

Effect of microstructure control on the reaction characteristics in Al/Ni reactive powder

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Abstract

A microstructure and reaction characteristics that appear in Al/Ni reactive materials and the correlation between those were investigated. 3 types of Al/Ni reactive material powders, that are clearly distinguishable in terms of microstructure, were prepared by using 3 kinds of mixing processes (i.e. turbula mixing, attrition milling, and planetary milling). The Al/Ni powder prepared by using turbula mixer shows that the shape was maintained from initial state of raw Al and Ni powder. In contrast, the Al/Ni powder prepared by using attrition mill shows that the shape was distorted and grain size largely decreased from the raw materials. And the powder prepared by using planetary mill was completely deformed from the initial state of raw materials and represents a new type of microstructure (i.e. nano-lamella structure). To compare the reaction initiation temperatures of these powders, differential scanning calorimetric analysis was performed. As a result, the initiation temperature varied more than 200 °C according to the changes in microstructure. In order to compare reaction rate, 3 types of compacts which is consolidated from the different powders were also observed for their reaction characteristics by high speed camera at a condition of 10,000 fps (frame per seconds). And it was found that the reaction rates also varies greatly depending on the microstructure of the powders. These results suggest that reaction characteristics of reactive materials can be controlled by tailoring their microstructure.

Keywords: reactive materials, mechanical alloying, nano-lamella, Al-Ni reactive powder, self-propagating reaction

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1. Introduction

Recently, the studies have been attracting attention to use Reactive Materials (RM) and Reactive Material Structures (RMS) for military purposes [1]. RM are usually classified into two categories. One is an intermetallic system in which an intermetallic reaction occurs between a metal and a metal such as Al-Ni [2], Al-Zr [3], and Al-Ti [4] and the other is a thermite system in which a thermite reaction occurs between a metal and a metal oxide such as Al-CuO [5], Al-MoO₃ [6], and Al-Fe₂O₃ [7]. The RMS are usually prepared by structuralizing RM of a powder state. For structuralizing, cold isostatic pressing and cold spray techniques are generally used.

RMS are also called as HDEM (High Density Energetic Materials) in a sense that

they are structurally very stable energetic materials, unlike conventional energetic materials such as explosives and propellants [8]. Since RMS are not only energetic materials but also structural materials, they are very attractive materials in that they can be utilized as energy-releasing structural materials [8]. For example, when RMS is used as a case of warhead, the energy per unit mass of the warhead can be increased up to two times compared to when conventional structural materials are used such as steel [1]. This is because the RMS is not a simple structural materials such as steel but an energetic structural material that can react in the explosion environment and thus release additional energy.

RMS could be utilized in a variety of military use as structural materials, but there are still many technical obstacles to overcome. In particular, the reaction rate of ordinary RMS is in a cm/s level [1], which is very slow compared to the reaction rate of common explosives (km/s), so it may not be suitable for military use as energetic materials that require a lot of energy release in a short time. However, if the microstructure of RMS is reduced to a nanometer level, the reaction rate could be increased more than 100 times [1], and the reaction initiating point could also be lowered. However, if we use just nano-sized raw materials to prepare the nanostructured RMS, first, it is dangerous to handle, second, it becomes very difficult to mix (due to agglomeration of nano-powder), and third, the manufacturing cost may also be increased.

It has been attempted to produce nanostructured RM without nano-powder. As a representative example, a high-energy ball mill such as Attrition Mill (AM) or Planetary Mill (PM) have been used to induce mechanical alloying of micro-sized raw powders [9]. The preparation of nanostructured RM using a high-energy ball mill is very useful in terms of that it is safer than using a nano-powder and the manufacturing cost could be lowered. In this study, RM powder were prepared with different mixing method (i.e. TM, AM and PM) in Al-Ni system, and microstructural changes were analyzed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). And the reaction initiation temperatures and the reaction rates of the prepared RMS were also compared according to the microstructural changes of the RM powders.

2. Experimental procedures

2.1. Materials preparation. RM powder samples were prepared using Al powder (10SF, ChangSung, South Korea) with a 99.0% purity and 10 μm average particle size and Ni powder (T123, Vale, Canada) with a 99.8% purity and 4 μm average particle size. The Al powder and Ni powder were mixed with 31.5 wt.% Al - 68.5 wt.% Ni composition, using TM, AM, and PM. The method of each mixing process are shown in Table 1. It is note that a cooling step of 10 minutes was added between each mixing step to reduce the heat generated by the mixing process. When preparing RM powder using TM (TM-powder), 100 g of Al/Ni powder, 500 g of stainless steel ball (10 mm) and inert gas (3 bar of Ar) were added in a cylindrical jar of 2L, and the mixture was mixed twice at 60 rpm for 15 minutes. When preparing RM powder using AM (AM-powder), 100 g of Al/Ni powder, 500 g stainless steel ball (10mm), inert gas (3 bar of Ar), and 360cc hexane were added in a 2L size cylindrical jar, and the mixture was milled twice at 400 rpm for 10 minutes. When preparing RM powder using PM (PM-powder), 70 g of Al/Ni powder, 350 g of stainless steel ball (10 mm), and inert gas (3 bar of Ar) were added to a 500 ml cylindrical jar, and the

mixture was milled twice at 600 rpm for 5 minutes. And then 40 cc of hexane was added to the milling jar, and the mixture was further milled twice at 600 rpm for 5 minutes. The prepared three types of RM powders were uniaxially compacted at 300 MPa to form pellets having a diameter of 5 mm and a height of 2 mm.

Table 1. Processing conditions according to mixing methods (TM: Turbula Mixing, AM: Attrition Milling, PM: Planetary Mill, RPM: Rotation per Minute, BPR: Ball to Powder Ratio)

Method	Conditions	1st step	2nd step	3rd step	4th step
TM	PCA	-	-	No action	
	Atmosphere	Ar (3 bar)	Ar (3 bar)		
	RPM	60	60		
	BPR	5:1	5:1		
	Duration (min)	15	15		
AM	PCA	Hexane (360 cc)	Hexane (360cc)	No action	
	Atmosphere	Ar (3 bar)	Ar (3 bar)		
	RPM	400	400		
	BPR	5:1	5:1		
	Duration (min)	10	10		
PM	PCA	-	-	Hexane (40 cc)	Hexane (40 cc)
	Atmosphere	Ar (3 bar)	Ar (3 bar)	Ar (3 bar)	Ar (3 bar)
	RPM	650	650	650	650
	BPR	5:1	5:1	5:1	5:1
	Duration (min)	5	5	5	5

2.2. Material characterization. Internal microstructure of the RM powder was analyzed by SEM (S-4800, Hitachi, Japan) and TEM (Tecnai G² F30 S-twin, FEI, Netherlands). TEM samples were prepared using a FIB (Focus Ion Beam; Nova 200, FEI, Netherlands). Phase analysis of the prepared RM powders was performed using HR-XRD (High Resolution X-ray Diffraction, X' Pert-Pro MRD, PANalytical, Netherlands) equipped with Ni-filtered Cu K α radiation.

2.3. Reaction characterization. DSC (STA 449 F5, Netzsch, Germany) analysis was also performed for the thermal characterization of the RM powder and the RMS. The thermal analysis was carried out under the conditions of a heating rate of 10 ° C/min and an atmosphere of pure Ar (5N) with a flow rate of 20 cc/min. The obtained DSC data were analyzed using Netzsch proteus thermal analysis software. In order to compare the reaction rate of RMS pellets, the samples were heated for 100 seconds on a torch set at 1000 ° C, and the occurred reaction phenomenon was observed by high speed camera (dimax HS4, PCO co., Germany) set at 10,000 frames/sec.

3. Results and discussion

3.1. Material characterization. Figure 1 shows the microstructure of the Al and Ni raw powder used in this study. The Al particles show a smooth spherical shape (Fig. 1 (a)), and one particle is consisted of one crystal (Fig. 1 (b)). In contrast, the surfaces of the Ni particles show spiky shapes (Fig. 1 (d), (e)), and one particle is consisted of several grains with different orientations, and then several grain boundaries were observed in the particle as shown in fig. 1 (f). In addition, a passivation layer of about 5 nm, which is regarded as Al₂O₃, was uniformly observed on the surface of the Al particle (Fig. 1 (c)), but additional

layer such as an oxide film was not observed on the Ni particle surface. (Fig. 1 (f)).

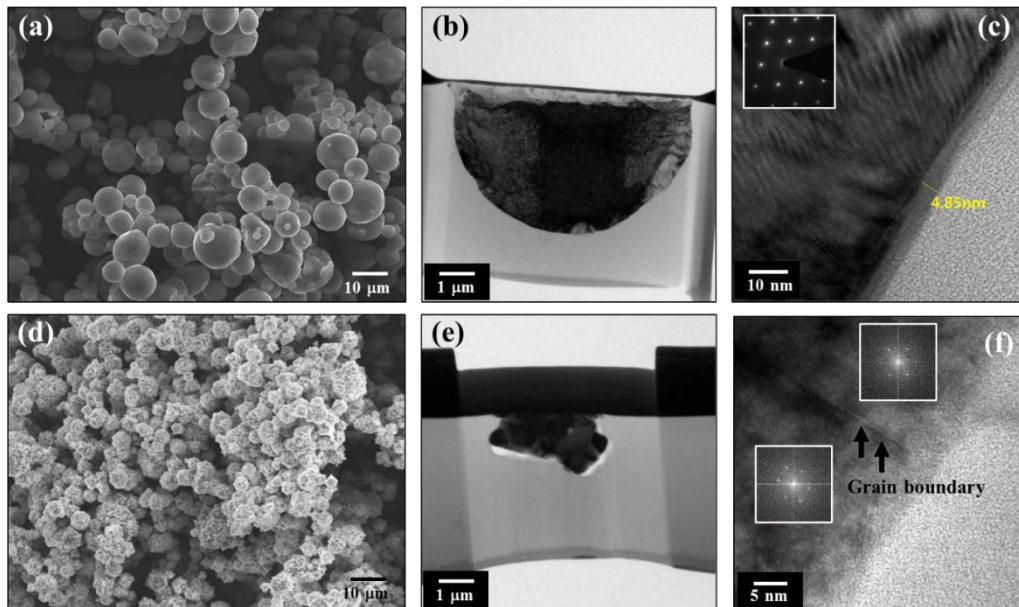


Fig 1. (a) SEM, (b) BF-(bright field-) TEM, and (c) HR-(high resolution-) TEM image of Al powder and (d) SEM, (e) BF-TEM, and (f) HR (high resolution) TEM image of Ni powder

The XRD peaks of the prepared RM powders were examined in order to confirm whether a secondary phase such as Al_mNi_n intermetallic formed during the mixing process. As a result, no visible peaks were observed except for Al and Ni peaks as shown in Fig. 2, and it was also difficult to recognize the differences in XRD patterns acquired from the different RM powders.

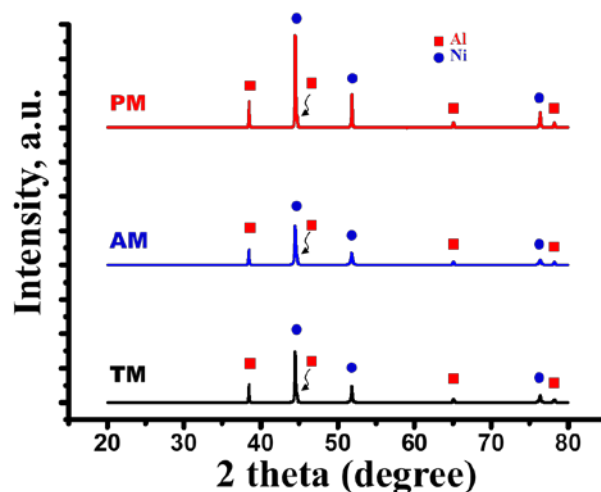


Fig. 2. XRD patterns for RM powders prepared by TM, AM, and PM.

In order to investigate the changes in microstructure according to the mixing methods, the RMS pellets were cut, the cut surfaces were polished, and the cut surfaces were observed by SEM. As a result, the microstructure of each powder are clearly distinguishable. The microstructure of TM-powder shows the original shape of Al and Ni raw powder. However, the microstructure of AM-powder is significantly

different from the shape of raw powder. In particular, the needle shape of the Ni raw powder disappear, and the overall shape is also elongated. In the case of PM-powder, the original shape of the raw material is completely collapsed and mixed at the nano-level.

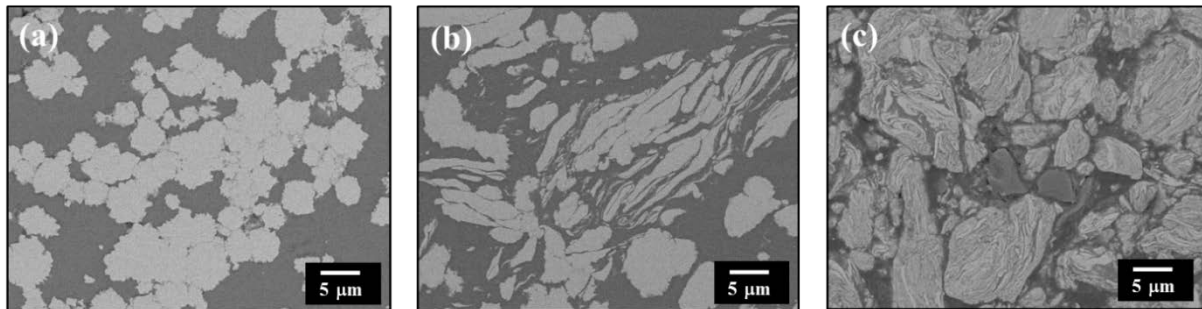


Fig 3. Back scattered SEM images for (a) TM- (b) AM- (c) PM- powders (in the figures, grey areas represent Al and white areas represent Ni)

The crystallographic microstructure of each RM powder was observed by TEM, and the results are shown in fig. 4. In the case of TM-powder, the needle shape which was observable in the Ni raw powder is maintained even after the mixing. However, Al particles which were confirmed as one grain, are broken into several grains of ca. 1 μm after the mixing. In the case of AM-powder, Al grain refinements are more pronounced, and most of the grains are found as ca. sub-micron size, and the needle shapes of Ni surface almost disappear. In addition, a number of lamella - type microstructures is observed in which several tens of nanometers of Al layer and Ni layer are alternately stacked. In the case of PM-powder, a typical mechanical alloying microstructure, in which Al layers and Ni layers are alternately stacked, that is, nano-lamella microstructure, is observed throughout the specimen.

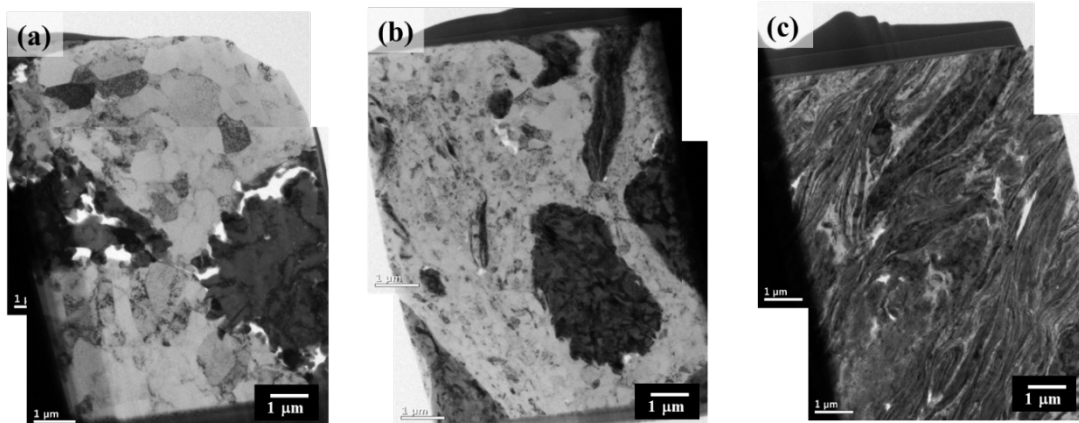


Fig 4. BF-TEM images for (a) TM- (b) AM- (c) PM- powders (bright areas represent Al and dark area represent Ni in these figures)

3.2. Reaction characterization. DSC analysis was carried out to analyze the thermal characteristics of RM powders and RMS pellets with the change of microstructure. The results are shown in Fig 5. The exothermic curve of PM-powder is much broader than that of TM-powder and AM-powder, and the reaction initiation temperature of PM-powder is found to be at least 200 degrees lower than that of other powders as shown fig. 5 (a). The decrease in reaction initiation temperature

is thought to be due to the decrease in grain size of RM powders. The total heat formation is gradually decreased in the order of TM-powder (720 J/g), AM-powder (630 J/g), and PM-powder (540 J/g). The reduction of heat formation is thought to be due to the partial reaction that capable to occur during milling (although any intermetallic phase could not be observed in XRD analysis).

The decrease of the reaction initiation temperature and the reduction of heat formation of the PM-powder were similarly observed in the DSC curves of the RMS pellets as shown fig. 5 (b). In the analysis of the RMS pellets, the reaction initiation temperature of the TM-pellet or the AM-pellet tends to decrease by more than 100 degrees from the reaction initiation temperature in the analysis of the RM powder. These results suggest that the changes of reaction initiation temperature is not only related to grain size reduction but also related to whether the reactant materials are contacted each other. In order for the intermetallic reaction, inter-diffusion between Al and Ni materials should occur smoothly. However, in a powder state, there is no direct contact interface between Al and Ni, and the paths of inter-diffusion are surely limited. In order words, in a powder state, the reaction proceeds only through the evaporation diffusion path, whereas in a consolidated pellet state, the reaction can proceed through the grain boundary diffusion path and the surface diffusion path, and hence, the reaction initiation temperature could be greatly reduced below the Al melting temperature.

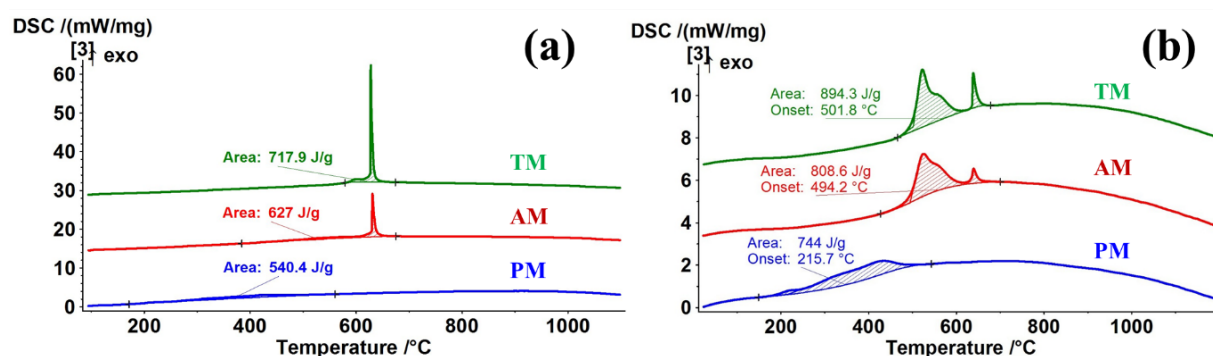


Fig 5. DSC curves obtained using (a) RM powders and (b) RMS pellets

In order to observe the self-propagation reaction [10] of three kinds of RMS pellets, the reaction phenomena occurred by heating one side of the pellet was photographed with high speed camera at 10,000 fps condition. In the case of the TM-RMS pellet, the reaction did not occur even after 100 seconds of heating. In the case of the AM-RMS pellet, a reaction started at the heated surface of the pellet after about 12 seconds of heating, and the reaction propagation was completed within 100 ms as shown fig. 6 (a)-(c). On the other hand, in the case of the PM-RMS pellet, the reaction started after about 2 seconds of heating, and the reaction propagation was completed before 10 ms as shown fig. 6 (d)-(f). That is, the reaction propagation rate of the PM-RMS pellet was about 10 times faster than that of AM-RMS pellet. In addition, the AM-RMS pellet showed a mild reaction propagation with maintaining the original shape, but the PM-RMS pellet showed a very rapid reaction propagation by splashing the fragments in all directions as shown fig. 6. These differences in the propagation phenomena were thought to be due to the microstructural differences of RMS.

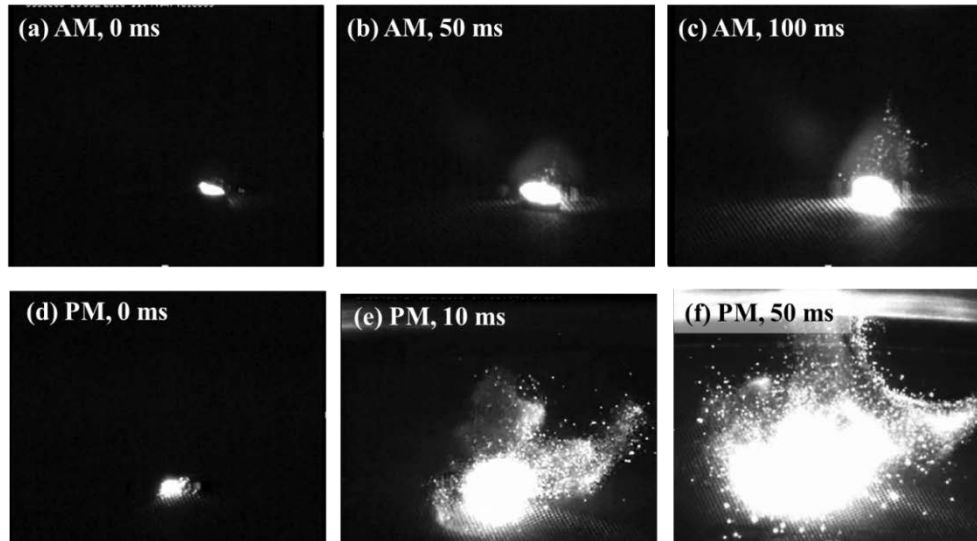


Fig 6. Self-propagation reaction images observed at (a) 0 ms, (b) 50 ms, and (c) 100 ms for AM-RMS pellet and (d) 0 ms, (e) 10 ms, and (f) 50 ms for PM-RMS pellet.

4. Conclusions

Three types of Al/Ni RM powders were prepared by varying mixing methods, and their reaction characteristics were compared. The TM powder showed just mixed microstructure with maintaining the shape of the Al and Ni raw powder. In contrast, the AM powder showed a distorted microstructure deviating from the original shape of raw powder. And PM powder showed a completely new microstructure (i.e. nano lamella structure) deviating from the shape and average size of the raw powder. Three kinds of Al/Ni RM powders are clearly distinguishable in terms of microstructure. DSC analysis was performed to compare the reaction initiation temperature of these RM powders. As a result, the reaction initiation temperatures of RM powders and RMS pellets varied more than 200 °C with changing the microstructure. In order to compare the self-propagation reaction phenomena of the three kinds of RMS pellets, the generated reactions resulting from heating one side of the pellet were recorded with high speed camera at 10,000 fps condition. As a result, it is confirmed that the reaction propagation rate varies greatly depending on the microstructure of RMS. These results suggest that the reaction characteristics of the RMS could be controlled by tailoring the microstructure of RM and RMS.

Acknowledgements

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