

PARTICULAR FEATURES OF COMBUSTION, STRUCTURE AND PHASE FORMATION DURING SHS

H.E. GRIGORYAN, L. PISMENSKAYA, A.S. ROGACHEV, and A.E. SYTSCHEV

Institute of Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka, Moscow, 143432 Russia

Introduction

Self-propagating high-temperature synthesis (SHS) is an attractive technique to synthesize a variety of advanced materials [1]. It is based on the concept that once initiated locally by means of a thermal source of short-term-service, highly exothermic reactions become self-sustaining and yield the final product progressively without requiring additional heat. We studied gasless combustion in self-propagating and thermal explosion modes in order to recognize the kinetic features and mechanisms of heterogeneous combustion. Various systems, such as Ni-Al, Ti-Al and Ti-C-Si, were investigated. These systems are characterized by intense melting of the reactants at the combustion temperature. In the first system, both Ni and Al melted in the combustion wave; in the second system only Al melted while metal Ti remained solid; and, finally, Ti-C-Si system represents an example when two components (Si and Ti) melt while nonmetal component (carbon) remains solid at the combustion temperature.

This work is focused on establishing the role of melts in the macrokinetic reaction mechanism. It is known that diffusion-controlled reaction and dissolution in the melt are two most probable mechanisms of gasless combustion. When the process is diffusion-controlled, combustion may proceed at temperatures even below the melting point of reactant. In the other case, reaction starts only above the melting point of at least one reactant

Experimental

Powders of Ti (PTOM grade, particle size $d \sim 20 \mu\text{m}$, 99.8% pure), graphite ($d - 1-2 \mu\text{m}$, Alrdich), electronic grade Si (pure for electronics, $d < 10 \mu\text{m}$), Ni (Cerac, $d = 44-80 \mu\text{m}$) and Al (ASD-1, $d < 20 \mu\text{m}$) were used in preparation of the reaction mixtures. Chemically pure SiC powders (irregularly shaped particles with $d \sim 5 \mu\text{m}$, Johnson Matthey Electronics) and whiskers (about $0.1-0.5 \mu\text{m}$ in diameter and a few microns in

length, TaTeHo Chem. Co., Ltd) were also used in our experiments. The powders in appropriate mass ratios were mixed and carefully ground in a china stamp to have a homogeneous green mixture. Then parallelepiped-like samples (1 x 1.3 x 3 cm) of a desired density were obtained by cold pressing in a steel mold. The uniform density was achieved by pressing perpendicular to the sample larger axis. The sample was put vertical into the reaction chamber, which was then evacuated and filled with argon (1.5 atm). The combustion wave initiated by an electrically heated tungsten wire from the top of the sample propagated downwards. The combustion velocity and the front shape could be read at any moment, since the process was monitored with a video-recorder Panasonic NV-SD450, video camera Panasonic WV-BL600 connected to a microscopic head OGME-P3 (x15). The sample temperature was registered with W/Re thermocouples (junction thickness 200 μ m). The Ni+Al, 3Ni+Al, Ti+Al, and 3Ti+Al mixtures were pelleted into parallelepiped-shaped samples and uniformly heated by an electric furnace up to the point of self-ignition. Phase composition was monitored continuously during the heating, thermal explosion, and cooling by Time-Resolved X-ray Diffraction (TRXRD) [2].

1. Gasless Combustion in the Ni-Al and Ti-Al Systems

The results are presented in Figures 1, 2. Figure 1 shows evolution in the diffraction patterns of the Ni + Al mixture (3 : 1) during thermal explosion. Thermal explosion occurred at the 192 s and drastically changed the green structure, which resulted in formation of NiAl (Fig. 1a).

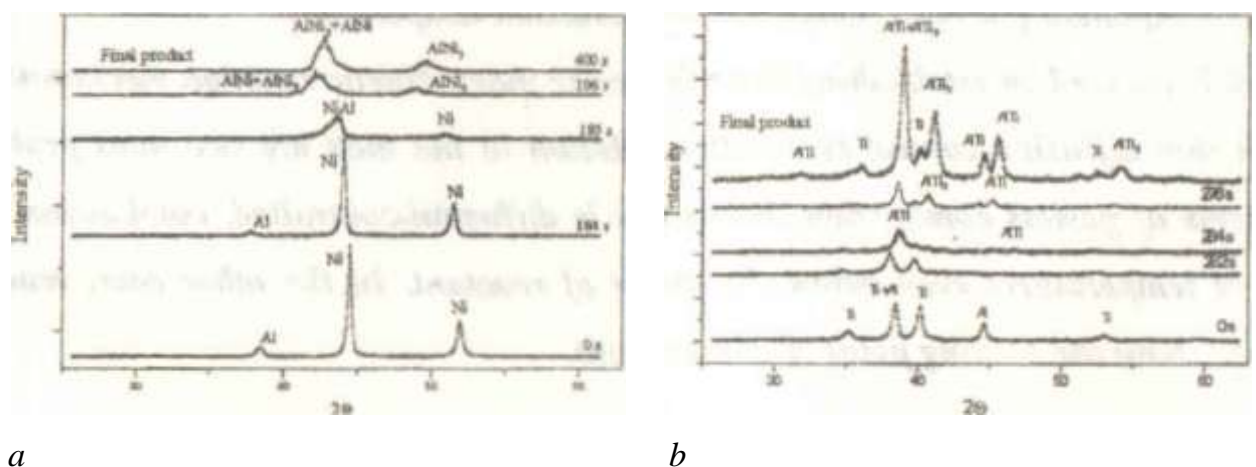
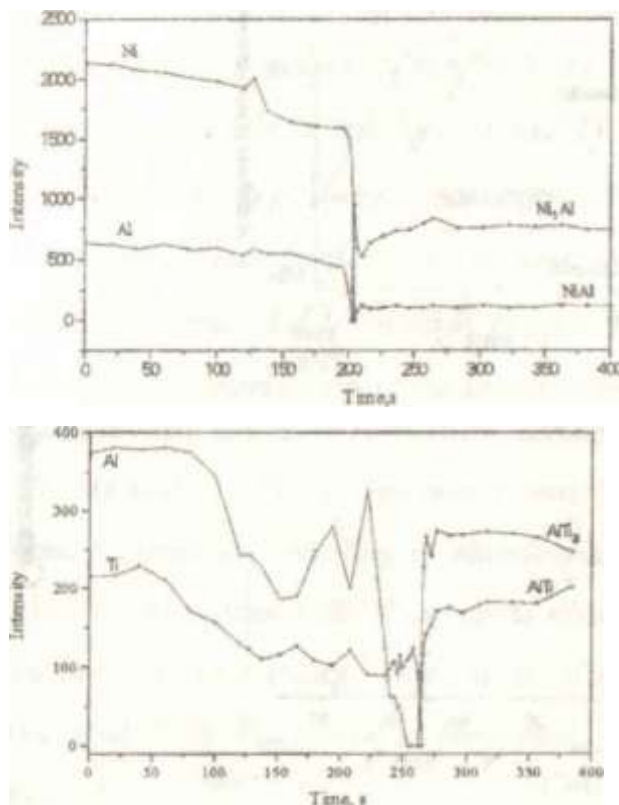


Fig. 1. Sequences of TRXRD patterns obtained directly during thermal explosion for Ni - Al (a) and Ti - Al (b) systems.

This is followed by the formation of cubic Ni_3Al . During cooling, the crystal lattice

undergoes gradual ordering. The RT diffraction pattern exhibits cubic AlNi_3 and NiAl . The kinetics of phase changes is illustrated in Fig. 2b. In the heat-affected zone, the crystal lattice of starting reactants undergoes only partial disordering. Thermal explosion leading to formation of new phases occurs at the moment of Al melting. The diffraction patterns of the Ti-Al system are presented in Fig. 1b. Initially, AlTi is formed. Then ordering of AlTi and formation of AlTi_3 take place. These phases are also present in cooled end product. Combustion in the Ti-Al (3 :1) system yield predominately AlTi_3 Figure 2b presents the kinetics of phase changes during thermal explosion in the Ti—Al system.



a

b

Fig.2. Kinetic phase transformation for a Ni - Al (a) and Ti - Al (b) systems during thermal explosion according to TRXRD analysis.

The results clearly show that combustion gets started immediately after melting of the low- melting reactant (Al). It allowed us to assume that dissolution of the refractory compound in the melt is a rate-controlling step of the gasless combustion.

2. Gasless Combustion in the Ti-Si-C System

The compositions were varied along the pseudo binary section $\text{TiC-Ti}_5\text{Si}_3$ of the ternary system. The reaction mixtures the composition $(100-x)(\text{Ti} + \text{C}) + x(5\text{Ti} + 3\text{Si})$,

where x ranged between 0 and 100 wt %. The results of the velocity measurements are presented in Figure 3.

A clearly pronounced minimum is exhibited for the mass ratio $x/(100 - x) = (5\text{Ti} + 3\text{Si})/(\text{Ti} + \text{C})$ between 20/60 and 50/50, i.e., for $x = 20-50$ wt %. The combustion velocity is seen to decrease by a factor of 3 to 3.5, compared to the binary compositions. This probably evidences for some interdependence between the $\text{Ti} + \text{C} = \text{TiC}$ and $5\text{Ti} + 3\text{Si} = \text{Ti}_5\text{Si}_3$ reactions rather than for their independent run.

The steady-state mode of combustion was observed within the entire range of compositions [3]. The most noticeable deviations from the perfect flat front were observed for the mixtures close to the binary $\text{Ti} + \text{C}$ and $5\text{Ti} + 3\text{Si}$ compositions. The combustion velocity in the compositions $(100-x)(\text{Ti} + \text{C}) + x(5\text{Ti} + 3\text{Si})$ containing two exothermic and fast-burning mixtures decreases by 3 and 3.5 times as compared to that in the $\text{Ti} + \text{C}$ and $5\text{Ti} + 3\text{Si}$ mixtures (Fig. 3). Consequently, the two combustion reactions are somehow retarding each other.

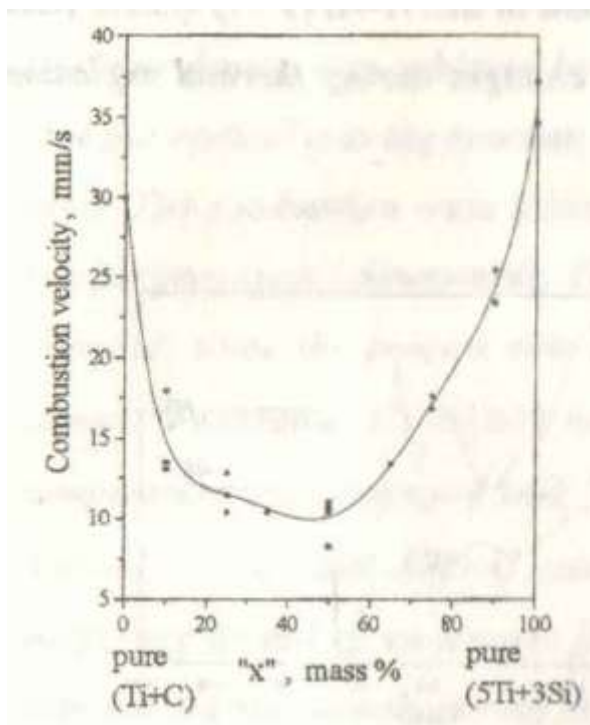


Fig.3. The combustion velocity vs. x for the $(100-x)(\text{Ti} + \text{C}) + x(5\text{Ti} + 3\text{Si})$ mixture temperature and at a green porosity of SOX. of products for the mixture.

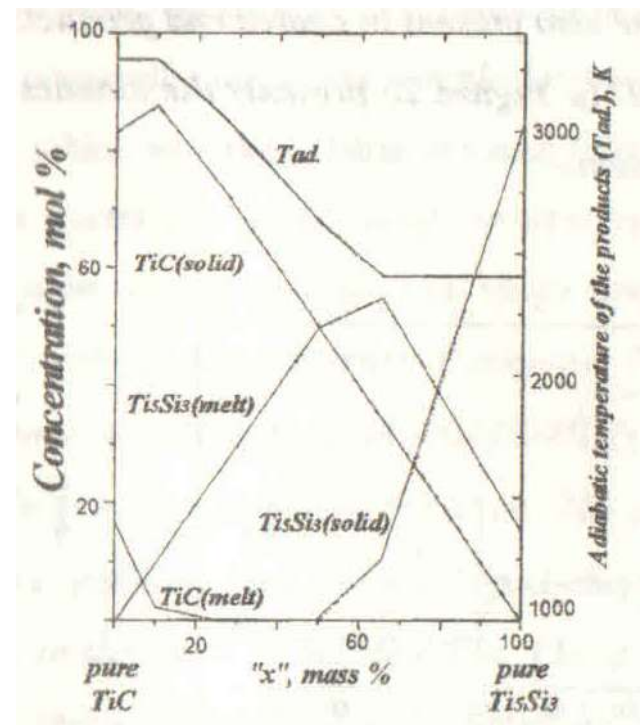


Fig. 4. The results of thermodynamic calculations of the combustion equilibrium concentration $(100-x)(\text{Ti} + \text{C}) + x(5\text{Ti} + 3\text{Si})$

Let us consider the results of thermodynamic calculations of the combustion temperature of the $(100-x)(\text{Ti} + \text{C}) + x(5\text{Ti} + 3\text{Si})$ mixture and the product composition (Fig.

4). At the addition of the Ti + C composition to the 5Ti + 3Si mixture, the volume portion of the solid product Ti_5Si_3 decreases, while the melt portion in the equilibrium products increases at the combustion temperature. The minimum of the combustion temperature (Fig. 3) is observed in the region of $x = 30-50$, within which the portion of solid Ti_5Si_3 turns to zero (Fig. 4) and all silicon gets dissolved in the titanium melt. When keeping in mind that all of the titanium is melted in the combustion wave ($Ti_{m.p.} = 1940$ K), one can propose the following mechanism of the relationship between the $Ti + C = TiC$ and $5Ti + 3Si = Ti_5Si_3$ reactions. The formation of Ti_5Si_3 at gasless combustion was shown to be the result of coalescence of the Ti and Si melts ($Si_{m.p.} = 1678$ K) precipitation of fine crystals of Ti_5Si_3 (the mechanism of reaction coalescence). For TiC to be formed in the SHS regime, the Ti melt should necessarily spread over solid carbon. The latter is dissolved in the melt up to its saturation and fine grains of TiC are crystallized both at the solid carbon surface and in the melt bulk. Thus, carbon and silicon dissolution in the titanium melt may be competing processes exerting an inhibiting effect on their reactions with titanium. Summarizing the above said, it can be supposed that the relationship between the $Ti + C = TiC$ and $5Ti + 3Si = Ti_5Si_3$ reactions is provided by the stage of dissolution of both non- metals in the titanium melt A more detailed description of the proposed mechanism will become possible after investigations of the dynamics of phase formation and the microstructures of the product formed in this system.

Conclusion

In this work, we have investigated the mechanism of phase- and structure formation during self- propagating high-temperature synthesis of Ni - Al, Ti - Al and Ti - Si - C systems. It was found that thermal explosion in the Ni - Al and Ti - Al systems occurred after melting of aluminum. It is possible that at the beginning of phase formation in the Ti - Al system, solid titanium is dissolved In the Al melt Phase content of the end product depends on the starting composition of green mixture. In general, the formation of phase 1:1 (NiAl and TiAl) was found to form first. Then the processes of ordering or phase transformation occurred.

An investigation of the ternary system Ti-Si-C confirmed the assumption about the leading role of dissolution in the combustion mechanism. Both binary mixtures, Ti+C and 5Ti+3Si exhibits relatively high combustion rates. However, combination of these mixtures in the ternary system results in significant decreasing of the combustion velocity.

This effect may be explained taking into account the dissolution mechanism, when both non-metal reactants concurrently dissolve in the metal Ti melt. A study of the product microstructure also shown intermixed grains of TiC and Ti₅Si₃ indicating that these products were co-precipitated from the same matrix melt

Acknowledgements

This work was supported by the Russian Science Foundation (grand No. 96-03-34256a). We thank I.O. Khomenko for performing the TRXRD experiments.

Nomenclature

RT- room temperature, $T_{i,m.p.}$ -melting point for titanium, Si_{mp} - melting point for silicon.

References

- 1. A.G. Merzhanov, I.P. Borovinskaya, Dokl. Akad. Nauk SSSR, 204, 2, 336-369 (1972).*
- 2. A.G. Merzhanov, I. P. Borovinskaya, V.I. Ponomarev, I.O. Khomenko, U.V. Zanevskiy, Dokl. Akad. Nauk SSSR, 328, 2, 72-74, (1993).*
- 3. H.E. Grigoryan, A.S. Rogachev, A.E. Sytschev, International Journal of Self-Propagating High- Temperature Synthesis, 5,1, (1997), in press.*