Synthesis of ZrO2-Al2O3 Composite Beads by Wet Titration Technology

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Research Article

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Abstract

In this work, based on the wet titration technology, an innovative method to prepare the ZrO_2-Al_2O_3 composite beads which can greatly improve the bead properties is proposed. Using this process, the ZrO_2-Al_2O_3 composite beads samples with different proportions of alumina component were prepared and tested. The bulk density test results show that the new method can prepare the beads with high compactness and without containing pores. The hardness test results show that the hardness of the composite beads is higher than zirconia beads without adding alumina. The SEM analyses show that the average grain size of the composite beads is about 180 nm, much smaller than the beads prepared by conventional rolling process. The XRD results show that there is no monoclinic phase in the composite beads after sintering at 1250 ℃. The EDS analyses show that the aluminum element exists in composite beads and the alumina grains are evenly distributed. Furthermore, the sintering temperature using this new process can achieve low-temperature sintering which is about 1250 ℃ much lower than the sintering temperature of conventional rolling process.

Introduction

In recent years, the ZrO_2-Al_2O_3 composite materials which include the advantages of high toughness characteristics inherited from zirconia and high hardness characteristics inherited from alumina have been widely used and researched [1–5]. However, the conventional rolling process to prepare the zirconia, alumina, ZrO_2-Al_2O_3 composite beads is by grinding zirconia and alumina powder, granulating and rolling them to form beads [6–7]. The main defects of the prepared beads using this method are containing many pores, large size of grains, low crushing load and small hardness characteristics, etc. These problems can be significantly improved by wet process technology [8].

Pure ZrO_2 exists in three polymorphs at low pressure (monoclinic, tetragonal and cubic) and in an orthorhombic form at higher pressure. While the monoclinic structure is stable at room temperature, the tetragonal and cubic forms crystallize at higher temperatures. By doping with larger ions such as Y^{3+}, Er^{3+}, or Ce^{4+}, the cubic structure of ZrO_2 can be stabilized at room temperature [8]

In this work, based on wet titration technology, an innovative method to prepare the ZrO_2-Al_2O_3 composite beads is proposed. The ZrO_2-Al_2O_3 composite beads are prepared by sol preparation, titration molding process, organic compound discharging and sintering [5–8]. From the test results, it can be seen that alumina grains are evenly distributed in the beads. The average grain size of the composite beads is about 180 nm, much smaller than the beads prepared by the conventional rolling process which average grain size is about 400 nm. The composite beads which inherit the excellent properties of zirconia and alumina have the advantages of high toughness and high hardness. Furthermore, the sintering temperature can achieve low-temperature sintering which is about 1250 ℃. XRD results show that there is no monoclinic phase in the beads after sintering at 1250 ℃, the results also show that monoclinic

phase exists in the ZrO_2-Al_2O_3 composite power at the same sintering temperature. This further reflects the advanced of the wet titration technology.

⊠ Process Method

The methods of synthesis ZrO_2-Al_2O_3 composite beads are:

Step 1: Preparing solution

Weighing zirconium oxychloride, aluminum chloride, and yttrium chloride by certain proportion, the proportions of zirconium oxychloride and aluminum chloride component are decided by the final products needed to be prepared; the proportion of yttrium oxide in the composite material is 5.5%. Then mixing them with deionized water and stirring the mixture to fully dissolve.

Step 2: Adding ammonia

Adding ammonia into the solution prepared in step 1, the concentration of ammonia used in this step should be 5–7%, and it must be added slowly. The final PH value of the solution should be up to 8.5-9, then waiting 30 minutes for the solution subsiding.

Step 3: Removing chlorine

Handling the sediment prepared in step 2 with filter-press method, after then mixing it with deionized water and well stirring. To fully remove the chlorine, this step needs to be repeated 3–4 times.

Step 4: Sediment dissolution

Preparing the zirconium oxychloride solution, heating to 80 ℃, then placing the sediment (prepared in step 3) into solution, stirring until fully dissolve. The weight of zirconium oxychloride used in this step should be about half of the step 1's.

Step 5: Adding organic solvent

Adding some binder and defoamer into the solution (prepared in step 4), stirring the mixture to fully combine. The weight of binder used in this step should be about 1/50, and the defoamer should be about 1/100 of the dissolution.

Step 6: Titration

Placing the solution (prepared in step 5) into titration equipment, dropping it into ammonia (The concentration of ammonia used here should be about 10%). Before dropping, we need to pour some oil (n-Alkanes) into the ammonia, about 2 mm on the surface of ammonia. The diameter of the ZrO_2-Al_2O_3 composite beads can be controlled by adjusting the port size of titration equipment.

Step 7: Cleaning beads

Placing the beads into teflon grinding can, adding some ammonia in it. Then placing the can into planetary mill and rotating. The concentration of ammonia used in this step should be about 10%, and the rotating speed of planetary mill should be 100–150 RPM. This step needs to be repeated 3–4 times.

Step 8: Baking beads

Placing the beads (prepared in step 7) into oven and baking. The temperature of the oven should be 120 ℃.

Step 9: Discharging organic compound

Placing the beads (prepared in step 8) into debinding furnace and discharging. The rising time-temperature curve of debinding furnace should be: 2 hours to 160 ℃, keeping 1 hour, 25 hours to 600 ℃, and keeping 2 hours.

Step 10: Sintering

Placing the beads (prepared in step 9) into sintering furnace. The rising time-temperature curve of sintering furnace should be: 11 hours to 1250 ℃, and coolling naturally to room temperature.

▯ Sample Preparation

The samples using the new process method were prepared and marked as: A Sample, B Sample, C Sample and D Sample, the proportion of alumina component in the ZrO_2-Al_2O_3 composite beads was 0%, 1.5%, 5% and 10%, respectively. Meanwhile, to make comparison, the zirconia beads sample which prepared with the conventional rolling process was also prepared. It was marked as E Sample.

▯ Characterization And Discussion Of Experimental Results

4.1 Bulk density test

Using the Archimedes method, the bulk densities of the five samples were tested. The test results are shown in Table 1. From the results, it can be got that:

1) When the ceramic beads are dense and without pores, the measured bulk density value of the ceramic beads will be close to the theoretical density value. From the literatures, the tested bulk density value of zirconia beads using the conventional rolling process is generally below 6.0 g/cm^3 [5–8], and the tested bulk density value of E Sample is 5.91 g/cm^3. It can be seen in the literature that there are some defects and pores in the traditional rolling method, which leads to the density lower than the theoretical density [7]. The tested bulk density value of the A Sample prepared with the new method is 6.05 g/cm^3, which is higher than E Sample. This implies that the new method can prepare the beads which are more denser and containing fewer pores. From the SEM results of Fig. 2, we can see there are no obvious defects and pores between grains. Less defects and internal pores are beneficial to the density. The bulk density test results further illustrate the advanced of the wet titration technology.

2) Meanwhile, from the results of A, B, C, and D Sample, the bulk density of the ZrO_2-Al_2O_3 composite beads declines with the proportion of alumina component rising. For the theoretical density of alumina (3.97g/cm^3) is lower than zirconia (5.85g/cm³), and the increase of alumina content will decrease the density of the composite beads.

Table 1
The bulk density test results of five samples. For each sample, three groups were tested.

Materials	A Sample (g/cm^3)	B Sample (g/cm^3)	C Sample (g/cm^3)	D Sample (g/cm^3)	E Sample (g/cm^3)
Number 1	6.06	6.01	5.92	5.81	5.92
Number 2	6.05	6.00	5.91	5.79	5.91
Number 3	6.04	6.01	5.93	5.8	5.89
Average value	6.05	6.01	5.92	5.80	5.91

Notes: A Sample was the zirconia beads prepared by wet titration method. The alumina component of B, C, and D Sample was 1.5%, 5%, 10% respectively; the prepared method for them was wet titration method. E Sample was the zirconia beads prepared by the conventional rolling process.

4.2 The hardness test

For the ZrO_2-Al_2O_3 composite beads, the hardness characteristics is an important index. In this work, using the Vickers hardness test method, the five samples were tested. The results are shown in Table 2. From the results, it can be got that: 1) With the increasing proportion of alumina component, the hardness value increased along with the increase of alumina content. The composite beads fully show the high hardness characteristics of alumina ceramic. 2) With the increasing proportion of alumina component, the increasing trend of hardness will decline, especially, when the proportion of alumina component is

larger than 5%. 3) In Table 2 column E, we also show the hardness test results of the zirconia beads prepared by the conventional rolling process. Compared the results with A Sample prepared by the new wet titration method (shown in Table 2, column A), we can see that the new process method can also improve the hardness characteristics of zirconia beads. Less defects and internal pores are beneficial to the hardness of ceramic. The hardness test results also further illustrate the advanced of the wet titration technology.

Table 2
The hardness test results of five samples. For each sample, three groups were tested.

Materials	A Sample	B Sample	C Sample	D Sample	E Sample
1	1259	1345	1401	1391	1125
2	1259	1346	1401	1411	1166
3	1275	1391	1421	1471	1156
Average value	1264	1361	1408	1424	1149

Notes: A Sample was the zirconia beads prepared by wet titration method. The alumina component of B, C, and D Sample was 1.5%, 5%, 10% respectively; the prepared method for them was wet titration method. E Sample was the zirconia beads prepared by the conventional rolling process.

4.3 Morphologies in microsphere

4.3.1 Optical microscope tests

From Fig. 1 (A), we can see the beads are transparent after the titration molding process, which implies that the beads are dense and without containing pores. After drying, the beads are still transparent, but slightly yellow showing in Fig. 1 (B), because there is organic matter in the sol. The organic matter will be removed in the later glue discharging and sintering process which shows in Fig. 1 (C). The surface of the beads prepared by rolling method is rough, and it needs polishing to achieve smooth surface. Through the new preparation process, the surface of the beads after sintering is bright and do not need polishing process [9].

4.3.2 SEM tests

The SEM analyses were made to A, B, C, and D Sample. To give full description about the samples, we took the four samples SEM analyses in 50 times and 20K times, respectively. The results are shown in Fig. 2–5.

Form the SEM analysis results, the surface grains are compact, no obvious pores and defects appear between the grains of the ZrO_2-Al_2O_3 composite beads. However, there are many pores and defects between the grains of the zirconia beads, alumina beads prepared by the conventional rolling process in Fig. 6. The average grain size is about 180 nm through the grain test, and the average grain size is about

400 nm of zirconia by the conventional rolling process [10–13]. By comparison, it can be seen that the average grain size of the new process is much smaller than that of the traditional process. The zirconia beads of A sample were broken, and the cross section was tested by SEM. It can be seen that the cross section grains of the beads which show in the Fig. 7 are similar to the surface grains of the Fig. 2 (b), and no defects and pores were found between the grains. The surface and cross section SEM images show that there is a good consistency between the inside and outside of the beads. The beads prepared by the conventional rolling process have poor consistency inside and outside. With the use of the beads, the performance of the beads will be worse and worse.

4.3.3 XRD tests

Figure 8 shows the XRD patterns of the A, B, C, and D beads Sample. Figure 9 shows the XRD patterns of the A-Power, B-power, C-power, and D-power Sample. The composition of the four powder samples is identical with A, B, C and D. The same sol is used, and the other process routes are identical except without Step 6 of titration. It can be seen from the comparison between Fig. 8 and Fig. 9 that the diffraction peak intensity of the beads is lower because the beads is directly used for testing, not a plane, and the diffraction peak intensity of the powder is obviously higher than that of the beads. There is no monoclinic phase in beads before and after 30 ℃, but there are two small peaks in powder before and after 30℃, which are monoclinic phase [14–18]. XRD analysis shows that the same components, the same sol, through the new wet titration process monoclinic phase zirconia in beads can convert to tetragonal phase after sintering at 1250 ℃, which fully demonstrates the advanced nature of the wet titration process [19].

4.3.4 EDS tests

To analyse the content and distribution of each element in the ZrO_2-Al_2O_3 composite beads, the EDS analyses were made to the B, C, and D Sample. The results are shown in Fig. 10, Fig. 11 and Fig. 12. From the figures: 1) It can be seen that the aluminum element exists in B, C and D Sample. For the B Sample, the alumina content is less, and the alumina peak is low and not obvious. However, the little mixing of alumina has a great influence on the characteristics of the composite beads, especially for the hardness of the beads. 2) By the EDS analyses, it can be seen that the aluminum element is evenly distributed [20], and there is no aluminum enrichment in the three surface scanning results. This result is consistent with SEM test.

5 Conclusion

In this work, based on the wet titration technology, we proposed a new innovative method to prepare the ZrO_2-Al_2O_3 composite beads, which can greatly improve the properties of the beads. The surface of the sintered composite beads is bright. The bulk density and the hardness of the composite beads is higher than traditional rolling technology. The SEM analysis results show the surface and cross section of the beads are consistent, and there are no pores in the beads. The XRD results show that there is no monoclinic phase in the composite beads, which are tetragonal phase and cubic phase after sintering at

1250 ℃. The EDS analysis results show that aluminum element exists and is evenly distributed in B, C and D Sample. Furthermore, the sintering temperature of using the new method is only 1250 ℃ which is much lower than the sintering temperature of traditional process.

Declarations

Acknowledgements

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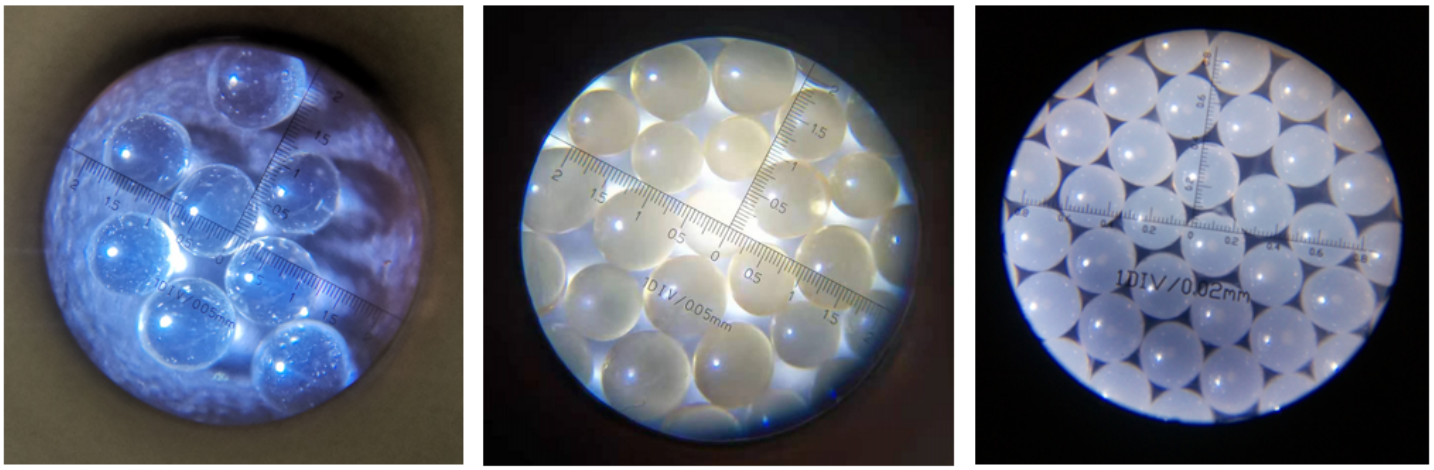
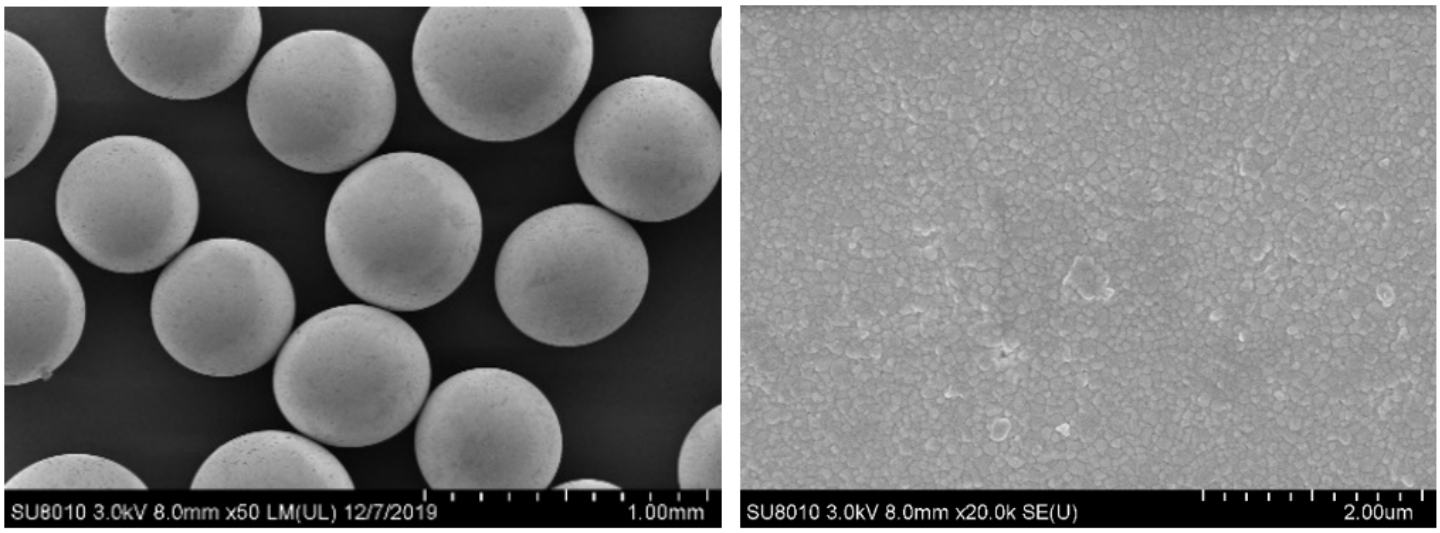
Figures



(A) (B) (C)

Figure 1

The morphologies of the beads in low-power amplifier: (A) After titration molding process step; (B) After baking process step; (C) After sintering process step.



(a) (b)

Figure 2

The SEM images of A Sample: (a) Amplified in 50 times; (b) Amplified in 20K times.

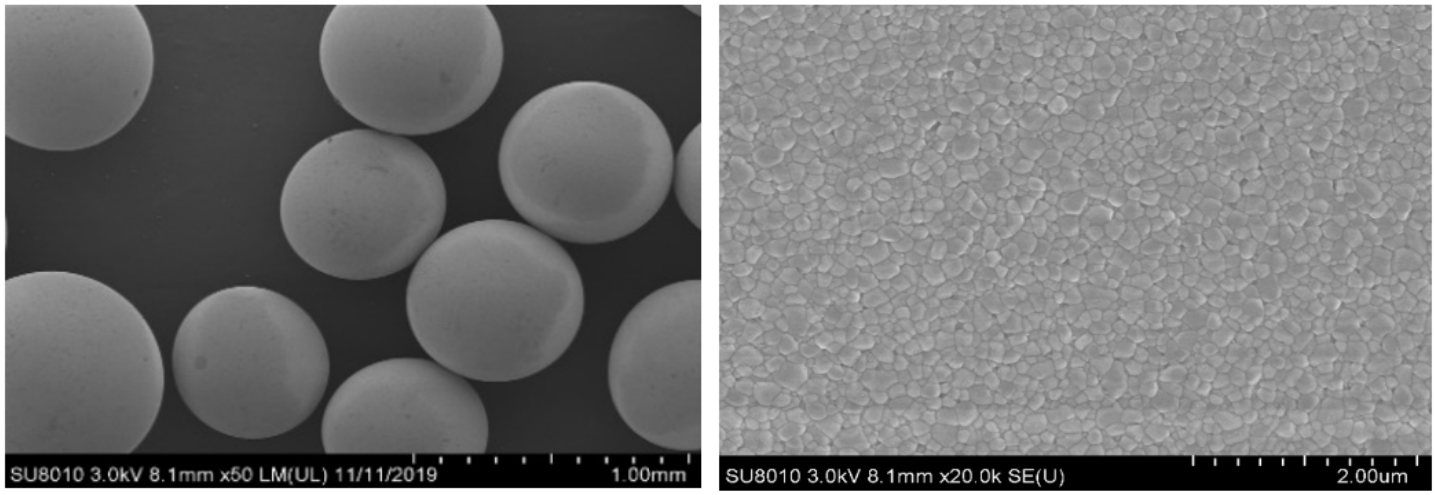


Figure 3

The SEM images of B Sample: (a) Amplified in 50 times; (b) Amplified in 20K times.

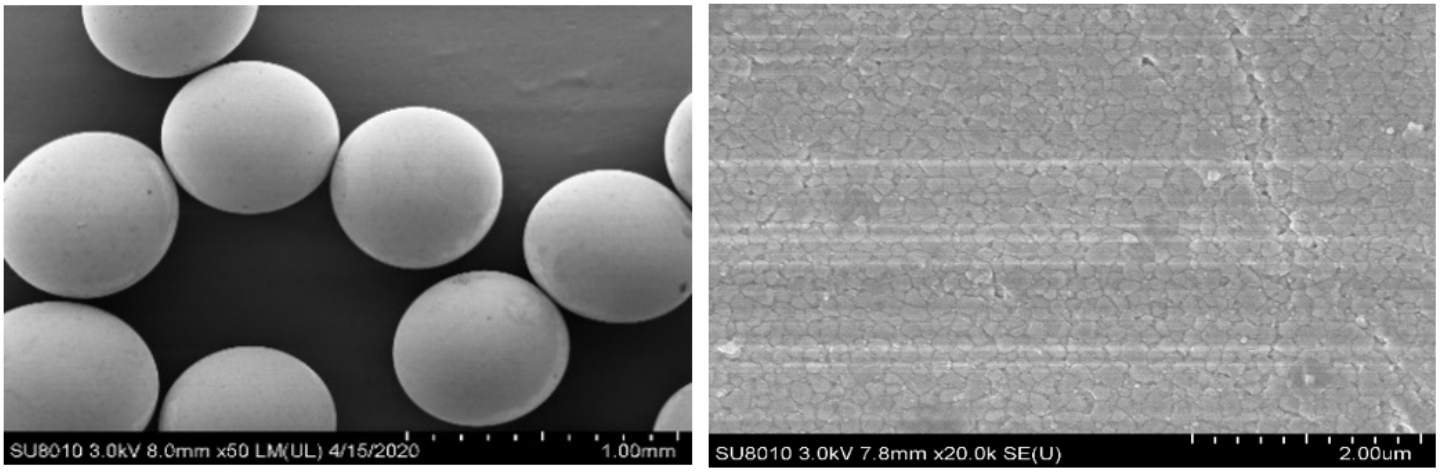
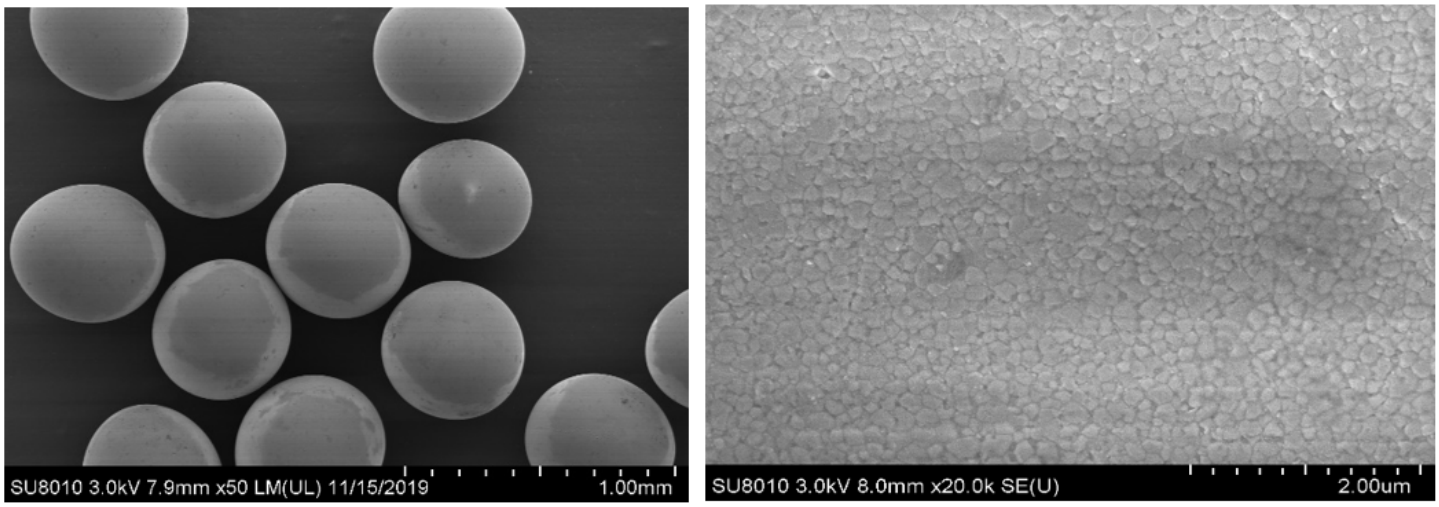


Figure 4

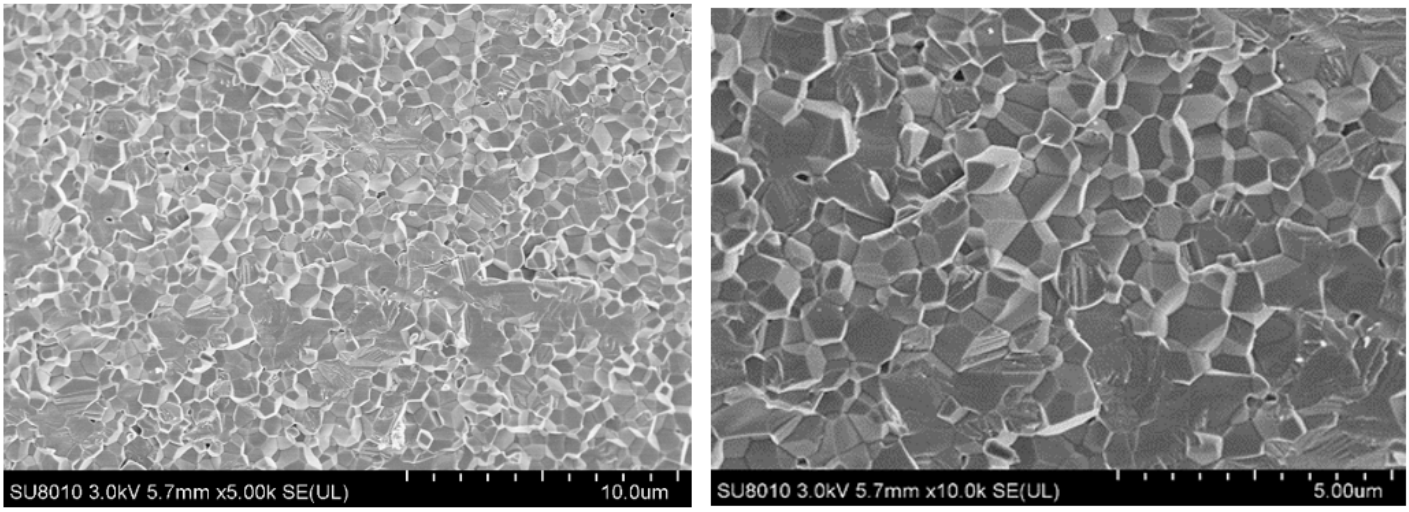
The SEM images of C Sample: (a) Amplified in 50 times; (b) Amplified in 20K times.



(a) (b)

Figure 5

The SEM images of D Sample: (a) Amplified in 50 times; (b) Amplified in 20K times.



(a) (b)

Figure 6

The SEM images of alumina beads prepared by the conventional rolling process (a) Amplified in 5K times; (b) Amplified in 10K times.

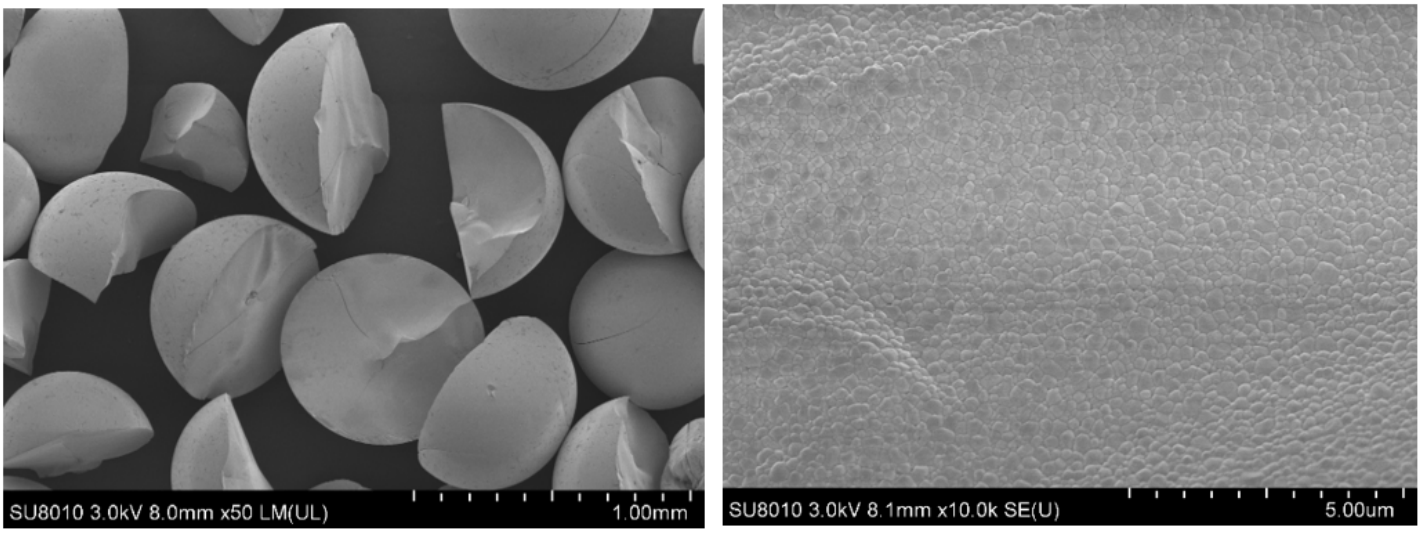


Figure 7

The SEM images A Sample: (a) Amplified in 50 times; (b); (b) Amplified in 10K times.

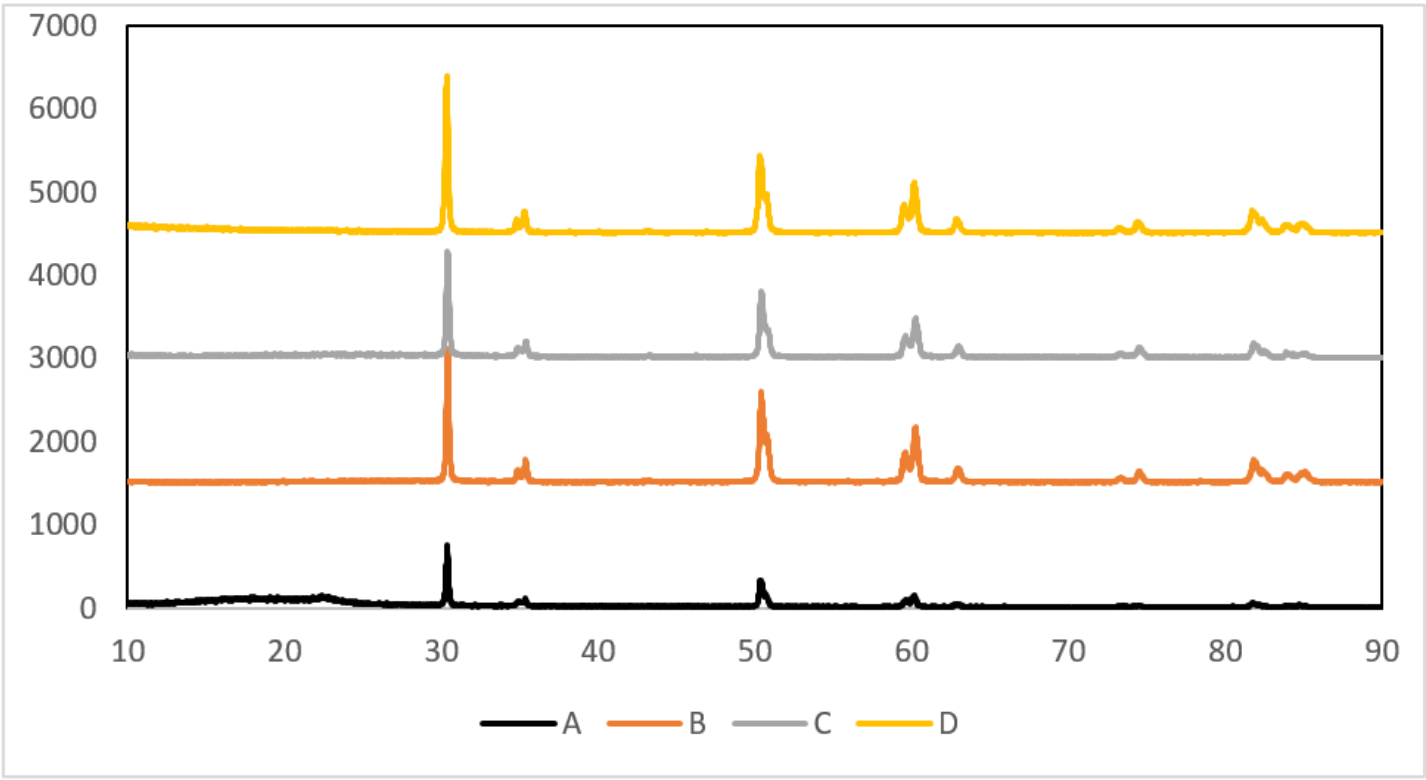


Figure 8

XRD pattern of the A, B, C, and D Sample.

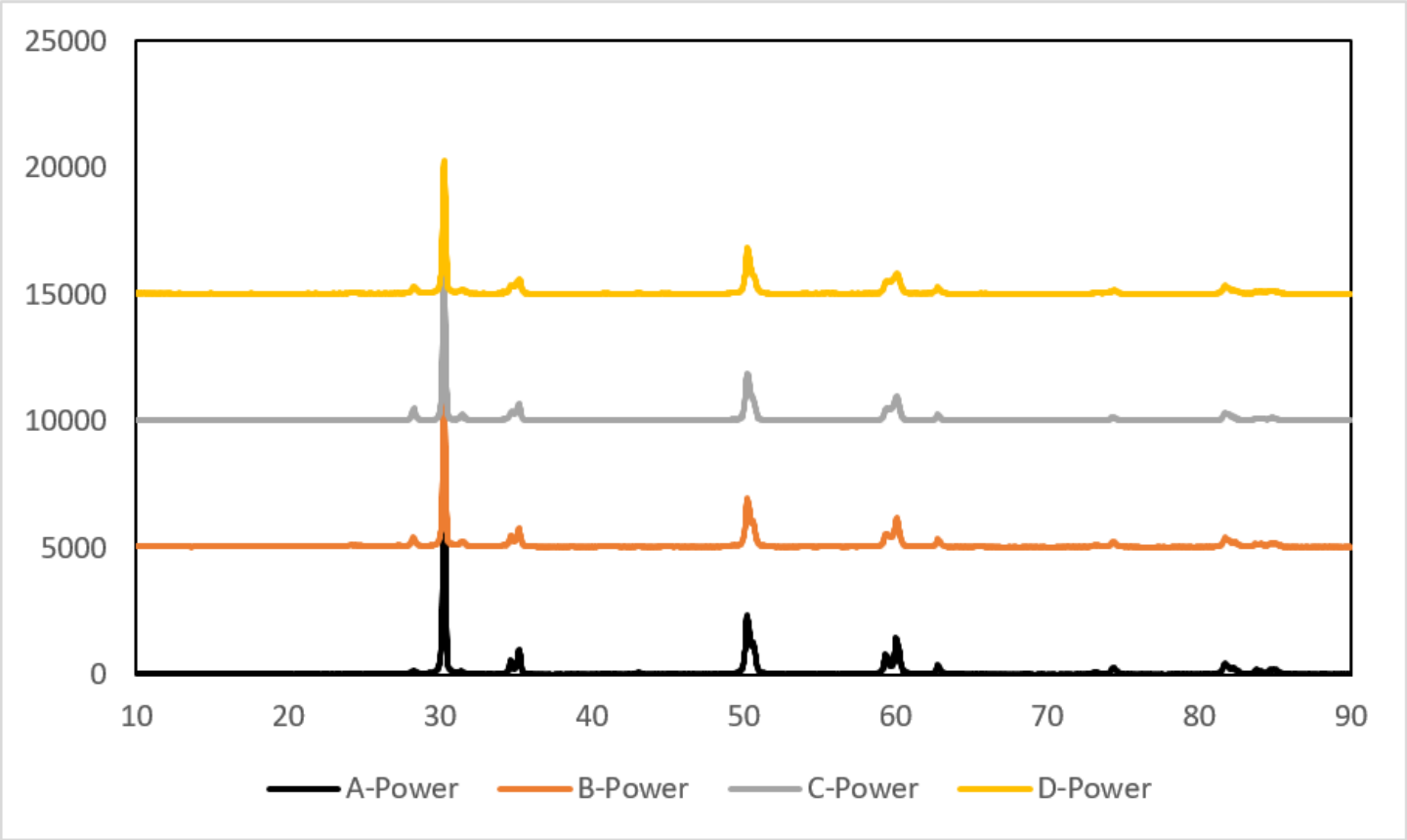
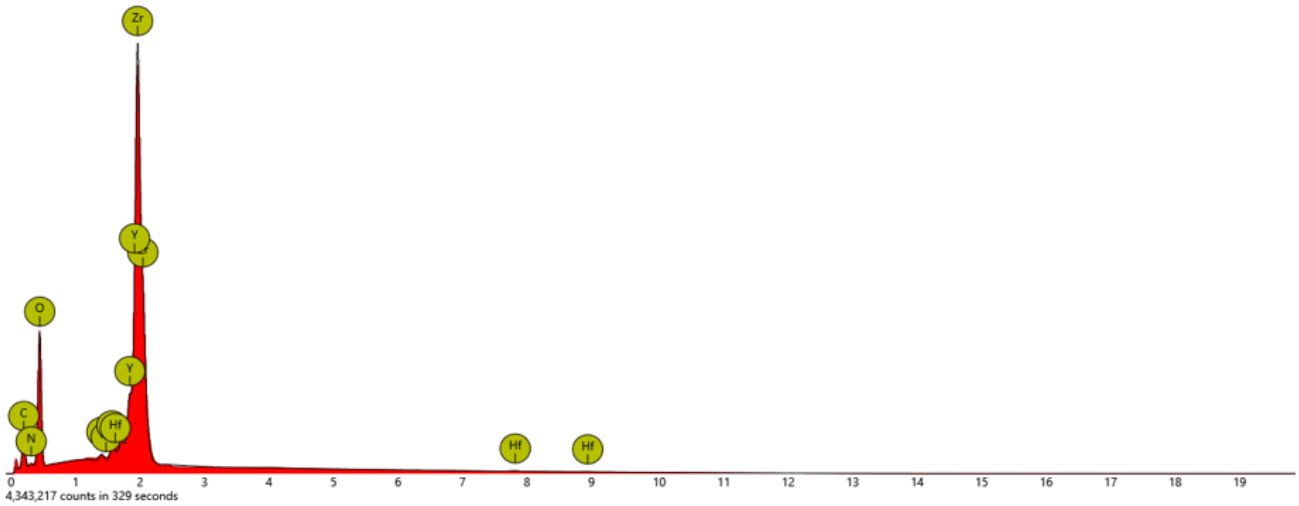
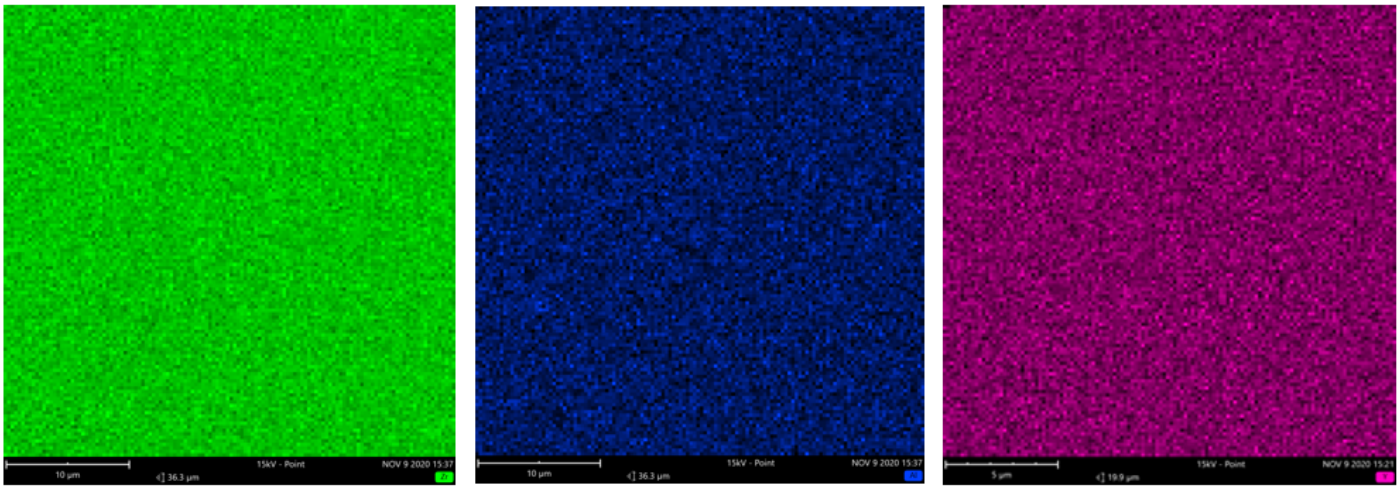


Figure 9

XRD pattern of the A-power, B-power, C-power, and D-power Sample.



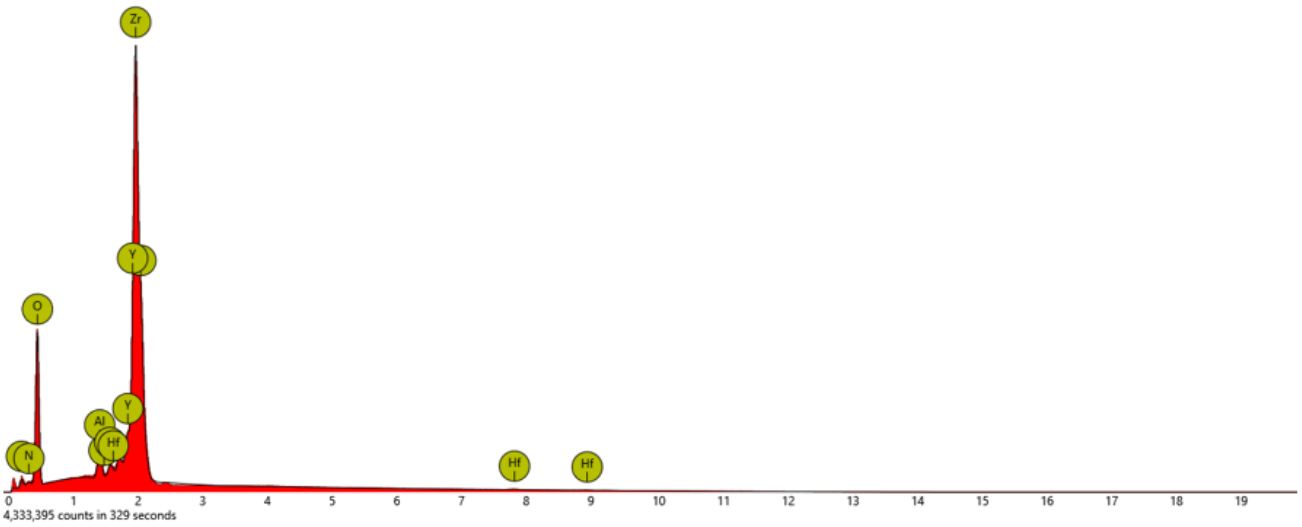
(a)



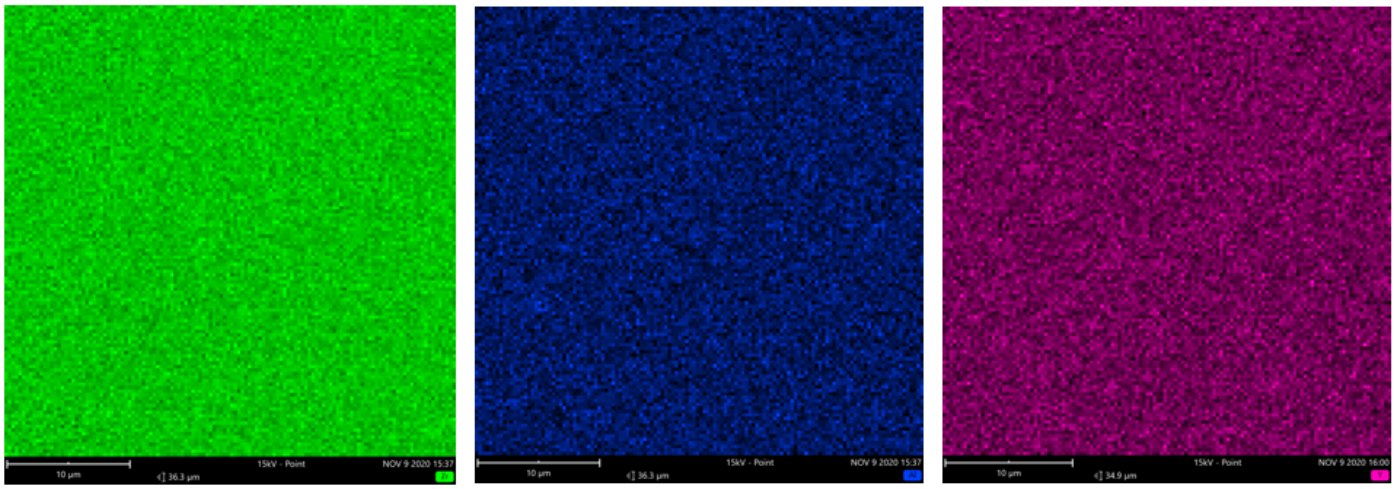
(b) (c) (d)

Figure 10

The results of B Sample using the EDS analysis: (a) Energy dispersive X-ray analysis spectrum; (b) Zr, (c) Al, (d) Y EDS-derived elemental distributions of B Sample.



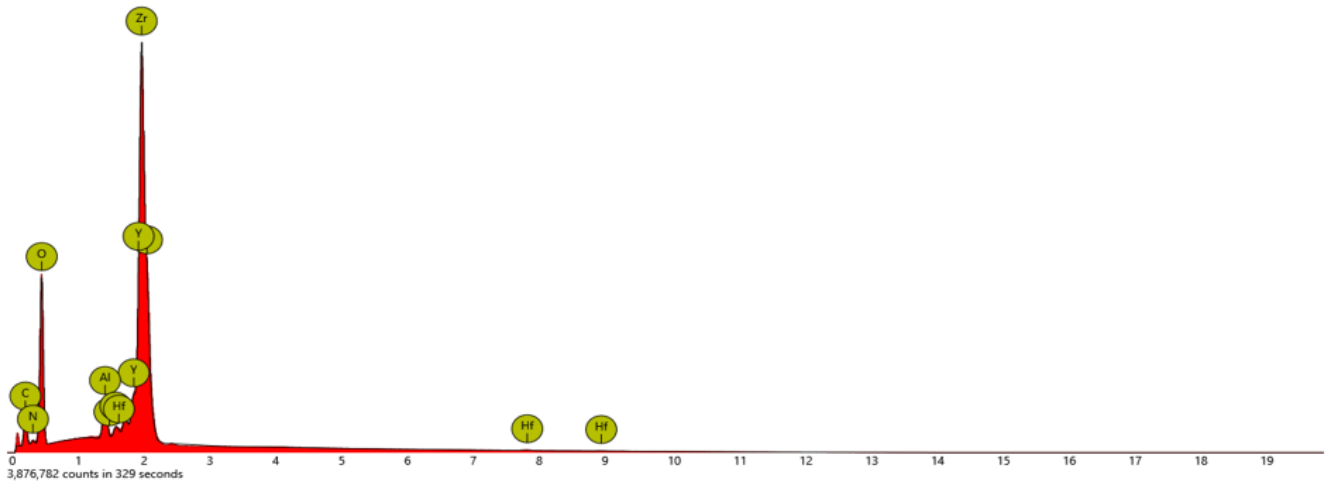
(a)



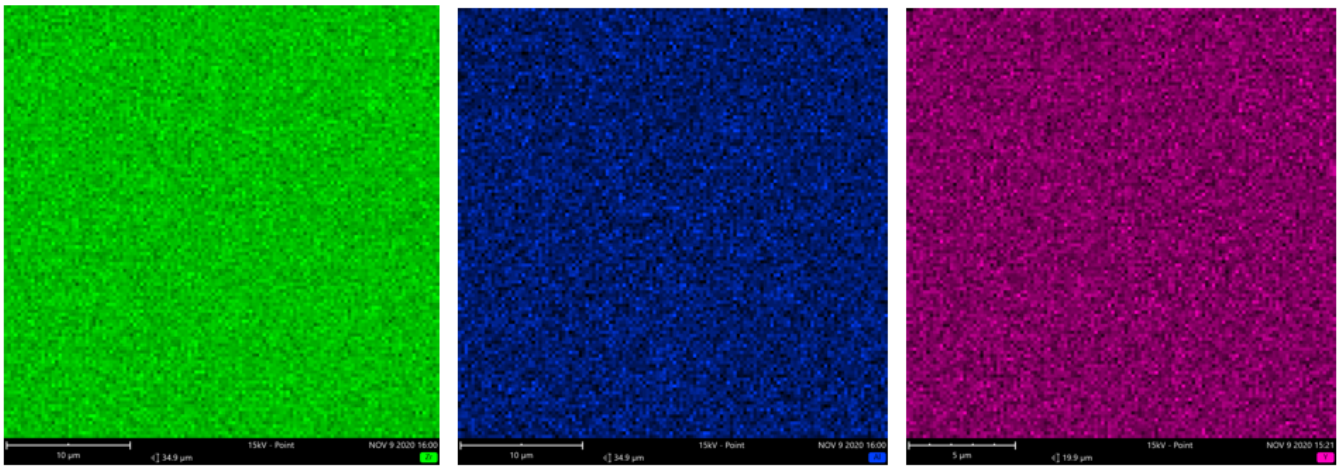
(b) (c) (d)

Figure 11

The results of C Sample using the EDS analysis: (a) Energy dispersive X-ray analysis spectrum; (b) Zr, (c) Al, (d) Y EDS-derived elemental distributions of C Sample.



(a)



(b) (c) (d)

Figure 12

The results of D Sample using the EDS analysis: (a) Energy dispersive X-ray analysis spectrum; (b) Zr, (c) Al, (d)Y EDS-derived elemental distributions of D Sample.