon the measured data of this study, the activation energy with a value of 121.7 kJ/mol was deduced for the synthesis of CoAl by SHS.

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## 1. Introduction

Intermetallic compounds, especially metal aluminides (such as nickel, titanium, cobalt, and niobium aluminides), have been considered as promising materials for high-temperature structural applications [1–4]. This is due to their physical and mechanical properties, which include low density, high specific strength, excellent creep resistance, and good oxidation and corrosion resistance. Conventional processing techniques used to produce intermetallic compounds are generally through a combination of melting, casting, powder grinding, and consolidation by hot pressing. However, these techniques such as melting and casting methods are inapplicable to the fabrication of many intermetallic alloys due

to, for example, a large difference between the melting points of constituent elements [5].

An alternative method, known as combustion synthesis, represents an attractive technique for the preparation of intermetallics and a variety of other materials, including carbides, borides, nitrides, silicides, hydrides, composites, etc. [6–9]. Combustion synthesis of intermetallic compounds can be conducted in either of two modes, the self-propagating high-temperature synthesis (SHS) and the thermal explosion. The former is possible only when the exothermic enthalpy of formation of the desired intermetallic is sufficiently large, which is usually not the case for most intermetallics. The latter conducts a gradual heating of the sample uniformly in a controlled manner until the reaction occurs simultaneously throughout the entire sample. Due to the relatively low exothermicity of reactions between metal interactions as compared to the synthesis of ceramic materials, preheating the sample prior to ignition or applying an electric field

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across the sample have been proved as the effective approach to achieve the self-sustained combustion [9]. Previous studies on the combustion synthesis of intermetallic compounds have focused to a large extent on the aluminides and in particular the nickel aluminides, NiAl and Ni<sub>3</sub>Al [1,10–13]. The preparation of titanium aluminides (TiAl, Ti<sub>3</sub>Al, and TiAl<sub>3</sub>) [14–16] and niobium aluminides (NbAl<sub>3</sub>) [4,17] by combustion synthesis has also been broadly investigated. However, there has been a lack of study on the synthesis of cobalt aluminide, CoAl, by self-propagating combustion or thermal explosion.

The objective of the present study was to experimentally investigate the synthesis of cobalt aluminide by SHS using compacted samples from elemental powders. Effects of the initial sample density, particle size of the reactants, and the initial sample temperature on the combustion characteristics, as well as on the composition and morphology of combustion products were studied. The influence of processing variables on the dynamics of combustion wave (i.e. flame-front propagation velocity and combustion temperature profile) was also explored. In addition, the activation energy associated with the combustion synthesis of the CoAl compound was deduced from the experimental data of this study.

## 2. Experimental methods of approach

Two types of cobalt (Co) powders with different particle sizes of 325 mesh (<45 μm, Cerac Incorp., 99.8% purity) and 2 μm (Aldrich, 99.8% purity) were used as one of the reactants. Similarly, two types of aluminum (Al) powders (Showa

Chemical Co.) with particle sizes of 350 mesh (<40 μm, 99% purity) and 10 μm (99.9% purity) were adopted as the other reactant. Co and Al powders at equiatomic stoichiometry were dry mixed in a ball mill for 10 h. The XRD pattern of blended mixtures exhibited no peaks other than those of the starting elements, with an indication that no mechanical alloying of powders occurred during the milling operation. Mixed powders were then cold-pressed into cylindrical samples with a diameter of 7 mm and a height of 12 mm. In order to study the effect of sample green density on the synthesis of the CoAl compound, the powder compacts were formed with initial packing densities equal to 55, 60, 65, and 70% of the theoretical maximum density (TMD) of the reactant mixture.

The SHS experiments were conducted in a stainless-steel windowed combustion chamber, as shown in Fig. 1, under an atmosphere of high purity argon (99.99%). The sample holder was equipped with a 600 W cartridge heater used to preheat the test sample prior to ignition. The ignition was accomplished by a heated tungsten coil with a voltage of 60 V and a current of 1.5 A. In order to understand the effect of initial sample temperature on the combustion synthesis of the CoAl intermetallic, the experiments were conducted with samples either without preheating or at a preheating temperature ( $T_p$ ) of 100 °C.

The propagation rate of combustion wave was measured by recording the whole combustion event with a color CCD video camera (Pulnix TMC-7) at 30 frames per second. The exposure time of each recorded image was set at 0.1 ms. To facilitate the accurate measurement of instantaneous locations of the combustion front, a beam splitter (Rolyn Op-

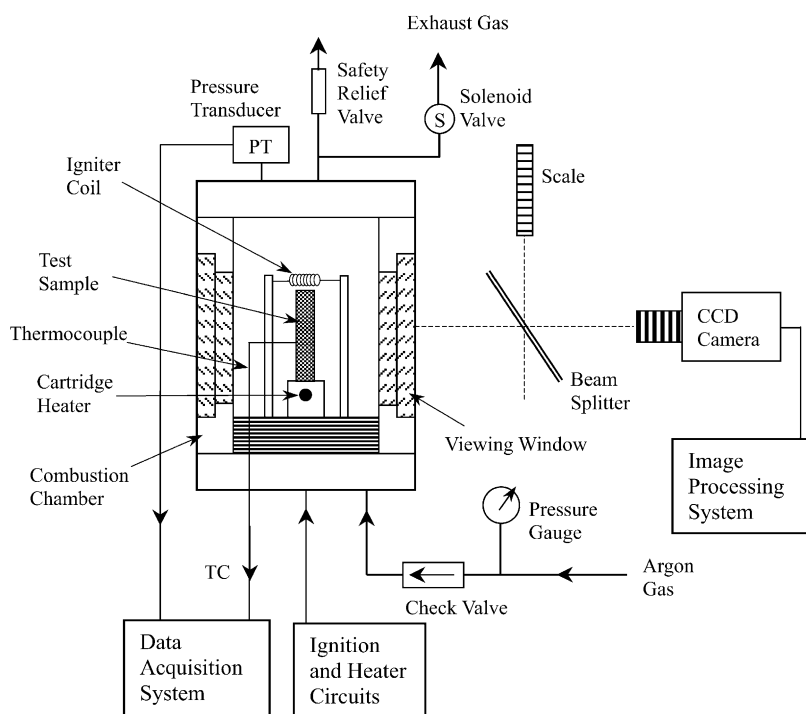


Fig. 1. Schematic diagram of experimental setup to synthesize CoAl intermetallic compound by SHS.

tics), with a mirror characteristic of 75% transmission and 25% reflection, was used to optically superimpose a scale onto the image of the test sample. The combustion temperature of powder compact was measured by a fine-wire (125  $\mu\text{m}$ ) Pt/Pt-13%Rh thermocouple (Omega Inc.) attached on the sample surface. After the SHS process, the density of the recovered sample was measured. In addition, the chemical composition of combustion products was identified by an X-ray diffractometer with Cu K $\alpha$  radiation operating at 40 kV.

### 3. Results and discussion

#### 3.1. Observation of combustion characteristics

Experimental observations of this study indicate that the combustion behavior associated with the CoAl synthesis is not affected by the variation in experimental parameters, including the sample green density, particle size of the reactants, and the initial sample temperature. Unlike most of the intermetallic reactions (such as in the synthesis of NiTi [18], Ni<sub>3</sub>Al [19], and TiAl [14]) which require preheating the sample or electric-field activation to attain the self-propagating flame-front, the self-sustained combustion was achieved on

the CoAl compact in this study even without any preheating. This implies the reactions between Co and Al are sufficiently exothermic so as to support the combustion in the self-sustained mode. Fig. 2(a) shows a typical SHS process recorded from the combustion of an unpreheated sample composed of coarse Co (325 mesh) and Al (350 mesh) powders at 65% TMD. It is evident in Fig. 2(a) that upon ignition a distinct and self-sustained flame-front propagates downward as a nearly parallel combustion wave from the ignited top plane, and transforms the cold reactant into an incandescent combustion product. According to the flame-front trajectory constructed upon the recorded film images, the combustion front was found to propagate in a steady manner. As also indicated in Fig. 2(a), the duration of the flame-propagation period is quite short. It took approximately 0.3 s for the combustion wave to arrive at the bottom of the sample, beyond which the sample remained glowing in white from  $t = 0.3$  to 0.9 s. Afterwards, the luminosity on the sample gradually faded away due to the heat loss to the surroundings. These observations suggest that the reaction is not restricted to the combustion front but continues vigorously in bulk after the passage of the flame-front. In the case of using fine reactant powders (i.e. 2  $\mu\text{m}$  Co and 10  $\mu\text{m}$  Al), a set of recorded images illustrating the typical combustion process at a preheating temperature of 100 °C is presented

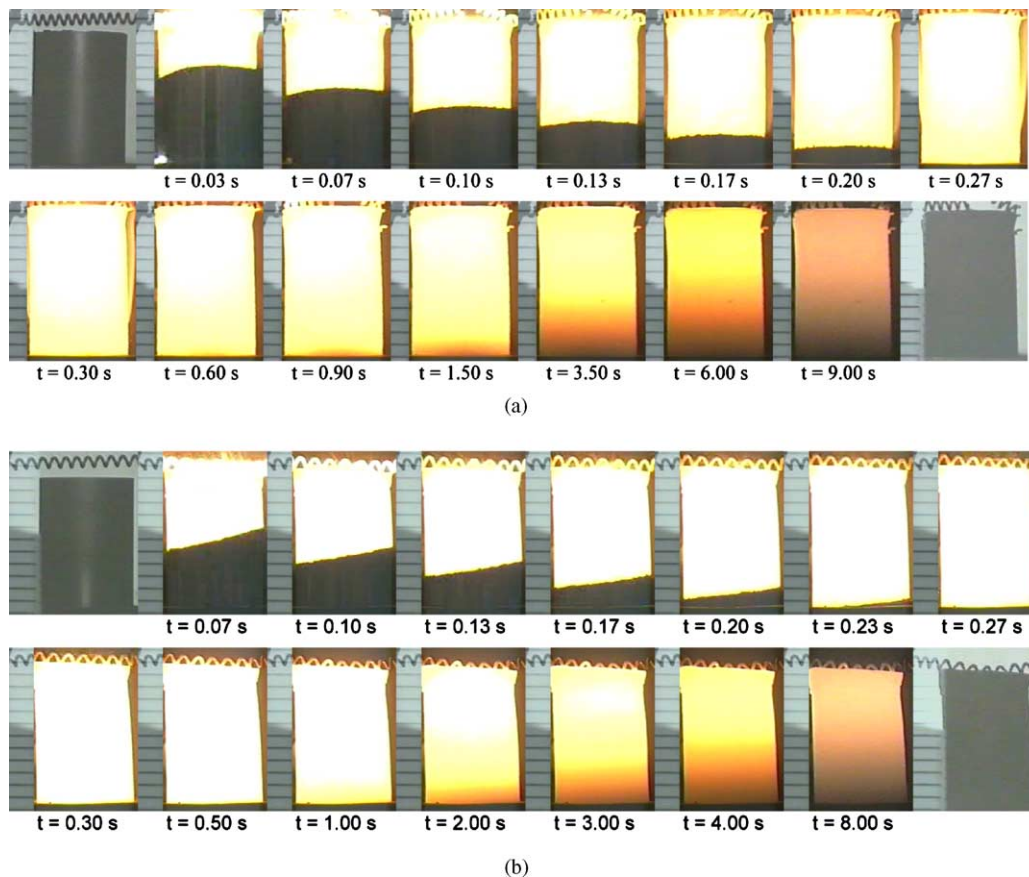


Fig. 2. Recorded combustion images of SHS processes associated with (a) a 65% TMD sample using 325 mesh Co/350 mesh Al ignited without preheating, and (b) a 60% TMD sample using 2  $\mu\text{m}$  Co/10  $\mu\text{m}$  Al ignited at  $T_p = 100^\circ\text{C}$ .

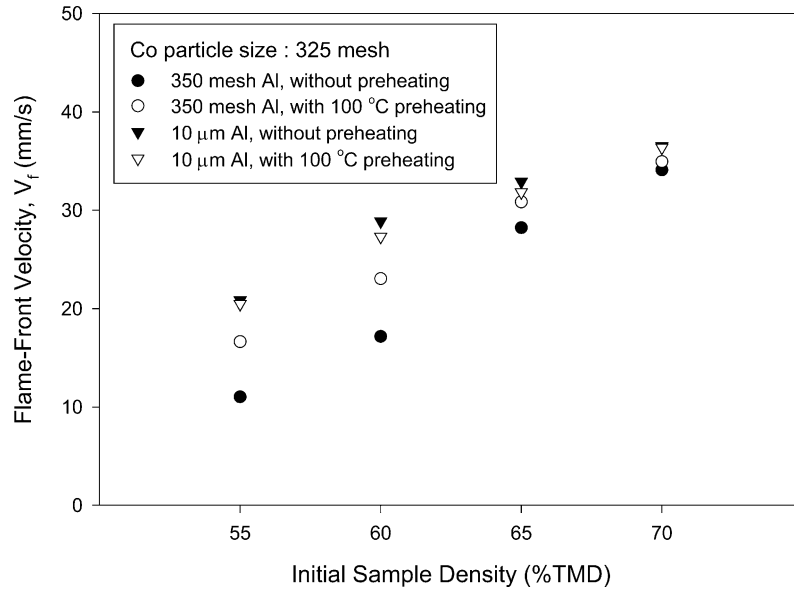


Fig. 3. Effects of initial sample density and preheating temperature on flame-front propagation velocity of samples using Co particles of 325 mesh.

in Fig. 2(b), where the wave propagation and the subsequent bulk reaction are essentially consistent with those observed in Fig. 2(a).

In contrast to the similarity in the combustion process, the sample shown in Fig. 2(a) exhibited an expansion in volume after combustion, while the burned sample in Fig. 2(b) was slightly shrunk. As can be seen in Fig. 2(a), the height of the burned sample is noticeably increased, leading to an increase in the sample volume. The volume expansion observed in Fig. 2(a) was likely attributed to the use of coarse Al powders (350 mesh), which could not form a connected network in the compact after melting due to a poor degree of contact

between reactant particles [1,12]. Consequently, the reaction occurred non-uniformly in the sample, causing the presence of large pores in the end product and thus the volume expansion. It is also accepted that due to the rapid spreading and reaction of the transient liquid, pore formation at prior particle sites is common especially in systems with large Al particle sizes and great exotherms [20]. Therefore, when starting with fine Al powders (10 μm) it was found that the burned samples exhibited a small shrinkage in size or retained essentially the original shape. The comparison of sample densities before and after combustion will be discussed later in this paper.

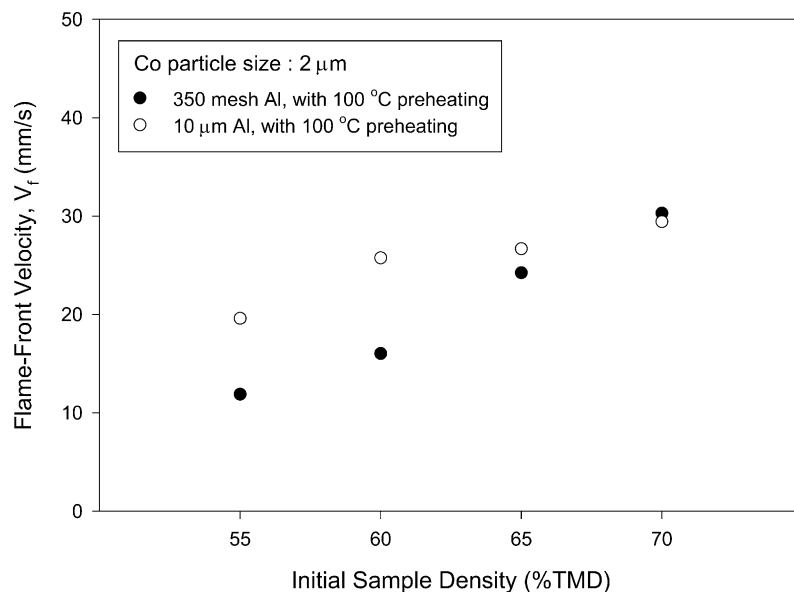


Fig. 4. Effect of initial sample density on flame-front propagation velocity of samples using Co particles of 2 μm.

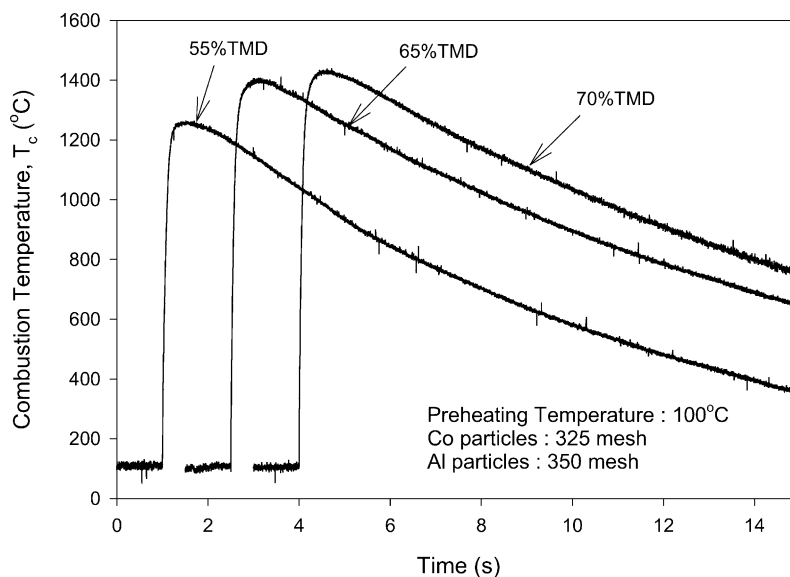


Fig. 5. Effect of initial sample density on combustion temperature of sample compacts using 325 mesh Co/350 mesh Al at  $T_p = 100^\circ\text{C}$ .

### 3.2. Measurement of flame-front propagation velocity

The flame-front propagation velocity ( $V_f$ ) was determined from the measured flame-front trajectory, which was constructed upon the recorded film images. The dependence of the flame-front propagation velocity on the sample green density for test compacts using coarse (325 mesh) and fine ( $2\ \mu\text{m}$ ) Co powders is shown in Figs. 3 and 4, respectively. It was found that an increase in the sample density led to a substantial increase in the flame-front velocity for both conditions. This was due to the fact that the sample with a higher compact density corresponds to the possession of a better degree of contact between reactant powders, which in turn enhances the heat transfer rate from the combustion front to the un-

burned region. As also shown in Figs. 3 and 4, the use of fine Al particles ( $10\ \mu\text{m}$ ) in the sample compacts brings about an increase in the flame-front velocity when compared to those using large Al particles (350 mesh), in particular for the samples with lower compact densities. This was believed to be caused by the fact that the interconnectivity of the liquid aluminum phase was present when the fine Al particles were adopted [1]. As a result, the dissolution of solid Co into the molten liquid was enhanced, leading to an increase in combustion wave velocity. Moreover, when compacts of relatively low green density are reacted, because of the lack of contact between the reactants the uniform spreading of the transient liquid phase around the cobalt particles plays an important role in the rate of reaction. Therefore, it is reasonable to see

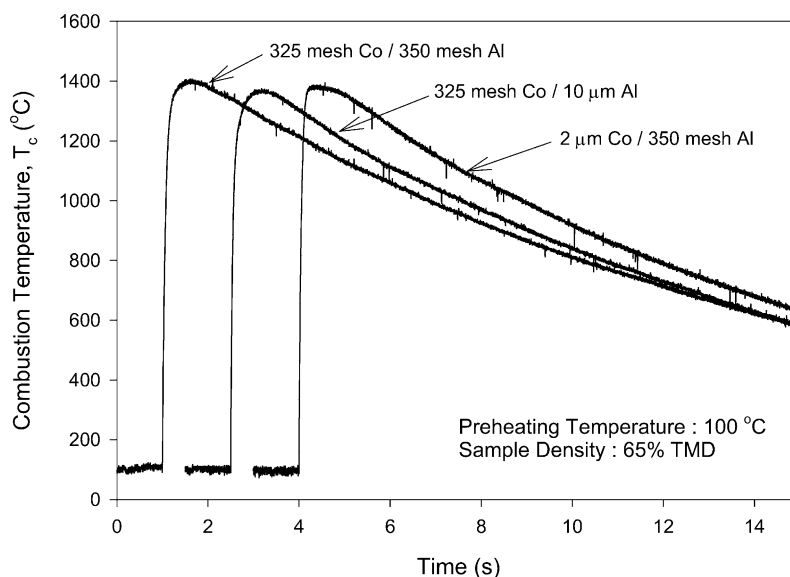


Fig. 6. Effect of particle size of reactants on combustion temperature of 65% TMD sample compacts at  $T_p = 100^\circ\text{C}$ .

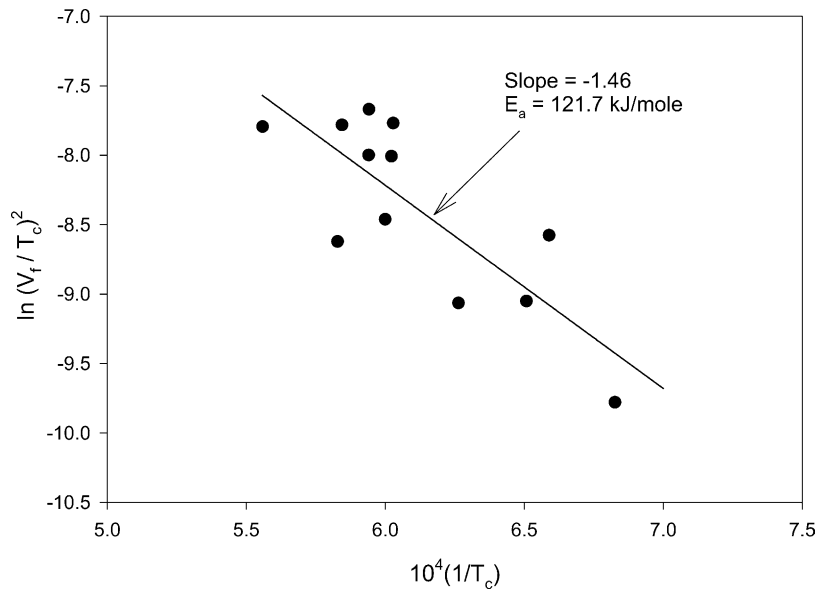


Fig. 7. Relation between flame-front velocity and combustion temperature for determination of activation energy of CoAl synthesis.

that the influence of Al particle size on the flame-front velocity becomes less pronounced as the initial sample density is increased, as shown in Figs. 3 and 4.

The effect of initial sample temperature on the flame-front velocity is presented in Fig. 3. In comparison with the condition without preheating, preheating the sample at 100 °C

prior to ignition was found to increase the flame-front velocity of the samples using large Al particles (350 mesh). Additionally, the influence of preheating on the combustion wave velocity was gradually diminished with the increase of sample green density. When small Al powders (10 μm) were used, the flame-front velocity was not affected by the initial

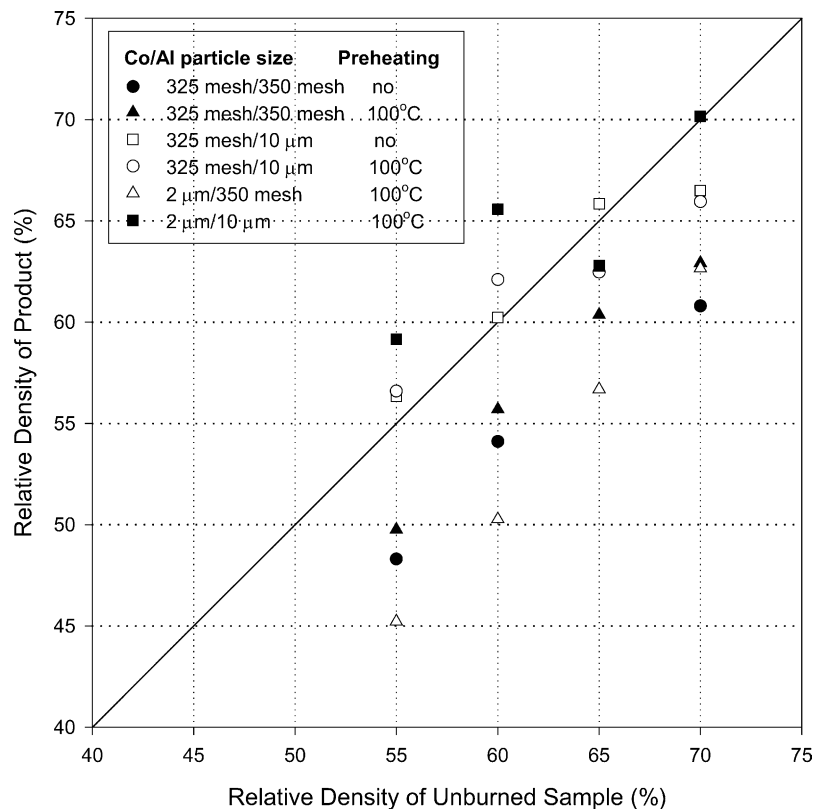


Fig. 8. Comparison of relative densities between unburned samples and combustion products.

sample temperature. Based upon the above observations, it was found that the flame-front velocity was dominantly increased by the increase of sample green density, and that for the 70% TMD compact the flame-front velocity was almost independent of either the initial sample temperature or the particle size of aluminum powders.

### 3.3. Measurement of combustion temperature

Typical combustion temperature profiles are shown in Fig. 5 for test compacts (with 325 mesh Co and 350 mesh Al) under different initial sample densities. The temperature profile starts with the initial sample temperature followed by an abrupt rise representing the rapid arrival of the flame-front. After reaching its maximum, the temperature profile reveals a gradual decline due to the heat loss to the surroundings. As shown in Fig. 5, the maximum combustion temperature increases with initial sample density, which further justifies the increase of flame-front velocity with sample green density. It was also found that during the synthesis reaction the combustion temperature did not reach as high as the melting point of cobalt (1495 °C). Analogous to the reaction mechanism proposed for the synthesis of titanium and nickel aluminides [14,21–23], it was believed that the combustion reaction of the CoAl powder compact is preceded by the melting of aluminum, followed by the dissolution of solid Co into the molten liquid to yield the cobalt aluminide and a great amount of heat. Fig. 6 shows the measured temperature profiles of three 65% TMD sample compacts made up of different particle sizes of reactants. Similar temperature profiles and comparable maximum temperatures were observed in Fig. 6, suggesting that the combustion temperature was not influenced by the variation in the particle size.

A typical approach to the determination of the activation energy of a self-sustained reaction is through the dependence of the reaction front velocity on combustion temperature. Such a relationship is expressed in the following simplified form [6,24]

$$\left(\frac{V_f}{T_c}\right)^2 = f(n) \left(\frac{R}{E_a}\right) K \exp\left(-\frac{E_a}{RT_c}\right)$$

where  $V_f$  is the velocity of combustion front,  $T_c$  the combustion temperature,  $E_a$  the activation energy of the reaction,  $R$  the universal gas constant,  $f(n)$  a function of the kinetic order of the reaction, and  $K$  a constant which includes the heat capacity of the product, thermal conductivity, and the heat of reaction. As a result, the slope of a plot of  $\ln(V_f/T_c)^2$  versus  $1/T_c$  can provide the activation energy of the process, as depicted in Fig. 7. From the slope of the best-fit line of all the data in Fig. 7, the activation energy of about 121.7 kJ/mol was obtained for the combustion synthesis of cobalt aluminide.

### 3.4. Analysis of morphology and composition of combustion products

Fig. 8 shows a comparison of relative density between unburned and burned samples. The relative density of the end product was defined as the ratio of the product density to the density of the intermetallic compound CoAl. Due to the volume expansion, the density of final product obtained from the sample using coarse Al particles (350 mesh) was obviously lower than that of the unburned compact. In general, the samples prepared by the mixture of fine Co (2  $\mu\text{m}$ ) and coarse Al particles (350 mesh) yielded the products with a relatively low density, signifying that the volume expansion during the combustion was correspondingly apparent. With the use of fine Al powders (10  $\mu\text{m}$ ), the density of end product

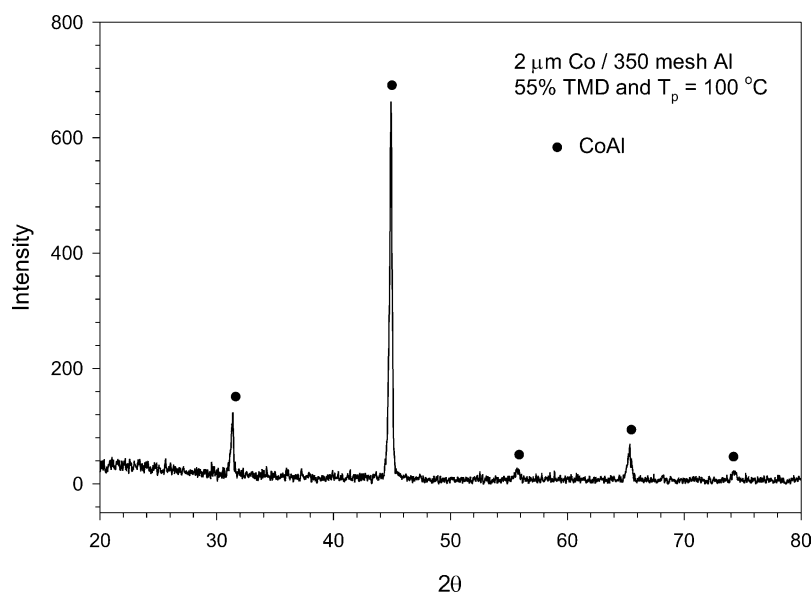


Fig. 9. XRD spectrum of combustion product obtained from 55% TMD sample using 2  $\mu\text{m}$  Co/350 mesh Al at  $T_p = 100$  °C.

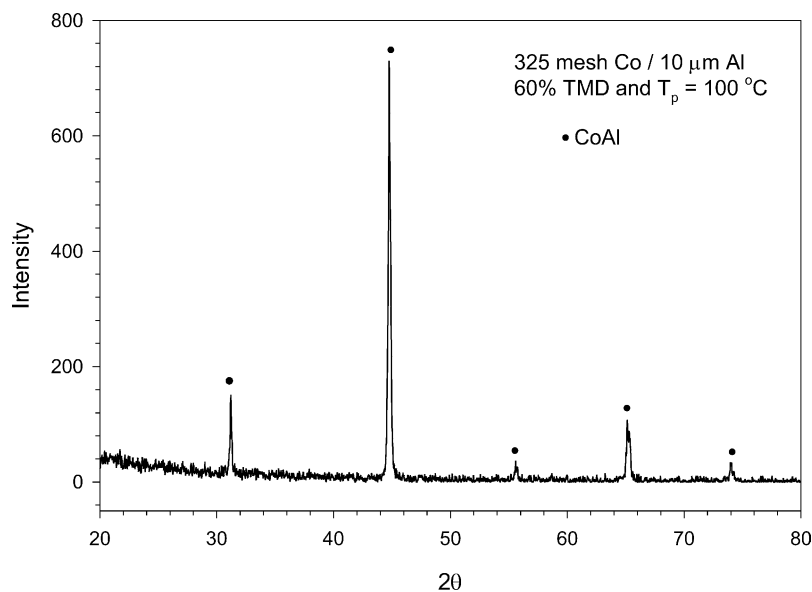


Fig. 10. XRD spectrum of combustion product obtained from 60% TMD sample using 325 mesh Co/10  $\mu\text{m}$  Al at  $T_p = 100^\circ\text{C}$ .

remained close to that of the original compact, or increased slightly owing to the sample shrinkage.

Fig. 9 shows the XRD spectrum of a combustion product synthesized from the 55% TMD sample composed of fine Co (2  $\mu\text{m}$ ) and coarse Al particles (350 mesh). According to Fig. 8, the product shown in Fig. 9 experienced a volume expansion during the synthesis reaction and was highly porous. On the other hand, Fig. 10 presents the XRD spectrum of a slightly shrunk product, which was obtained from the sample made up of coarse Co (325 mesh) and fine Al (10  $\mu\text{m}$ ) powders. It was found that the pattern of both spectra is identical and matches with that of the CoAl compound. That is, the XRD analysis of combustion products indicates the formation of a single-phase product, CoAl, without any secondary phases or unreacted constituent elements. It should be noted that complete conversion yielding fully reacted products composed of the CoAl phase was achieved under all test conditions adopted in this study.

#### 4. Conclusions

This study presents a comprehensive investigation of the SHS process associated with the formation of the CoAl compound from elemental powder compacts. It was found that the combustion wave velocity and combustion temperature were affected by the initial sample density to a great extent. Moreover, the particle size of Al powders was found to have an effect on the flame-front velocity, as well as the morphology of final products.

The combustion process in the CoAl synthesis was characterized by the rapid propagation of a self-sustained combustion front. Moreover, even without preheating the combustion was self-sustained upon initiation in the CoAl sample, which

is indicative of the highly exothermic reaction between Co and Al particles. After the passage of the flame-front, the burned sample remained extremely incandescent, implying the reaction taking place not only in the combustion front but also in the bulk region behind the flame-front. Preheating the sample at  $100^\circ\text{C}$  had no influence on the combustion synthesis of CoAl, other than increasing the flame-front propagation velocity of samples with green densities of 55–65% TMD.

The increase of initial sample density was found to cause a significant increase in the flame-front propagation velocity, because of the increase of combustion temperature with sample green density. The use of fine particles (10  $\mu\text{m}$ ) of Al, which melt and formed a continuous network of liquid phase in the compact, facilitated the dissolution of solid cobalt particles and thus increased the flame-front velocity. Consequently, the end products synthesized from the sample using fine Al particles was slightly shrunk or almost retained the original shape. On the contrary, the samples using coarse Al particles (350 mesh) yielded final products with an expansion in volume, since the interconnectivity of liquid Al phase was lost and large pores were generated during the reaction.

The combustion temperature was found to increase with sample green density, due to an increase in the heat flux from the combustion front to the unburned region. However, the variation in particle size of the reactants produced nearly no effect on the combustion temperature. Based upon the dependence of flame-front velocity on combustion temperature, the activation energy with a value of 121.7 kJ/mol was obtained for the combustion synthesis of CoAl in this study. The XRD analysis identified the synthesized product obtained in this study as a single-phase compound, signifying an achievement of complete conversion from the CoAl powder compact to the CoAl intermetallic compound.



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## References

- [1] K. Morsi, *Mater. Sci. Eng.* A299 (2001) 1–15.
- [2] M.N. Mungole, R. Balasubramaniam, A. Ghosh, *Intermetallics* 8 (2000) 717–720.
- [3] B.M. Warnes, N.S. DuShane, J.E. Cockerill, *Surf. Coat. Technol.* 148 (2001) 163–170.
- [4] V. Gauthier, F. Bernard, E. Gaffet, D. Vrel, M. Gailhanou, J.P. Larpin, *Intermetallics* 10 (2002) 377–389.
- [5] C. Nishimura, C.T. Liu, *Scripta Metall. Mater.* 26 (1992) 381–385.
- [6] Z.A. Munir, U. Anselmi-Tamburini, *Mater. Sci. Rep.* 3 (1989) 277–365.
- [7] A.G. Merzhanov, *Ceram. Int.* 21 (1995) 371–379.
- [8] J.J. Moore, H.J. Feng, *Prog. Mater. Sci.* 39 (1995) 243–273.
- [9] P. Mossino, *Ceram. Int.* 30 (2004) 311–332.
- [10] P. Zhu, J.C.M. Li, C.T. Liu, *Mater. Sci. Eng.* A329–331 (2002) 57–68.
- [11] A. Biswas, S.K. Roy, K.R. Gurumurthy, N. Prabhu, S. Banerjee, *Acta Mater.* 50 (2002) 757–773.
- [12] J.P. Lebrat, A. Varma, *Combust. Sci. Technol.* 88 (1992) 211–221.
- [13] A. Hibino, S. Matsuoka, M. Kiuchi, *J. Mater. Process. Technol.* 112 (2001) 127–135.
- [14] R. Orru, G. Cao, Z.A. Munir, *Chem. Eng. Sci.* 54 (1999) 3349–3355.
- [15] E.G. Kandalova, V.I. Nikitin, J. Wanqi, A.G. Makarenko, *Mater. Lett.* 54 (2002) 131–134.
- [16] N. Bertolino, M. Monagheddu, A. Tacca, P. Giuliani, C. Zanotti, U. Anselmi-Tamburini, *Intermetallics* 11 (2003) 41–49.
- [17] V. Gauthier, F. Bernard, E. Gaffet, C. Josse, J.P. Larpin, *Mater. Sci. Eng.* A272 (1999) 334–341.
- [18] C.L. Yeh, W.Y. Sung, *J. Alloys Comp.* 376 (2004) 79–88.
- [19] C.L. Yeh, W.Y. Sung, *J. Alloys Comp.* (2004) in press, doi:10.1016/j.jallcom.2004.04.116.
- [20] W. Misiolek, R.M. German, *Mater. Sci. Eng.* A144 (1991) 1–10.
- [21] P. Zhu, J.C.M. Li, C.T. Liu, *Mater. Sci. Eng.* A239–240 (1997) 532–539.
- [22] P. Zhu, J.C.M. Li, C.T. Liu, *Mater. Sci. Eng.* A329–331 (2002) 57–68.
- [23] Q. Fan, H. Chai, Z. Jin, *Intermetallics* 9 (2001) 609–619.
- [24] N. Bertolino, U. Anselmi-Tamburini, F. Maglia, G. Spinolo, Z.A. Munir, *J. Alloys Comp.* 288 (1999) 238–248.