Research paper

# Synthesis of nitrides through the reaction of a metal jet induced in conical shaped charge penetrated into liquid nitrogen

Kazuyuki Hokamoto*†, Naoyuki Wada**, Shin–ichiro Tsutsumi**, Kazunori Akiyoshi**, Shigeru Tanaka***, Shoichiro Kai****, and Yasuhiro Ujimoto****

*Shock Wave and Condensed Matter Research Center, Kumamoto University, 2–39–1 Kurokami, Kumamoto 860–8555, JAPAN
TEL +81–96–342–3292 FAX +81–96–342–3293
†Corresponding address : hokamoto@mech.kumamoto–u.ac.jp

**Graduate School of Science and Technology, Kumamoto University

***Faculty of Engineering, Kumamoto University

****Chikushino Plant, Asahi–Kasei Chemicals Corp., Yamae, Chikushino, Fukuoka 818–0003, JAPAN

Received : April 16, 2010 Accepted : May 13, 2010

## Abstract

A new approach for synthesizing nitride intermetallics is proposed in the present investigation. The source of nitrogen is liquid nitrogen and the reaction was induced by a metal jet generated by conical shaped charges. An aluminum jet, generated by an aluminum cone, was penetrated into liquid nitrogen mixed with titanium powders. Under a moderate condition, some small sized blocks of 2–3 mm were recovered and the blocks were characterized. The results confirmed the evidence of inducing intermetallics, and the intermetallics formed were titanium nitride and titanium–aluminum nitrides.

***Keywords*** : synthesis of intermetallics, reaction synthesis, conical shaped charge, metal jet, liquid nitrogen

## 1. Introduction

Shock–induced chemical reaction has been investigated to synthesize various intermetallics by researchers [1)–4)]. This technique has good potential for obtaining ultra–fine grained structure which is expected to improve the properties of the synthesized materials [5) 6)]. The ultra–fine grained structure in the order of nanometer size can be obtained by the intensive deformation in a short period of time caused by the rapid change in the physical state including pressure as well as the temperature. The synthesis of intermetallics by the use of an extremely high pressure has been investigated by gas–gun or explosively accelerated assembly [1)–4)]. Using such system, pressures up to the order of several tens of GPa can be applied to the mixed elemental powders placed in a metal capsule to induce chemical reaction to form various intermetallics.

A different method for synthesizing nitrides through high–velocity chemical reaction was developed by some of the authors [7)]. The method uses wire explosion by an electrical discharge. In this case, a titanium wire was exploded in liquid nitrogen and reaction products were fully reacted into titanium nitride powders whose size was several tens of nanometers. The same type of reaction may be possible when a metal is accelerated to the same range of velocity. The use of high–velocity collision of elements is essential to induce such reaction. The authors have developed a new method for shock–induced synthesis using conical shaped charge. Conical shaped charges are well known for making holes on a thick metal plate [8)]. A metal jet formed by an extremely high–velocity material flow having an extremely high kinetic energy is generated ahead of the collision point of the metal cone. This metal jet plays an impor-

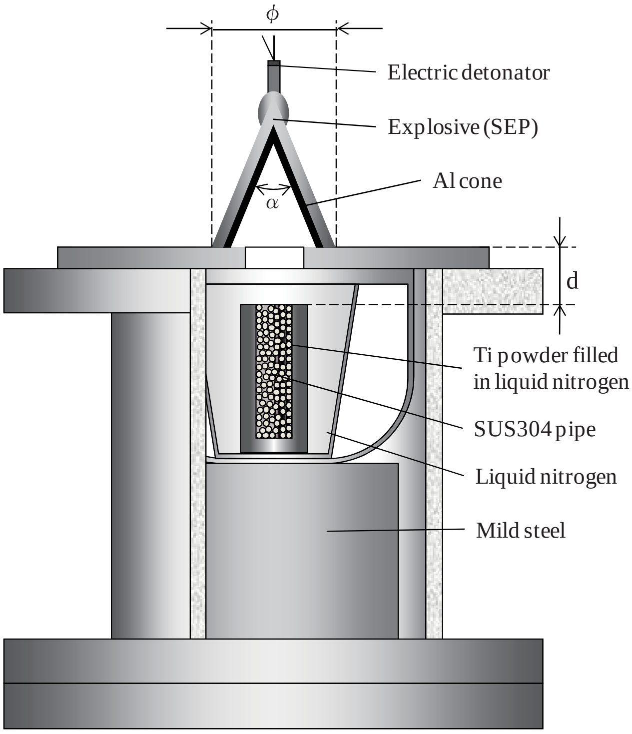


**Fig. 1** Assembly used for recovery experiments.

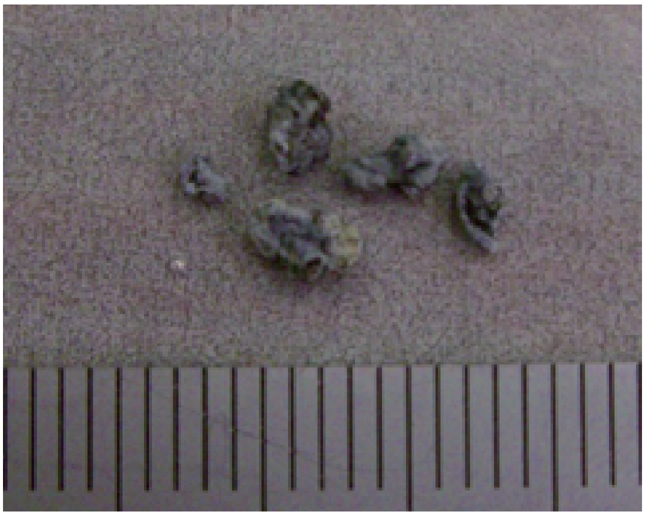

**Fig. 2** Appearance of small blocks recovered (d = 10 mm).

tant role to remove the collided metal part. In this investigation, an aluminum metal jet was penetrated into liquid nitrogen mixed with titanium powders. Since the ceramics namely, titanium nitride, aluminum nitride and titanium–aluminum nitride, are well known for its application in engineering [9) 10)], the authors tried to investigate the basic phenomenon from the recovered samples.

## 2. Experimental

The assembly used for the experiments is illustrated in Fig. 1. The thickness of the aluminum cone was 1.2 mm and the cone angle α was fixed at $45^0$. The diameter of charge ϕ was 33.5 mm. An explosive SEP, produced by Kayaku Japan Co., Ltd, of 5 mm thickness was set on the cone. The detonation velocity and the density of the SEP explosive are about 7.0 km $s^{-1}$ and 1300 kg $m^{-3}$, respectively. The mass of the explosive used for the recovery experiment was 24 g and the explosive was detonated by an electric detonator placed on the upper side of the cone. Prior to the recovery experiments, the assembly was used for penetration experiment in which the metal jet fully penetrated 10 layers of steel plates, each of 2 mm thickness. Two experiments were conducted by changing the distance ***d*** between the cone base and the liquid nitrogen mixed with spherical titanium powders (average diameter 45 μm, OSAKA Titanium technologies Co., Ltd.). The distance ***d*** was set at 10 and 20 mm for the experiments, but only in the experiment when ***d*** = 10 mm small reacted blocks were recovered as shown in Fig. 2. The blocks were small fragments in the order of several mm in length.

The velocity of the jet is estimated based on a simple geometrical relationship as illustrated in Fig. 3. At first, the velocity of the metal plate $V_p$ was estimated based on the Gurney equation [8)] expressed as follows,

$$V_p = \sqrt{2E}\,\{3R^2/(R^2+5R+4)\}^{1/2} \quad (1)$$

where $E$ is Gurney energy and $E = 2.16 \times 10^6$ J $kg^{-1}$ [11)] for SEP explosive used, and $R$ (= $c\,m^{-1}$) is the mass ratio of explosive $c$ and metal plate $m$. Then, the velocity of the metal jet $V_j$ is estimated based on the Brikhoff's equation [12)] as follows,

$$V_j = V_p\,\{\cos(\beta/2)/\sin\gamma + \cos(\beta/2)/\tan\gamma + \sin(\beta/2) \quad (2)$$

where $\beta$ is the dynamic bending angle and $\gamma$ is the collapse angle of the cone. Using the equation, the velocity of the aluminum jet was estimated as 5999 m $s^{-1}$ which is

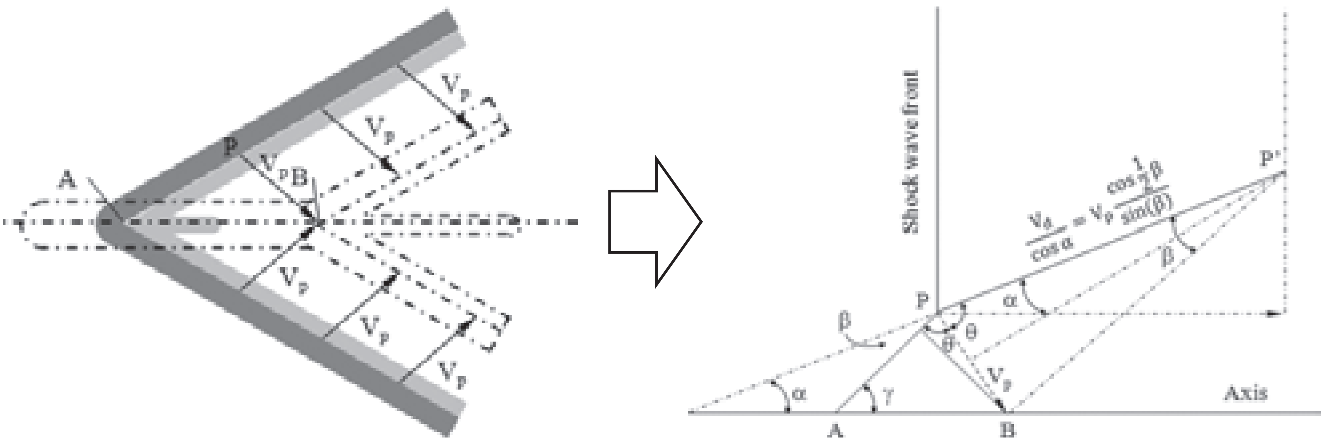


**Fig. 3** Geometrical relationship for estimation of jet velocity.

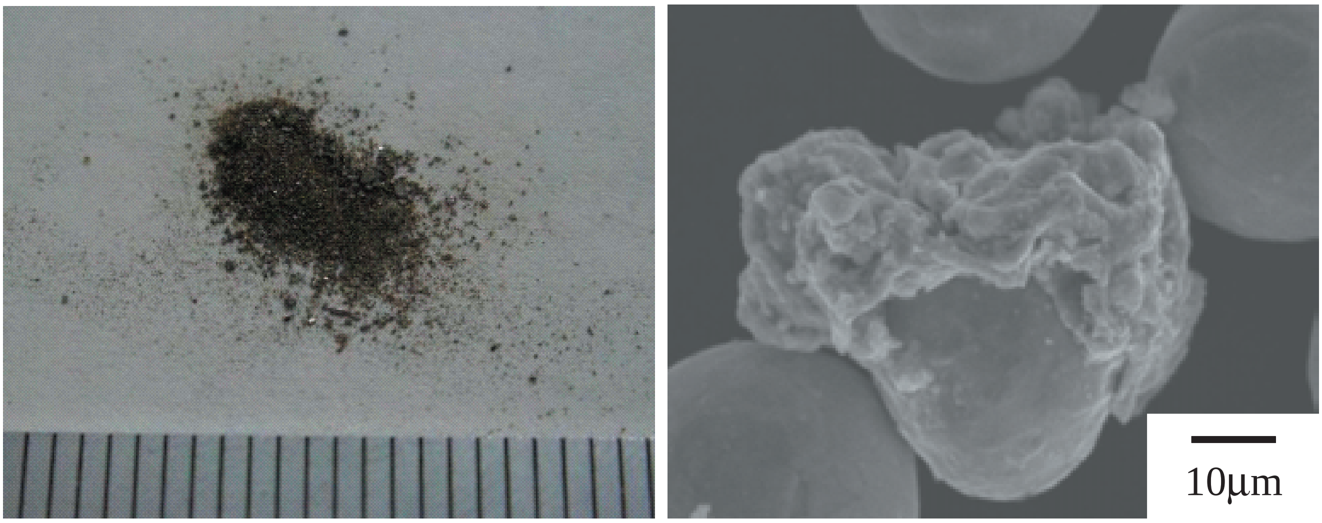


**Fig. 4** Appearance of recovered powders (a) and its SEM image (b) (d = 20 mm).

high enough to induce chemical reaction. Optical observations are required to estimate the actual velocity of metal jet. However, it is quite difficult to observe and measure, so we focused only on detecting a chemical reaction caused by a metal jet.

The samples recovered were characterized for the microstructure using optical and scanned electron microscopes (SEM), and electron probe microanalyzers (EPMA).

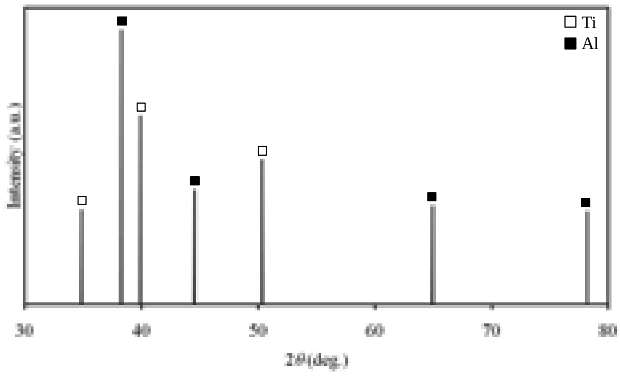


**Fig. 5** X−ray diffraction pattern (Cu−Kα) for recovered powders (d = 20 mm).

## 3. Results and discussion

As shown in Fig. 2, the reaction seems induced only for the case *d* = 10 mm. Figure 4 shows the macro− and microscopic structure when *d* = 20 mm. The SEM image (Fig. 4 (b)) shows recovered powder for the condition *d* = 20 mm, and it seems that an aluminum droplet was trapped on a spherical titanium powder. As seen in the X−ray diffraction pattern shown in Fig. 5, no reacted product was confirmed by this experiment. It is considered that the reaction was not induced due to the decrease in the velocity of the metal jet during relatively long travelling distance in air. From these results, it is clear that the reactivity is effected by the distance *d* which causes the change of velocity and pressure for inducing chemical reactions. The velocity and pressure of metal jet for inducing the chemical reaction require more research.

One of the recovered samples obtained under the condition *d* = 10 mm was cut and polished to characterize its microstructure. The picture taken by optical microscope is shown in Fig. 6 and it is confirmed that the cross−section contains many pores. These pores are formed during the cooling from the molten phase. The average micro−Vickers hardness under load 0.098 N (10 g) was in the order of 650−1200 HV, which is quite harder than the metals, and this fact is considered as one of the evidences to form nitride ceramic(s). The details of the hardness distribution will be discussed later.

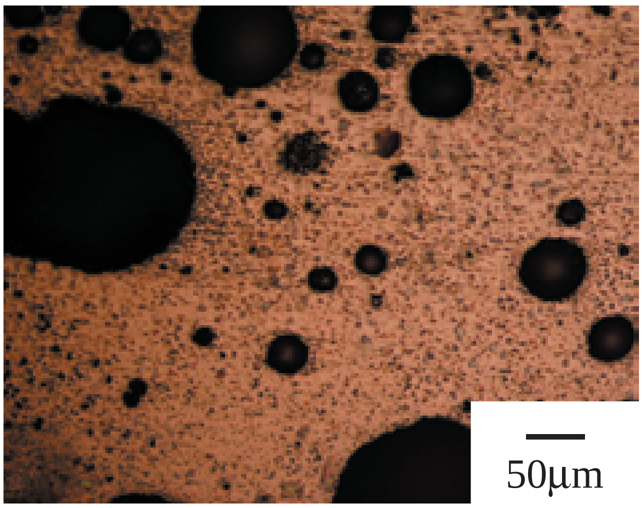


**Fig. 6** Microstructure of cross−section of reacted sample (d = 10 mm).

The X−ray diffraction pattern for the sample *d* = 10 mm, is shown in Fig. 7. In the figure, no aluminum or titanium peaks are found and the peaks of titanium nitride (TiN) and titanium−aluminum nitrides are confirmed. The titanium−aluminum nitrides are identified as $Ti_2AlN$ and $Ti_3AlN$. It is interesting to note that aluminum is not the major component of the reaction products even though an aluminum jet was used. It is considered that the aluminum jet plays a role to ignite a sustainable reaction between the components placed at the position based on the SHS (Self−propagating High−temperature Synthesis) [13) 14)] process.

A SEM image is shown in Fig. 8. Figure 8 (a) shows the cross−section of one block and the central large cavity

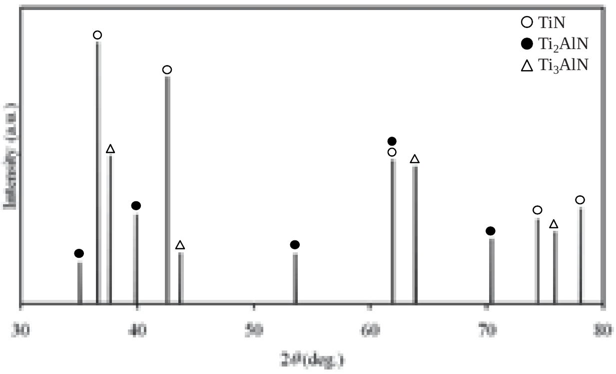


**Fig. 7** X−ray diffraction pattern (Cu−Kα) for recovered block (d = 10 mm).

**Table 1** Chemical composition measured by EPMA for recovered block (d = 10 mm).

| Position No. | Ti content (at %) | Al content (at %) | N content (at %) |
|---|---|---|---|
| 1 | 40.30 | 4.07 | 55.63 |
| 2 | 60.86 | 18.22 | 20.92 |

suggests that the block is formed by cooling from a molten part. The backscattered image (Fig. 8 (b) and (c)) illustrates the distribution of the elements where bright area is composed of heavy element(s) and dark area includes light element(s). In Fig. 8 (c), there are two compositionally different areas. Since the bright region is composed of heavy element(s), such region close to the central cavity seems to be titanium nitride. The other area close to the edge of a block is considered as titanium−aluminum nitride(s). The mapping of elements taken by EPMA is shown in Fig. 9, and the results of point analysis by EPMA are listed in Table 1. The number (1 or 2) corresponds with it as shown in Fig. 8 (c) and in Fig. 9. The results of the analysis also suggest that the central area is composed of titanium nitride (TiN) and the other area is composed of titanium−aluminum nitride whose composition is closer to $Ti_3AlN$. The area composed of $Ti_2AlN$ is not clearly confirmed by the SEM and EPMA images because of the slight difference in the chemical composition in the area containing titanium, aluminum and nitrogen. Since titanium−aluminum nitride was confirmed especially in the edge of the block, the location should be closer to the central axis of the powder container. Therefore, a process inducing reaction from center (aluminum jet part) to periphery (Ti−N reaction) as illustrated in Fig. 10 is suggested. During the cooling from liquid, the area was separated into small fragments (blocks) and central and other cavities as illustrated in the figure are formed.

The average micro−Vickers hardness of TiN was 767 HV (648 $HV_{min}$− 839 $HV_{max}$), and 1067 HV (876 $HV_{min}$− 1219 $HV_{max}$) for titanium−aluminum nitride part. These values are not in correspondence with the reported data for these materials [15) 16)]. These values are slightly lower than the reported data which may be caused by the presence of the cavities in the bulk region recovered after cooling from molten phase.

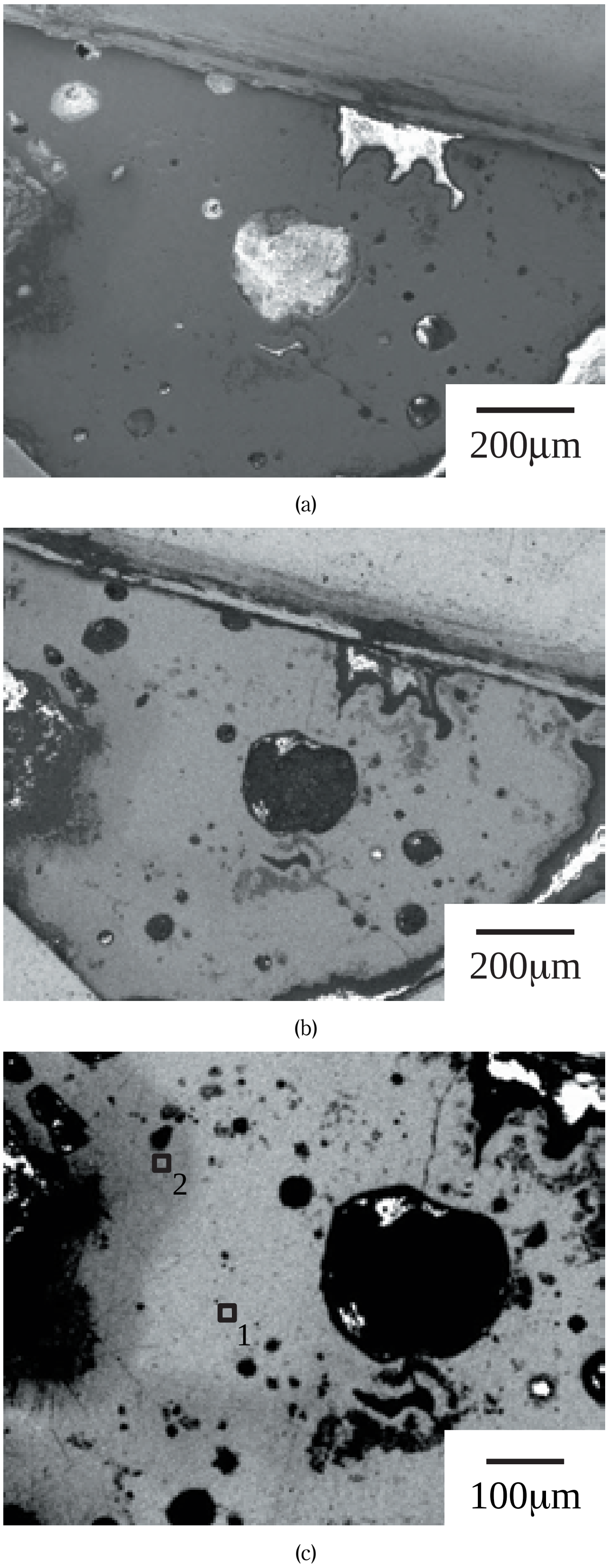


**Fig. 8** SEM image of recovered block (d = 10 mm) (a), its backscattered electron image (b), and enlarged backscattered image (c).

The velocity and pressure of the metal jet should be understood to describe the mechanism of the chemical reaction. However, without this understanding, the data from this experiment shows that the aluminum jet reacted with the titanium and nitrogen to achieve bulk nitrides with high hardness. The authors will describe the mechanism

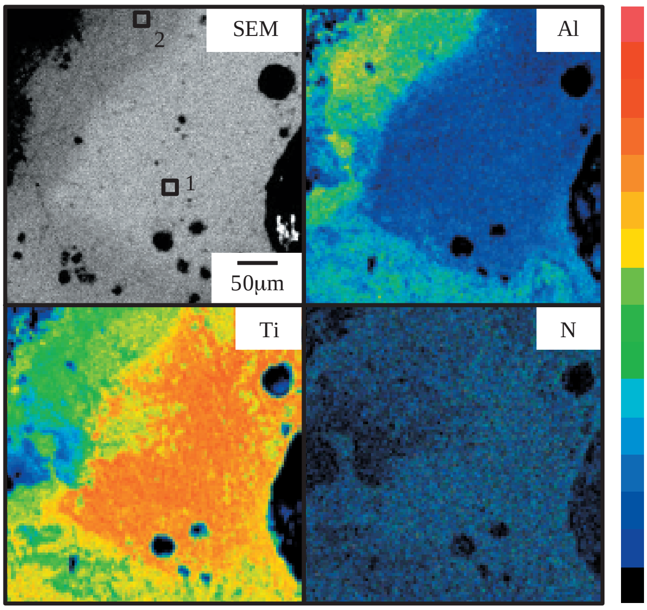


Fig. 9 Mapping of elements for recovered block (d = 10 mm) taken by EPMA.

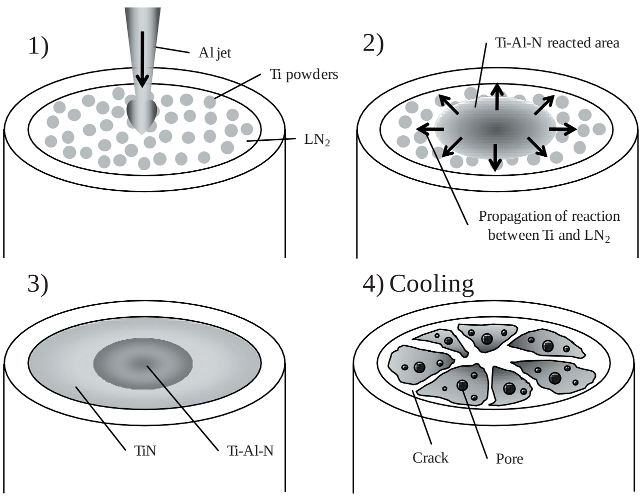


Fig. 10 Schematic illustration of reaction process.

after establishing measurement methods in future.

## 4. Conclusions

A new method to synthesize nitride ceramics using conical shaped charges is proposed and the possibility to induce chemical reaction of the elements is demonstrated. An aluminum cone was highly accelerated as metal jet in the order of 6 km $s^{-1}$ and collided with liquid nitrogen mixed with titanium powders. Under a moderate condition, some small blocks having high hardness were recovered and the blocks were composed of titanium nitride and titanium–aluminum nitrides formed by chemical reaction. The reaction process was discussed based on the chemical component analysis at different positions in the cross–sectional area.

## Acknowledgements

The research was supported by Global–COE Program "Pulsed Power Engineering". The help of the explosion experiments by Mr. Susumu Akimaru and Mr. Kenichi Matsuyama, Shock Wave and Condensed MatterResearch Center, Kumamoto University is gratefully acknowledged.

## References

1) N. N. Thadhani, J. Appl. Phys. 76, 2129 (1994).
2) N. N. Thadhani, R. A. Graham, T. Royal, E. Dunbar, M. U. Anderson, G. T. Holman, J. Appl. Phys. 82, 1113 (1997).
3) T. Aizawa, T. Kato, K. Tanaka, Y. Nakayama, Intermetallics 3, 369 (1995).
4) K. Hokamoto, J. S. Lee, M. Fujita, S. Itoh, K. Raghukandan, J. Mater. Sci. 37, 4073 (2002).
5) K. Uenishi, T. Matsubara, T. Shibutani, K. Kobayashi, Intermetallics 10, 105 (2002).
6) E. E. Zhurkin, T. V. Hoof, M. Hou, Phys. Rev. B 75, 224102 (2007).
7) K. Hokamoto, N. Wada, R. Tomoshige, S. Kai, Y. Ujimoto, J. Alloy. Compd. 485, 573 (2009).
8) M. A. Meyers, Dynamic Behavior of Materials, John Wiley & Sons Inc. (1994)
9) S. PalDey, S. C. Deevi, Mater. Sci. Eng. A 342, 58 (2003).
10) J. Shin, D. H. Ahn, M. S. Shin, Y. S. Kim, J. Am. Ceram. Soc. 83, 1021 (2000).
11) S. Itoh, Handbook of Shock Waves (Eds., G. Ben–Dor, O. Igra, Tov Elperin), Academic Press, 3, 263 (2001).
12) G. Brikhoff, D. P. Macdougall, E. M. Pugh, G. Taylor, J. Appl. Phys. 19, 563 (1948).
13) A. G. Merzhanov, Ceram. Int. 21, 371 (1995).
14) A. G. Merzhanov, J. Mater. Proc. Tech. 56, 222 (1996).
15) L. P. Ward, K. N. Strafford, C. Subramanian, T. P. Wilks, J. Mater. Proc. Tech. 56, 375 (1996).
16) T. Yamazaki, Y. Okumura, K. Desaki, T. Kikuta, H. Anada, N. Nakatani, Vacuum 83, 479 (2009).

# コニカルシェープトチャージによって生じた金属ジェットと液体窒素の反応による窒化物の合成

**外本和幸*†，和田直之**，堤慎一郎**，秋吉一徳**，田中茂***，甲斐彰一郎****，氏本泰弘****

本研究では，新しい窒化物化合物の合成法について研究を行った。本方法における窒素の供給源は液体窒素であり，これとコニカルシェープトチャージによって生じる金属ジェットとの間に生じる反応を誘起させることを行った。アルミニウム製コーンを用いたアルミニウムジェットをチタニウム粉末を混ぜた液体窒素中へ打ち込む実験が実施された。その結果，ある条件において２－３mmの寸法を有するいくつかの塊状物が回収され，それらは解析の結果，窒化チタンや窒化チタンアルミニウムといった金属間化合物からなることが確認された。

*熊本大学衝撃・極限環境研究センター　〒860-8555　熊本市黒髪2-39-1
TEL：096-342-3292　FAX：096-342-3293
†Corresponding address：hokamoto@mech.kumamoto-u.ac.jp

**熊本大学大学院自然科学研究科

***熊本大学工学部

****旭化成ケミカルズ㈱筑紫野工場　〒818-0003　福岡県筑紫野市山家