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Research Article

Effect of the Dispersibility of Nano-CuO Catalyst on Heat Releasing of AP/HTPB Propellant

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Kneading time is adjusted to change the dispersibility of nano-CuO in AP/HTPB (Ammonia Perchlorate/Hydroxyl-Terminated Polybutadiene) composite propellants. Nano-CuO/AP is prepared to serve as the other dispersing method of nano-CuO, named predispersing procedure. Several kinds of heat releasing, thermal decomposition by DSC, combustion heat in oxygen environment, and explosion heat in nitrogen environment, are characterized to learn the effect of dispersibility of nano-CuO catalyst on heat releasing of propellants. With pre-dispersing procedures, thermal decomposition temperature of nano-CuO/AP and its propellant are about 25°C and 8.6°C lower than that of AP simple mixed with nano-CuO and its propellant, respectively. Comparing propellant with simple mixed nano-CuO kneading 3 hours, combustion heat and explosion heat of propellant with nano-CuO/AP increase about 1.4% and 1.7%, respectively. However, because of the breaking of nano-CuO/AP structure during kneading procedure, combustion heat and explosion heat of all the samples are decreased with the increase of kneading time after 3 hours.

1. Introduction

In recent years, there has been an explosion of interest in the synthesis, structure, properties, and applications of nanomaterials, mainly because of the fact that materials confined in one or more dimension can exhibit interesting properties, such as catalysis. Copper oxide (CuO) has been reported as a thermal decomposition catalyst of AP (Ammonia Perchlorate, NH_4ClO_4) [1]. It naturally becomes a traditional combustion catalyst of AP/HTPB (Hydroxyl-Terminated Polybutadiene) composite propellants. As a result of the development of nanotechnology, researches on nanocatalysts, including nanometer CuO, are surged up. However, most researches tend to focus on the catalysis of the diameter or variety of nanomaterials [2, 3]. Although some of them emphasized the dispersibility improvement technologies of nanomaterials, little attention has been paid to the relationship between dispersibility and catalysis of nanomaterials.

Heat releasing or energy releasing is one of the most important properties of thermal decomposition and combustion of propellants. Catalysts always play a key role in heat releasing procedure of propellant. As one of the most important factors of nanomaterials, dispersibility plays a key role in the effect of catalysis of nanomaterials. Because of little diameter and proportion, nanocatalyst becomes the most difficult dispersing composition of many combustion systems. However, the excellent catalysis of nanocatalyst still attracts many researchers to study [4–6]. As nanocatalysts likely perform much higher catalysis efficiency than microcatalysts, the dispersibility of nanocatalysts is much important than that of microcatalysts. On the other hand, the dispersibility of nanocatalysts also affected its catalysis crucially [7–9]. Therefore, the dispersibility of nanocatalyst is very important to the heat releasing of propellants.

In this paper, kneading time has been ranged from 1 hour to 5 hours to improve the dispersibility of nano-CuO combustion catalyst in composite propellant. Predispersing procedure has been applied to the propellant by adding nano-CuO/AP composite particles instead of simple mixture of nano-CuO and AP. Several kinds of heat releasing, thermal decomposition by DSC, combustion heat in oxygen environment, and explosion heat in nitrogen environment, have been tested to check the relationship of heat releasing with the dispersibility of nano-CuO catalyst in AP/HTPB composite propellants.

Table 1: Thermal decomposition temperature of HTPB propellant with nano-CuO particles.

Kneading Time (h)	Area 1 (°C)	Area 2 (°C)	Area 3 (°C)	Mean Value (°C)	STD (°C)	RSD (%)
1 h	321.51	337.98	310.07	323.19	14.03	4.34
2 h	319.59	328.42	310.93	319.65	8.75	2.74
3 h	308.55	316.17	303.64	309.45	6.31	2.04
4 h	302.33	300.47	308.18	303.66	4.02	1.32
5 h	298.07	293.87	300.96	297.63	3.57	1.20

2. Experimental Procedures

Nanometer copper oxide (CuO), 40 nm in average diameter, was used as the combustion catalyst in AP/HTPB composite solid propellant. Kneading machine was used to disperse nanocatalyst as well as other compositions of AP/HTPB propellant. Kneading time ranged from 1 to 5 hours to change the dispersibility of nano-CuO catalyst in the propellant.

QM-ISP2-CL model planetary ball mill was used to prepare the nano-CuO/AP composite particles. The predispersing method was applied to improve the dispersibility of nano-CuO before adding it into the propellant. First, nano-CuO was dispersed in ethanol by ultrasonic. Then AP was mixed with the nano-CuO with the weight ratio of 4 : 1. The mixture was milled in the planetary ball mill for 30 minutes at 70 rpm. Nano-CuO/AP composite particles were obtained by drying and grinding the milled mixture. When the catalyst added in the propellant in the form of nano-CuO/AP composite, the amount of AP was deducted from the original proportion.

To test thermal decomposition temperature of AP and AP/HTPB propellant, DSC studies were performed with the USA SDTQ-600 differential scanning calorimeter under an atmosphere of N_2 (at a rate of 20 mL/min) and at a heating rate of 10 k/min. XRY-1C oxidation bomb calorimeter was applied to test combustion heat (in 3 MPa O_2 environment) and explosion heat (in 3 MPa N_2 environment) of AP/HTPB propellant.

3. Results and Discussions

3.1. DSC Thermal Decomposition of AP. Ammonia Perchlorate (AP) is one of the main compositions of AP/HTPB composite propellant. The content of AP is up to 70 percent in the composite propellant. Most catalysts in the composite propellant act on the composition of AP. Therefore, many researches study the catalysis of nanocatalyst on AP/HTPB propellant by testing the thermal decomposition of AP with nanocatalyst [10, 11]. Figure 1 shows thermal decomposition curves of AP tested by DSC.

High-decomposition temperatures of AP are decreased 112.83°C and 137.62°C by adding with simple mixed nano-CuO and nano-CuO/AP composite catalysts, respectively. The nanometer catalysts show excellent catalysis on the thermal decomposition of AP. While the thermal decomposition temperature of nano-CuO/AP composite is much lower than that of AP simple mixed with nano-CuO. Better catalysis on AP of nano-CuO can be attributed to better dispersibility of nano-CuO catalyst. Simple mixing method is difficult to

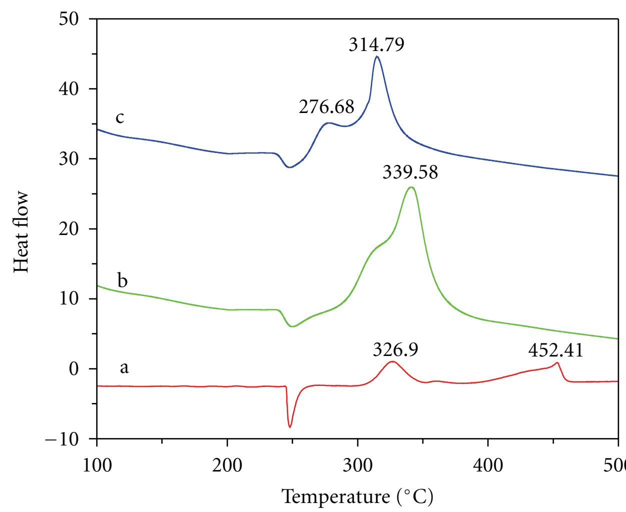

Figure 1: DSC thermal decomposition curves of AP. (a) pure AP; (b) nano-CuO simple mixed with AP; (c) nano-CuO/AP composite.

get enough dispersibility of nanocatalyst in AP, while the dispersibility of nano-CuO can be improved at a perfect level in the form of nano-CuO/AP composite particles.

3.2. DSC Thermal Decomposition of Propellant. Table 1 shows the thermal decomposition temperature data of HTPB propellant with nano-CuO catalyst. The kneading time of each sample ranged from 1 hour to 5 hours. Three representative areas of each sample were chosen to test its decomposition temperature by DSC. Standard deviation (STD) and relative standard deviation (RSD) of the test results of each sample were calculated and listed in Table 1.

Kneading procedures are always employed to improve the composition dispersity of HTPB propellants as well as nano-CuO catalyst. Because of little diameter and proportion, nanocatalyst becomes the most difficult dispersing composition of HTPB propellants. Therefore, the dispersity of nanocatalyst becomes one of the key factors of propellant properties, including its heat releasing amount and procedures. From Table 1, as the kneading time increase, the mean values of decomposition temperature of samples decease smoothly from 323.19°C to 297.63°C. HTPB propellants with higher dispersity of nano-CuO catalyst show lower decomposition temperature. Meanwhile, the RSD values of samples decrease from 4.34% to 1.20% with the increase of kneading time. It means that the increasing of nano-CuO dispersibility in HTPB propellant not only decreases the

Table 2: Thermal decomposition temperature of HTPB propellant with nano-CuO/AP composite.

Kneading Time (h)	Area I (°C)	Area II (°C)	Area III (°C)	Mean Value (°C)	STD (°C)	RSD (%)
1 h	310.11	327.39	309.17	315.56	10.26	3.25
2 h	308.66	303.32	316.84	309.61	6.81	2.20
3 h	302.81	308.53	301.17	304.17	3.86	1.27
4 h	296.72	293.43	295.03	295.06	1.65	0.56
5 h	293.81	292.29	294.78	293.63	1.26	0.43

Table 3: Combustion heat data of propellant with simple mixed nano-CuO.

Kneading Time (h)	Area A (J/g)	Area B (J/g)	Area C (J/g)	Mean Value (J/g)	STD (J/g)	RSD (%)
1 h	16156	15741	15562	15819	304.6	1.93
2 h	16201	15839	15690	15910	262.8	1.65
3 h	15752	16216	16037	16002	234.0	1.46
4 h	15836	16202	16011	16016	183.1	1.14
5 h	16139	16331	15949	16190	191.2	1.18

decomposition temperature, but also decreases the deviation of decomposition temperature.

The preparation of nano-CuO/AP composite is a pre-dispersing method to improve the dispersity of nano-CuO in HTPB propellant. The amount of AP in the nano-CuO/AP composite has been deducted before adding it into the propellant. Table 2 lists the decomposition temperature of HTPB propellant with nano-CuO/AP composite catalyst. With the similar tendency of Table 1, the mean value of decomposition temperature and RSD value in Table 2 decrease dramatically with the increase of kneading time of HTPB propellant, from 315.56°C to 293.63°C and from 3.25% to 0.43%, respectively.

However, when compared with Table 1 at the same kneading time, taking 3 hours for example, all the RSD values and mean values of decomposition temperature in Table 2 are much lower. It means that the pre-dispersing method, the preparation of nano-CuO/AP composite, can effectively improve the dispersity of nano-CuO catalyst in HTPB propellant and decrease the decomposition temperature of HTPB propellant.

Figure 2 shows the DSC curves of AP/HTPB propellant kneaded 4 hours. Compared with the blank sample, thermal decomposition peaks of the two other samples with nano-CuO are combined together as one peak. And the thermal decomposition temperatures are much lower than the low decomposition temperature of blank sample. With pre-dispersing procedures, the thermal decomposition temperature of propellant with nano-CuO/AP is 8.6°C lower than that of propellant with simple mixed nano-CuO.

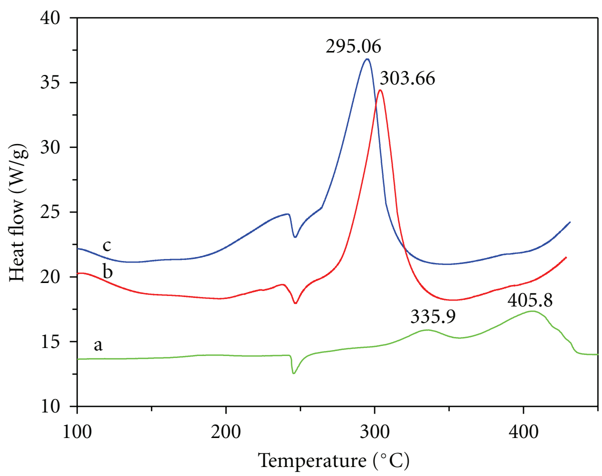

Figure 2: DSC curves of AP/HTPB propellant kneaded 4 hours. (a) Blank sample (b) Propellant with nano-CuO (Area 1); (c) Propellant with nano-CuO/AP (Area III).

3.3. Combustion Heat Testing. Combustion heat data of propellant with simple mixed nano-CuO catalyst and with nano-CuO/AP are contented in Tables 3 and 4, respectively. Three areas of each propellant sample have been chosen randomly to test combustion heat in 3 MPa O_2 environment. Every combustion heat data of the three areas is a mean value of three testing data. Take the data 16,201 J/g of area A kneading 2 hours in Table 3, for example it is the mean value of three data 15,351 J/g, 16,683 J/g, and 16,569 J/g.

From the combustion data in Tables 3 and 4, as the kneading time is increasing, the RSD of combustion heat is decreasing sharply. The mean value of combustion heat in Table 3 is increased steadily with the kneading time increase. The RSD of combustion heat in Table 4 is much lower than that of in Table 3 as a whole. However, after 3 hours kneading, the mean value of combustion heat in Table 4 decreases with the kneading increase. The strange phenomenon could be speculated that the composite structure of nano-CuO/AP in the propellant is broken gradually after 3 h kneading. The breaking of nano-CuO/AP leads to nano-CuO in the form of simple mixing in the propellant sample. Therefore, when kneading time increases to 5 hours, the combustion heat of propellant in Table 4 decreases to the value of propellant with simple mixed nano-CuO kneading 2 hours. It means that the

Table 4: Combustion heat data of propellant with nano-CuO/AP.

Kneading Time (h)	Area a (J/g)	Area b (J/g)	Area c (J/g)	Mean Value (J/g)	STD (J/g)	RSD (%)
1 h	15943	16230	15632	15935	299.2	1.88
2 h	16219	15788	16223	16077	250.2	1.56
3 h	16375	16259	16032	16222	174.5	1.08
4 h	16379	16003	16131	16171	191.2	1.18
5 h	16207	15722	15984	15971	242.8	1.52

Table 5: Explosion heat of propellant with simple mixed nano-CuO.

Kneading Time (h)	Area (1) (J/g)	Area (2) (J/g)	Area (3) (J/g)	Mean Value (J/g)	STD (J/g)	RSD (%)
1 h	5832	6089	6339	6087	253.5	4.16
2 h	6306	6402	6108	6272	149.9	2.39
3 h	6332	6517	6281	6377	123.9	1.94
4 h	6268	6049	6206	6174	110.9	1.80
5 h	6055	6121	6271	6149	110.6	1.80

Table 6: Explosion heat of propellant with nano-CuO/AP composite.

Kneading Time (h)	Area (I) (J/g)	Area (II) (J/g)	Area (III) (J/g)	Mean Value (J/g)	STD (J/g)	RSD (%)
1 h	5954	6336	6272	6187	211.8	3.42
2 h	6047	6371	6229	6216	162.4	2.61
3 h	6419	6491	6539	6483	60.4	0.93
4 h	6238	6281	6375	6298	70.0	1.11
5 h	6229	6245	6363	6279	73.2	1.17

kneading procedure promote the reunion of nano-CuO after the breaking of nano-CuO/AP composite structure.

3.4. Explosion Heat Study of Propellant. Tables 5 and 6 list the explosion heat data of propellant with simple mixed nano-CuO catalyst and with nano-CuO/AP, respectively. With the same testing procedures of combustion heat, three areas of each propellant sample have been chosen randomly to test explosion heat in 3 MPa N_2 environment. And each explosion heat data of the three areas is a mean value of three testing data.

In Table 5, the explosion heat of propellant with simple mixed nano-CuO is increased with the increase of kneading time, while the STD and RSD of explosion heat decreased. Meanwhile, the decrease ratios of STD and RSD of the explosion heat are very smooth when kneading time of propellant less than 3 hours. That is to say, after 3 hours kneading, the dispersibility of nano-CuO catalyst in propellant is improved to a maximum by kneading method. There is no use to improve the dispersibility of nanocatalyst by increasing kneading time for the simple mixed nano-CuO catalyst in AP/HTPB composite propellant. Other methods should be employed to improve the dispersibility of nanocatalyst in the propellant.

The tendency of the data, mean value of explosion heat, STD, and RSD, in Table 5, is very similar Table 6. The explosion heat value of these data increase with the kneading time before 3 hours, and the value decrease with the kneading time after 3 hours. The value of STD and RSD of explosion heat decreases with the kneading time less than 3 hours then increases smoothly. As the tendency of data in Table 6, one of the reasons should be the gradual breaking of the nano-CuO/AP composite particles after 3 h kneading, which result from the too long kneading time. The breaking changes the dispersity of nano-CuO in the propellant. And it provides new probabilities for reunion of nano-CuO catalyst particles.

However, as we can see in Table 2, there is no influence of the breaking of the nano-CuO/AP composite particles on the thermal decomposition temperature of HTPB propellant. Far from the situation in Table 6, the decomposition temperatures of the propellants, in Table 2, are still decreasing with the increase of kneading time after 3 hours. One possible reason for this is that because the decomposition rate, or heat releasing rate, of thermal decomposition of HTPB propellant is much slower than that of combustion and explosion; the effect of the breaking of nano-CuO/AP composite on combustion and explosion is more obvious than that of thermal decomposition of HTPB propellant. Therefore, it seems that there is no or little influence on the thermal decomposition temperatures of HTPB propellants in Table 2.

Similar with the data of combustion heat testing, the explosion heat data of propellant with nano-CuO/AP composite in Table 6 is much higher than the data in Table 5 at all the kneading times. With pre-dispersing procedures, added with nano-CuO/AP composite, propellants exhibit good performance on explosion heat releasing. And the RSD values in Table 6 are less than those in Table 5. Less

RSD value is the stand of less change, or less instability, of the explosion heat releasing of the propellant sample. It means that the propellants in Table 6 could be show higher explosion heat and more steady explosive procedures than samples in Table 5. It is only because of the pre-dispersing procedures by adding nano-CuO/AP composite in the propellants in Table 6.

From the data of Table 1 to Table 6, taking kneading efficiency and heat releasing into account, the preference kneading time should be set to 3 hour for AP/HTPB composite propellant added with nano-CuO, instead of the traditional kneading time, 2 hours, for micrometer catalyst of AP/HTPB composite propellant.

4. Conclusions

The dispersibility of nano-CuO has been adjusted by changing the kneading time of AP/HTPB composite propellant. Nano-CuO/AP composite has been prepared, as a pre-dispersing method of nano-CuO, to improve the dispersibility of nano-CuO in AP as well as AP/HTPB propellant. With the improvement of the dispersibility of nano-CuO, increasing kneading time or adding composite, DSC thermal decomposition temperature of AP and AP/HTPB propellant decreases markedly. However, the combustion heat and explosion heat of propellants with nano-CuO/AP, tested in O_2 and N_2 environment, increase then decrease on 3 hours of kneading time. This is partly because of the breaking of nano-CuO/AP composite structure and leads to the reunion of nano-CuO particles.

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References

[1] A. A. Said and R. Al-Qasmi, "The role of copper cobaltite spinel, $CuxCo_{3-x}O_4$ during the thermal decomposition of ammonium perchlorate," *Thermochimica Acta*, vol. 275, no. 1, pp. 83–91, 1996.

[2] L. Liu, F. Li, L. Tan, L. Ming, and Y. Yi, "Effects of nanometer Ni, Cu, Al and NiCu powders on the thermal decomposition of ammonium perchlorate," *Propellants, Explosives, Pyrotechnics*, vol. 29, no. 1, pp. 34–38, 2004.

[3] L.-J. Chen, G.-S. Li, P. Qi, and L.-P. Li, "Thermal decomposition of ammonium perchlorate activated via addition of NiO nanocrystals," *Journal of Thermal Analysis and Calorimetry*, vol. 92, no. 3, pp. 765–769, 2008.

[4] Z. Yu, Y. Sun, W. Wei, L. Lu, and X. Wang, "Preparation of $NdCrO_3$ nanoparticles and their catalytic activity in the thermal decomposition of ammonium perchlorate by DSC/TG-MS," *Journal of Thermal Analysis and Calorimetry*, vol. 97, no. 3, pp. 903–909, 2009.

[5] K. Zhang, C. Rossi, G. A. Ardila Rodriguez, C. Tenailleau, and P. Alphonse, "Development of a nano- AlCuO based energetic material on silicon substrate," *Applied Physics Letters*, vol. 91, no. 11, Article ID 113117, 2007.

[6] K. Zhong, P. Jin, and Q. Chen, "Ni hollow nanospheres: preparation and catalytic activity," *Journal of Nanomaterials*, vol. 2006, Article ID 37375, 7 pages, 2006.

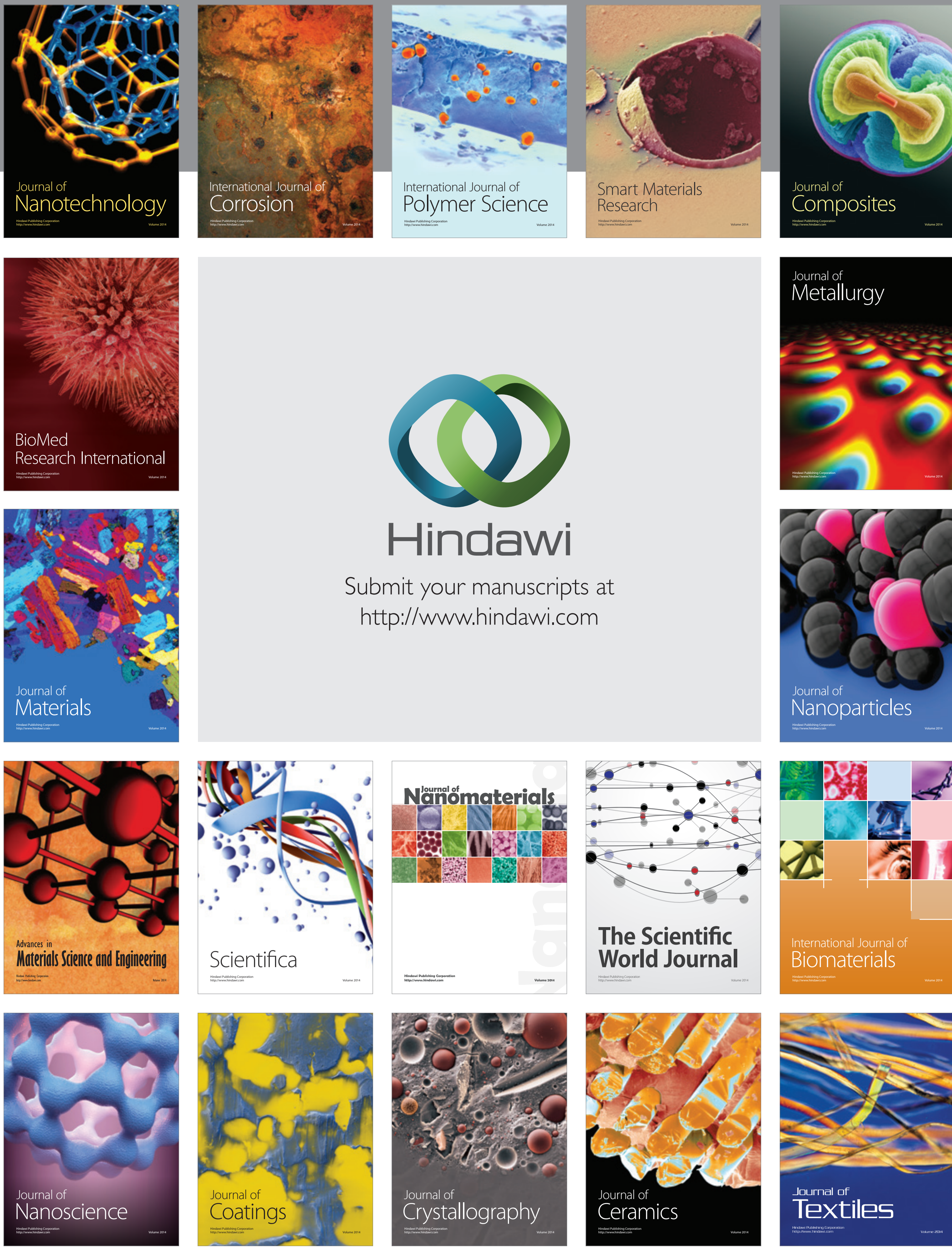
[7] Y.-H. Hu, J.-P. Liu, J. Xu, and D.-Z. Wang, "Dispersion mechanism of nano-magnetite coated with oleate in aqueous carrier," *Journal of Central South University of Technology*, vol. 15, no. 5, pp. 663–668, 2008.

[8] M. Kawaraya, "Dispersibility of nano-TiO_2 paste with fine ceramic beads and morphology of the mesoporous film," *Journal of Chemical Engineering of Japan*, vol. 40, no. 3, pp. 255–258, 2007.

[9] J. K. Kim, D. Z. Wo, L. M. Zhou, H. T. Huang, K. T. Lau, and M. Wang, "Dispersibility and degradation properties characterization of nano titanium dioxide photocatalysis material," *Key Engineering Materials*, vol. 334-335, pp. 565–568, 2007.

[10] G. Duan, J. Zhu, C. Kan, X. Yang, L. Lu, and X. Wang, "Preparation of novel structural nanosized Y_2O_3 powders and their catalytic activity on the decomposition of NH_4ClO_4," *Reaction Kinetics and Catalysis Letters*, vol. 92, no. 2, pp. 247–256, 2007.

[11] V. F. Komarov, "Catalysis and inhibition of the combustion of ammonium perchlorate based solid propellants," *Combustion, Explosion and Shock Waves*, vol. 35, no. 6, pp. 670–683, 1999.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