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CHARACTERISTICS OF ZrO_2 ADDED-$MgAl_2O_4$ CERAMICS FOR MATRIX OF INERT MATRIX NUCLEAR FUEL (IMF)

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ABSTRACT

CHARACTERISTICS OF ZrO_2 ADDED-$MgAl_2O_4$ CERAMICS FOR MATRIX OF INERT MATRIX NUCLEAR FUEL (IMF). Some ZrO_2 added-$MgAl_2O_4$ ceramics for inert matrix of inert matrix nuclear fuel (IMF) had been fabricated from powders prepared using precipitation method. Effect of ZrO_2 addition on crystal structure, microstructure and mechanical properties of the ZrO_2 added-$MgAl_2O_4$ ceramics was studied. The ceramics were prepared by mixing ZrO_2, MgO and Al_2O_3 followed by pressing and sintering. The concentrations of ZrO_2 additive were 0, 5, 10 and 15 mole %. The mixed powder was pressed into green pellets with pressure of 4 ton/cm^2. The green pellets were sintered at 1600 ^oC for 2 hours in air. The sintered pellets were evaluated visually. For microstructure examination, the fractured samples were examined using a scanning electron microscope (SEM). Crystal structure of the samples was analyzed using x-ray diffraction (XRD). Hardness and fracture toughness of the sintered pellets were determined using microindentation method with aid of a Vickers microhardness tester from Zwick. It was known that the sintered pellets were visually good. The XRD data showed that the ceramics crystallized in spinel cubic with second phase of ZrO_2. The hardness and fracture toughness of the ceramics increased with the increase of ZrO_2 concentration.

Keywords: ZrO_2, $MgAl_2O_4$, inert matrix, IMF, nuclear fuel

ABSTRAK

KARAKTERISTIK KERAMIK MgAl2O4 YANG DITAMBAH ZrO_2 UNTUK MATRIKS DARI BAHAN BAKAR MATRIKS INERT (IMF). Keramik $MgAl_2O_4$ yang ditambah ZrO_2 untuk matriks dari bahan bakar matriks inert (IMF) telah difabrikasi dari serbuk yang dibuat dengan metode presipitasi. Pengaruh penambahan ZrO_2 terhadap struktur kristal, mikrostruktur dan sifat mekanik keramik $MgAl_2O_4$ dipelajari. Keramik dibuat dengan mencampur ZrO_2, MgO dan Al_2O_3 diikuti dengan pengepresan dan penyinteran. Konsentrasi ZrO_2 adalah 0, 5, 10 and 15 mole %. Serbuk campuran dipres menjadi pelet mentah dengan tekanan 4 ton/cm^2. Pelet mentah disinter pada suhu 1600^oC selama 2 jam di udara. Pelet sinter dievaluasi secara visual. Untuk evaluasi mikrostruktur, patahan sampel diperiksa dengan SEM. Struktur kristal ditentukan memakai XRD. Kekerasan dan ketangguhan patah pelet sinter diukur menggunakan indentasi mikro dengan bantuan microhardness tester Zwick. Diketahui bahwa pelet sinter bagus secara visual. Data XRD memperlihatkan bahwa keramik berstruktur kristal kubik spinel dengan fase kedua ZrO_2 Kekerasan dan ketangguhan patah keramik bertambah dengan penambahan kandungan ZrO_2.

Kata kunci: ZrO_2, $MgAl_2O_4$, matriks inert, IMF, bahan bakar nuklir

1. INTRODUCTION

There is a trend in the future that plutonium (Pu) and other actinides having long half life such as Am, Np and Cm

accumulated in large amount as by product of nuclear power plants will be a problem. According to International Atomic Energy Agency (IAEA), until 2006 reactors around the world have produced plutonium about 2000 tones contained in spent fuel (1). In order to overcome this problem, a more efficient nuclear fuel that will produce only small amount of plutonium and other long-lived actinides is required. In this case, the fuel has to have capability to be a special containment for burning Pu and other actinides. By this burning, the amount of Pu and other actinides contained in the spent fuel will be small. One candidate of this kind of fuel is inert matrix fuel (IMF) (1-11). This fuel consists of matrix ceramic that is inert or transparent to neutron (inert matrix) and fissile material such as uranium dioxide that is dispersed or dissolved inside the matrix.

The inert matrix ceramic has to fulfill some conditions such as high density, high melting point and no change during its usage in the reactor. Some researches on $MgAl_2O_4$ projected for inert matrix have been carried out (1, 4-9). It is known that this ceramic has relatively good thermal conductivity (2), the property required by the inert matrix. The thermal conductivity of $MgAl_2O_4$ is even larger than that of ZrO_2 and UO_2 (2). However, the fracture toughness of the $MgAl_2O_4$ still has to be increased. One effort can be done to increase the fracture toughness of the ceramic is by adding additive into the ceramic.

The increase of the fracture toughness theoretically will be reached since the additive or the reaction product between the additive and the matrix is dispersed homogeneously. Regarding this assumption, one alternative is choosing the additive that will not react with the $MgAl_2O_4$ during sintering. Here, the additive of ZrO_2 was chosen. It is predicted that the ZrO_2 will not react with $MgAl_2O_4$. The ZrO_2 has high melting point (2677^oC) and large fracture toughness (12). On the other hand, the high density inert matrix $MgAl_2O_4$ ceramic needs powder having good reactivity (13). In this work the powders of MgO, Al_2O_3 and ZrO_2 as raw materials were prepared using precipitation method. The powder prepared by this method has small particle size (nano meter). It means that the powder has high reactivity. So, the aim of this work is to know the effect of ZrO_2 addition on crystal structure, microstructure and mechanical properties (especially hardness and fracture toughness) of $MgAl_2O_4$ ceramics for inert matrix made of powder prepared using precipitation method.

2. METHODOLOGY

Some amount of $Al(NO_3)_2$, $MgCl_2$ and $ZrOCl_2$ was separately dissolved with water. An amount of NH_4OH was poured into the three solutions untill forming precipitate. The precipitate then was separated, washed using water and dried by heating at 100^oC for 24 hours. After drying, the powder was calcined at 500^oC for 2 hours. The powder of Al_2O_3, MgO and ZrO_2 were formed. These three powders were mixed following composition of Table 1. The mixed powder was pressed with pressure of 4 ton/cm^2 into green pellets. The green pellets were sintered at 1600^oC for 2 hours. Density of the pellets was determined by weighing and

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dimension measurement.

Table 1. Composition for inert matrix ceramics in mole %.

No.	Al_2O_3 (mole %)	MgO (mole %)	ZrO_2 (mole %)
1.	50	50	0
2.	47.5	47.5	5
3.	45	45	10
4.	42.5	42.5	15

The crystal structure of the sintered pellet and phases present inside the pellet were analyzed using x-ray diffraction (XRD). The morphology or microstructure of fractured sample was investigated using a scanning electron microscope (SEM). Hardness and fracture toughness of the samples were determined using vickers microhardness testing with aid of equation [1] for hardness (8,14) and equation [2] for fracture toughness (8). Ilustration for vickers indentation is shown in Figure 1.

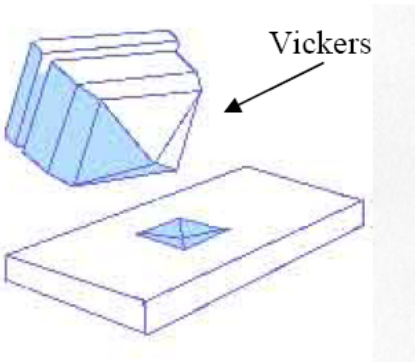

Figure 1. Indentor for Vickers and its indentation (14).

The unit for Vickers hardness of kg/mm^2 can be converted to GPa.

$$Hv = 1.8544.M/(2a)^2 \quad \text{.....} \quad [1]$$

Where :

Hv = Vickers hardness (kg/mm^2)
M = Load (kg)
2a = Diagonal length of indentation (mm).

$$K_{IC} = \{0.035Hv.a^{1/2}/\phi\}.\{E.\phi/Hv\}^{0.4}.\{l/a\}^{-0.5} \quad [2]$$

Where:

K_{IC} = Fracture toghness ($Mpa.m^{1/2}$),
Hv = Vickers hardness (kg/mm^2),
a = Half of diagonal length d (mm),
d = Average diagonal length of indentation (mm),
l = Crack length,
E = Young modulus
ϕ = Constraint factor of 2.7. Equation [2] is valid for $0.25 < l/a < 2.5$ (8)

The value of E of $MgAl_2O_4$ used for calculation here is 274 GPa (8).

3. RESULTS AND DISCUSSION

3.1 . Visual Appearance and Density

The sintered pellets were visually good as shown in Figure 2. The density of the pellets is shown in Table 2.

Table 2. Density of the sintered pellets as function of ZrO_2 concentration.

No.	Sample	Density (g/cm^3)
1.	$MgAl_2O_4$	3.20
2.	$MgAl_2O_4$-5 mole % ZrO_2	3.25
3.	$MgAl_2O_4$-10 mole % ZrO_2	3.30
4.	$MgAl_2O_4$-15 mole % ZrO_2	3.47

The density of sintered pellets is between 3.20 – 3.47 g/cm^3. The density increases following the increase of ZrO_2 concentration. It shows clearly the contribution of ZrO_2 additive. The increase is caused by the different theoretical density between $MgAl_2O_4$ ($3.58g/cm^3$) and ZrO_2 ($5.58g/cm^3$). This statement is supported by the XRD data described in another part of this paper. The increase trend can be predicted using equation [3]. According to this equation, the density of the sample will increase following the increase of ZrO_2 concentration.

$$\rho_{AV} = f(MgAl_2O_4).\rho(MgAl_2O_4)+f(ZrO_2).\rho(ZrO_2) \quad \text{.....} [3]$$

Where:

ρ_{AV} = Average density,
$f(MgAl_2O_4)$ = Vol fraction of $MgAl_2O_4$,
$\rho(MgAl_2O_4)$ = Theoretical density of $MgAl_2O_4$,
$f(ZrO_2)$ = Vol fraction of ZrO_2
$\rho(ZrO_2$ = Theoretical density of ZrO_2.

In order to know the inertness of the sintered pellets to water, an inertness testing was conducted by heating the pellets in the hot water (100°C) for 4 hours. Density of the pellets was measured before and after testing. According to the data in Table 3, there is no change in density observed. This means that all ceramics produced here are inert to water at 100°C.

Figure 2. Visual appearance of sintered pellets.

3.2 XRD

Diffraction profiles for ceramic with and without ZrO_2 addition are shown in Figure 3 to Figure 6, respectively. As can be seen in Figure 3, $MgAl_2O_4$ ceramic has been well produced at 1600°C. Majority peaks are from spinel $MgAl_2O_4$ (Analyzed using JCPDS standard for $MgAl_2O_4$ no. 21-1152). No peak from second phase was observed. Figure 4 to Figure 6 are diffraction profiles for $MgAl_2O_4$ added with ZrO_2 with concentration of 5-15 mole %. As shown in Figure 4-6, other than peaks from $MgAl_2O_4$, peaks from ZrO_2 are also observed (JCPDS standard for ZrO_2 No. 37-1484). This means that the additive of ZrO_2 does not dissolve in $MgAl_2O_4$ as matrix. The ZrO_2 is distributed inside the matrix of $MgAl_2O_4$ as inclusion. By considering this data, it can be stated that the analyses using equation [3] to explain the density increase is relevan.

Dissolution of ZrO_2 can be confirmed also by evaluating lattice constant data. Theoretically, since ZrO_2 dissolved in $MgAl_2O_4$ by substitution of Al^{3+}, the latice constant of the $MgAl_2O_4$ should change because ionic radius of Zr^{4+} (86 pm) is larger than ionic radius of Al^{3+} (67.5 pm) and no change in lattice constant since Zr^{4+} substitutes Mg^{2+} (86 pm) (12).

The lattice constant data in Table 4 which calculated using equation [4] (15) shows that no change in lattice constant was observed. It means that between the two conditions, the second one is possible. However, this can happen only when ZrO_2 dissolved and Zr^{4+} substitutes Mg^{2+}. Figure 4 to 6 shows that peaks from ZrO_2 were observed. This means that the ZrO_2 did not dissolved in the $MgAl_2O_4$

Table 3. Density of the sintered pellets before and after inertness testing.

No.	Sample	Before inertness to water testing (g/cm^3)	After inertness to water testing (g/cm^3)	$\Delta\rho$ (g/cm^3)
1.	$MgAl_2O_4$	3.20	3.20	0.00
2.	$MgAl_2O_4$-5 mole % ZrO_2	3.25	3.25	0.00
3.	$MgAl_2O_4$-10 mole % ZrO_2	3.30	3.30	0.00
4.	$MgAl_2O_4$-15 mole % ZrO_2	3.47	3.47	0.00

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Table 4. Data of lattice constant.

No.	ZrO_2 concentration (mole %)	Lattice constant (A)
1	0% ZrO_2	8.0584
2	5% ZrO_2	8.0574
3	10% ZrO_2	8.0523
4	15% ZrO_2	8.0783

$$a = d(h^2+k^2+l^2)^{0.5} \quad [4]$$

a = Lattice constant,
d = Inter crystal plane distance
h, k, l = Miller indices.

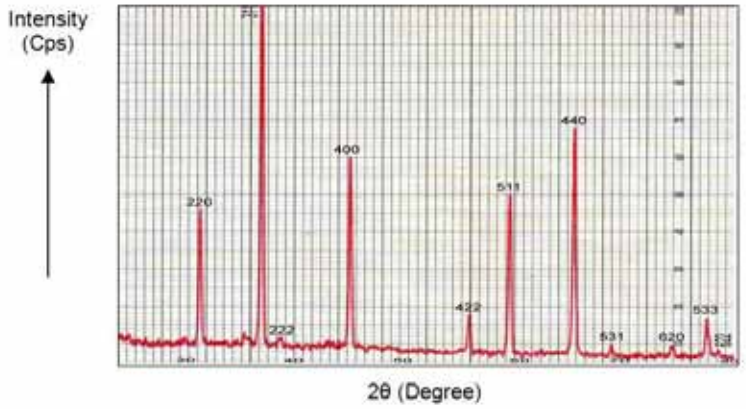

Figure 3. XRD profile of $MgAl_2O_4$ ceramic without additive.

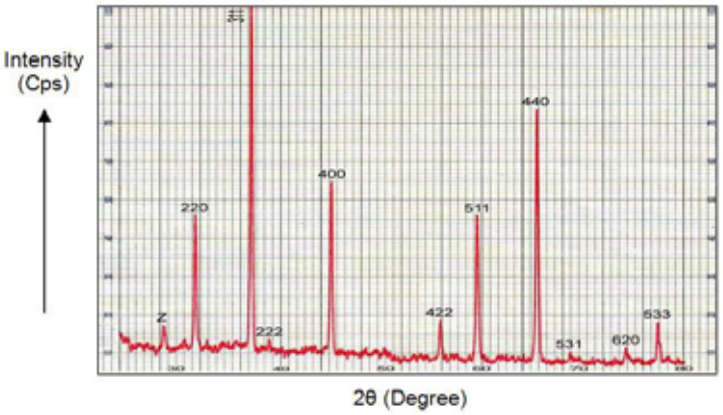

Figure 4. XRD profile of $MgAl_2O_4$ ceramic with 5 mole % ZrO_2 addition.

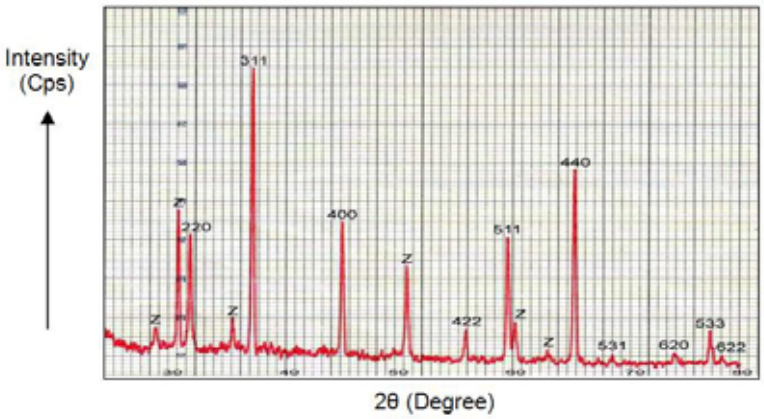

Figure 5. XRD profile of $MgAl_2O_4$ ceramic with 10 mole % ZrO_2 addition.

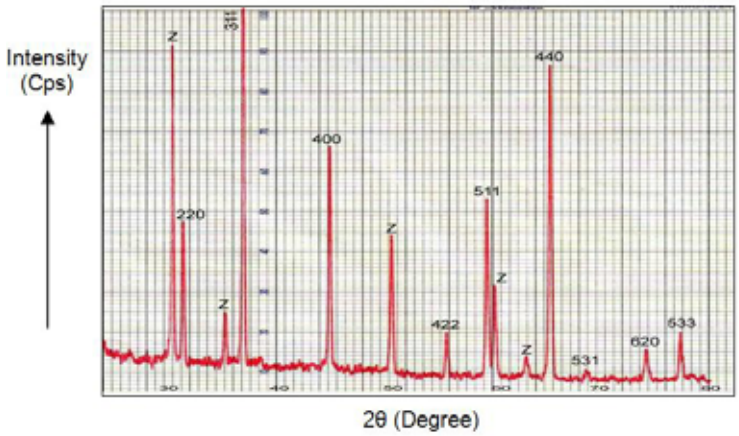

Figure 6. XRD profile of $MgAl_2O_4$ ceramic with 15 mole % ZrO_2 addition.

3.3. Microstructure

The images of SEM for $MgAl_2O_4$ ceramics with and without ZrO_2 addition are shown in Figure 7 to Figure 10. It can be seen that grains of the ceramics tend to be smaller when the ZrO_2 is present. The average grain size decreases following the increase of ZrO_2 concentration.

This data shows that the presence of additive inhibited grain growth during sintering. The additive of ZrO_2 is present as second phase as confirmed by the XRD data. The presence of the second phase makes the grains of the ceramic becomes smaller.

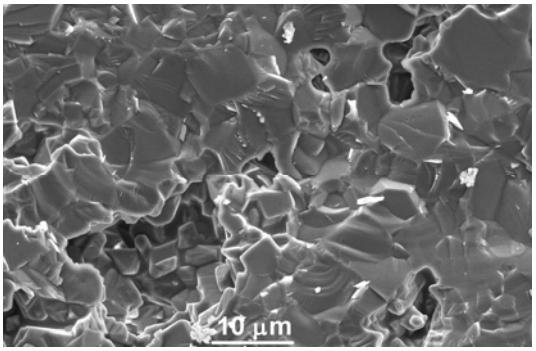

Figure 7. Microstructure of $MgAl_2O_4$ ceramic without additive.

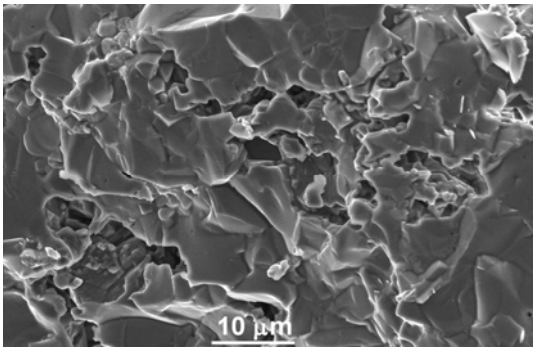

Figure 8. Microstructure of $MgAl_2O_4$ ceramic with addition of 5 mole % ZrO_2.

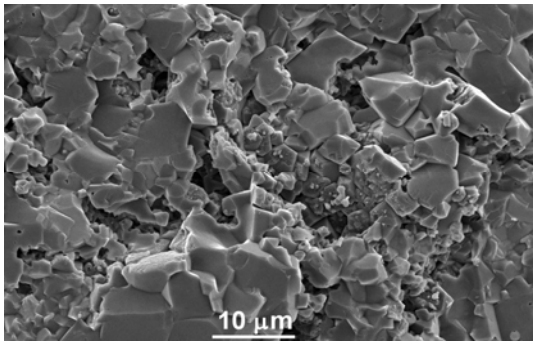

Figure 9. Microstructure of $MgAl_2O_4$ ceramic with addition of 10 mole % ZrO_2.

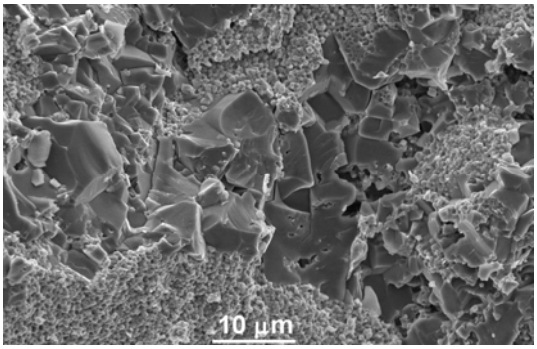

Figure 10. Microstructure of $MgAl_2O_4$ ceramic with addition of 15 mole % ZrO_2.

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3.4. Hardness and Fracture Toughness

Hardness and fracture toughness data for $MgAl_2O_4$ ceramics with and without ZrO_2 addition are shown in Table 5.

Table 5. Hardness and fracture toughness

No.	Sample	Hardness (kg/mm^2)	Fracture toughness (K_{IC}) ($MPa.m^{1/2}$)
1.	$MgAl_2O_4$	663	1.4
2.	$MgAl_2O_4$-5 mole % ZrO_2	714	1.5
3.	$MgAl_2O_4$-10 mole % ZrO_2	908	1.7
4.	$MgAl_2O_4$-15 mole % ZrO_2	1255	1.8

One can see that the hardness and fracture toughness of the $MgAl_2O_4$ ceramics increase with the increase of ZrO_2 concentration. The presence of ZrO_2 as second phase or inclusion as confirmed by the XRD and the microstructure data, and the small grains caused by the presence of the ZrO_2 are the cause of the hardness and fracture toughness increase. The inclusions of ZrO_2 and grain boundaries have changed the ceramics to become more stronger to deformation. The fracture toughness is lower than that found in literature, i.e. 2.5 $MPa.m^{1/2}$ (8). This is due to the lower density of our samples (90% theoretical density).

4. CONCLUSIONS

The ZrO_2 added-$MgAl_2O_4$ ceramics with density of 3.2 – 3.47 g/cm^3 have been produced at sintering temperature of 1600^oC. The ceramics crystallize in cubic spinel. The additive of ZrO_2 does not dissolve in $MgAl_2O_4$ and tends to form inclusion and inhibits grain growth. The addition of ZrO_2 increases the hardness and fracture toughness of $MgAl_2O_4$ ceramics through the change of microstructure. For example, the hardness of $MgAl_2O_4$ ceramic without ZrO_2 of 663 kg/mm^2 increases to 1255 kg/mm^2 after addition of 15 mole % ZrO_2 and the fracture toughness of $MgAl_2O_4$ ceramic without ZrO_2 of 1.4 $MPa.m^{1/2}$ increases to 1.8 $MPa.m^{1/2}$ after addition of 15 mole % ZrO_2.

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6. REFERENCES

1. International Atomic Energy Agency. Viability of inert matrix fuel in reducing plutonium amounts in reactors. IAEA-TECDOC-1516. Vienna: IAEA; 2006.
2. Medvedev P. Development of dual phase magnesia-zirconia ceramics for light water reactor inert matrix fuel. Doctor Thesis. Idaho: Idaho State University; 2004.
3. Medvedev P, Frank SM, Holleran TP, Meyer MK. Dual phase MgO-ZrO_2 for use in LWR inert matrix fuel. J Nucl Mat 2005; 342: 48-62.
4. Wiss TGA, Damen PMG, Hiernaut JP, Ronch Ci. Helium and xenon behaviour in irradiated Am-containing $MgAl_2O_4$ (Reactor experimenrt EFTTRA-T4). J Nucl Mat 2004; 334: 47.
5. Neeft EAC, Bakker K, Schram RPC, Conrad R, Konings RJM. The EFTTRA-

T3 irradiation experiment on inert matrix fuels. J Nucl Mat 2003; 320: 106.

6. Noirot J, Decgranges L, Chauvin N, Georgenthum V. Post-irradiation examinationsof THERMHET composite fuels for transmutation. J Nucl Mat 2003; 320: 117-25.
7. Nitani N, Kuramoto K, YamashitaT, Nihey Y, Kimura Y. In-pile irradiation of rock-like oxide fuels. J Nucl Mat 2003; 319: 102-7.
8. Neeft EAC, Bakker K, Belvroy RL, Tams WJ, Schram RPC, Conrad R, Veen AV. Mechanical behavior of macro-dispersed inert matrix fuels. J Nucl Mat 2003; 317: 217-25.
9. Neeft EAC, Bakker K, Schram RPC, Conrad R, Konings RJM. The EFTTRA-T3 irradiation experiment on inert matrix fuels. J Nucl Mat 2003; 320: 106–16.
10. Savchenko AM, Vatulin AV, Glagovsky EM, Ikonovalov I, Morozov AV, Kozlov AV, et al. Main results of the development of dispersion type IMF at A.A. Bochvar Institute. J Nucl Mat 2010; 396: 26–31.
11. Syarif DG, Sambodo GD, Yamin M, Setiadi Y. Characterization of $MgAl_2O_4$ ceramics for matrix of inert matrix nuclear fuel (IMF) made of high energy ball milling (HEM) powder at sintering temperature of 1500^{O}C. JSTNI 2009; 10(2):97-106.
12. Barsoum M. Materials science series: fundamental of ceramic. McGraw-Hill; 1997.
13. Lie JG, Ikegami T, Lee JH, Mori T, Yajima Y. Synthesis of Mg-Al spinel powder via precipitation using ammonium bicarbonate as the precipitant. J Europ Cer Soc 2001; 21: 139-48.
14. Yount HJ. Advanced ceramic materials for use as fuel coating and inert matrix materials in advanced reactors. Master Thesis. University of Wisconsin-Madison, USA; 2006.
15. Klug HP, Alexander LE. X-ray diffraction procedures (For Polycrystalline and Amorphous Materials). New York : John Wiley & Sons; 1974.