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Role of V_2O_5 on the formation of chemical mullite from aluminosilicate precursor

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Abstract

Aluminosilicate precursor for the processing of mulite ceramics was synthesized chemically from inorganic salts following colloidal route. V_2O_5 was used as a sintering additive in different ratios with the precursor powder. The powder mixes were compacted and sintered at different elevated temperatures. The sintered masses were characterized by measuring the bulk density, porosity, flexural strength and fracture toughness. The extent of mullitization and final microstructure of the sintered masses were investigated by scanning electron microscopy and XRD analysis. It was observed that V_2O_5 exhibited favourable effect on the formation of properly crystallized mullite and in the improvement of different mechanical properties.

Keywords: A. Sintering; B. Microstructure-final; D. Mullite; Powder-chemical preparation

1. Introduction

Mullite, having molecular formula $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$ is a major constituent in many industrial ceramic products. It is basically a non-stoichiometric compound where x denotes the number of missing oxygen and atoms per unit cell, varying between 0.17 and 0.59 [1]. Due to several technical advantages, like, low thermal expansion and thermal conductivity, good stability, high melting point, chemical resistance and creep resistance, mullite is an attractive engineering material for different high temperature applications [2]. Recent studies of mullite synthesis have emphasized more on the utilization of chemically synthesized precursors which are converted into mullite in a low temperature range from −850 to −1350 °C [3–7]. Mullite synthesized by this method is known as 'chemical mullite' [8]. The importance of these preparation methods has increased within the last few years and numerous methods have been developed.

Different transition metal oxides have been shown to have favourable mineralizing effect on the formation of mullite ceramics from the precursor materials [9–12]. Several works have been reported the role of different transition metal oxides on the processing of mullite ceramics. Baudin and Moya [13] investigated the influence of titanium dioxide on the sintering and microstructural evolution of mullite and observed that addition of TiO_2 under the solubility limit enhanced the initial sintering and grain size in mullite whereas an amount in excess of that limit inhibits sintering and drastically increased the total porosity and mean pore size. Nass et al. [14] investigated the influence of chromium on homogeneity of gels and on mullite formation at 980 °C by DTA coupled with quadrupole mass spectrometry, SEM, EDX and TEM analysis and observed that difference in chromium content affected the crystallization path of mullite. Mitra et al. [15] observed that Cr_2O_3 played a positive role in the formation of mullite at elevated temperatures from the aluminosilicate gel precursor. Bagchi et al. [16] studied the influence of copper ions on the synthesis of nano-crystalline mullite at a low temperature and observed that activated crystal lattice of copper catalyzed the reaction between alumina and silica to form mullite at a much lower temperature of 600 °C.

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In the present investigation effect of V_2O_5 on the crystallization of mullite from alumino silicate precursor powder will be investigated examining the microstructure and mechanical properties of mullite formed by the sintering of aluminosilicate gel precursor from inorganic salts.

2. Experimental

$Al(NO_3)_3{\cdot}9H_2O$ of analar quality and liquid sodium silicate (sp. Gr. 1.6 and molar ratio of Na_2O:SiO_2 = 1:3) were used as the starting materials for the synthesis of the aluminosilicate hydrogel. The chemical composition of the starting materials is given in Table 1. From sodium silicate solution silicic acid was prepared by ion exchange process. A dilute sodium silicate solution (7%, w/v) was passed through a column packed with Dowex-50 cation exchanger with a flow rate of 200 ml/min. The silicic acid sol thus generated was stored in a polythene container to avoid contamination and to maintain the stability of the sol.

The generated silicic acid sol and $Al(NO_3)_3{\cdot}9H_2O$ solution were mixed together stoichiometrically to attain a molar ratio Al_2O_3:SiO_2 = 3:2 in the mix. After mixing the pH of the solution was 2. To the mixed solution 1:1 ammonia solution was added slowly. The viscosity of the solution increased gradually and ultimately en block (throughout the mass) gel formation took place at pH 9. The gel was filtered, washed thoroughly, dried at 80 °C followed by calcination at 800 °C for a period of 2 h. The gel was characterized by chemical analysis, measurement of surface area and bulk density and the results are given in Table 2. The calcined gel was thoroughly ground with V_2O_5 (Reagent Grade) additive in different ratios in a pot mill to ensure proper homogeneity in the mixes. The composition of the different batches is given in Table 3. The powder mixes were compacted at 100 MPa. The samples were fired in an electrically heated muffle furnace at three different final temperatures, ca., 1400, 1500 and 1600 °C, with 2 h of soaking period in each case. Bulk density and apparent porosity of the sintered samples were measured following the procedures described in BS 1902, Part 1A, 1966. The flexural strength of the sintered samples were determined from a three point bending strength with a span of 30 mm and a loading rate of 0.5 mm/min. Fracture toughness was determined by using an indentation micro-crack method with a load of 5 kg [17]. XRD characterization of the samples was carried out with a Rigaku X-ray diffractometer with Cu target (Miniflex, Japan). Studies of photomicrograph and EDX analyses of the samples were carried out with FEI Quanta microscope (US).

Table 1
Chemical constituents of the ingredients.

Ingredients	SiO_2	Al_2O_3	Na_2O
Sodium silicate	29.75	–	17.41
Aluminum nitrate	–	12.98	–
Batch composition	27	73.	–

Table 2
Physicochemical properties of the hydrogel.

Composition	Properties
SiO_2	17.86
Al_2O_3	48.23
Ignition loss	33.91
Bulk density (g/cm^3)	0.27
Sp. surface area (m^2/g)	170

Table 3
Batch composition of the samples.

Batch no.	Al_2O_3–SiO_2 hydrogel	V_2O_5
1	100	0
2	99	1
3	98	2
4	97	3
5	96	4

3. Results and discussion

The precursor aluminosilicate was synthesized through an aqueous phase colloidal interaction of the starting materials under optimum condition to achieve molecular level mixing among the constituents. Silicic acid was generated by ion exchange process. As it is a positively charged colloid, it did not exhibit the tendency of polymerization. When silicic acid sol was mixed with $Al(NO_3)_3$ solution, the solution became acidic. After the addition of ammonia, $Al(OH)_3$ was formed and silicic acid was polymerized by condensation. It resulted in the formation of diphasic aluminosilicate gel.

The precursor powder had a very low bulk density (0.27 g/cm^3) and a considerable surface area (170 m^2/g), which is an indication of its relative surface activity. The hydrogel contained significant amount of water (33.91%). To prevent excessive shrinkage during sintering, it was calcined at 800 °C. From the chemical analysis of the powder (Table 2) it was apparent that the composition lies slightly in the alumina-rich zone of the mullite. It was done intentionally to eliminate the glassy phase formation as far as possible. There was no deviation from the parent batch composition. In this system discrete aluminum hydroxide gel particles was likely to be distributed uniformly in the high molecular weight polysilicic acid gel network, thereby forming a typical diphasic gel system.

It has been reported by other workers that mullite formation in diphasic aluminosilicate gel is controlled by dissolution–precipitation reactions, where Al_2O_3 species dissolve in the co-existing SiO_2 liquid until a critical Al_2O_3 concentration is reached [18,19]. Higher Al_2O_3 concentrations induce random mullite nucleation in the bulk of the SiO_2-rich phase. Therefore, the dissolution velocity of Al_2O_3 into the SiO_2 liquid is the rate limiting step for the nucleation and subsequently growth of mullite crystals. Both the formation temperature of the SiO_2-rich liquid phase and the velocity of the Al_2O_3 dissolution into the liquid phase are related to the nature (activity) of SiO_2 and Al_2O_3 used and the presence of other compounds. V_2O_5 has a very low melting point (690 °C). It is likely to develop a liquid

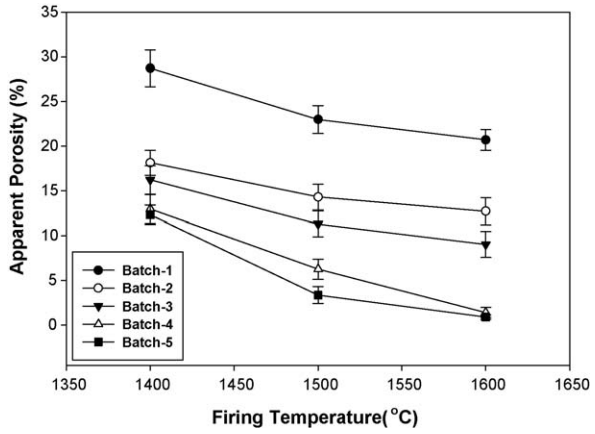

Fig. 1. Variation in apparent porosity (%) with V_2O_5 content.

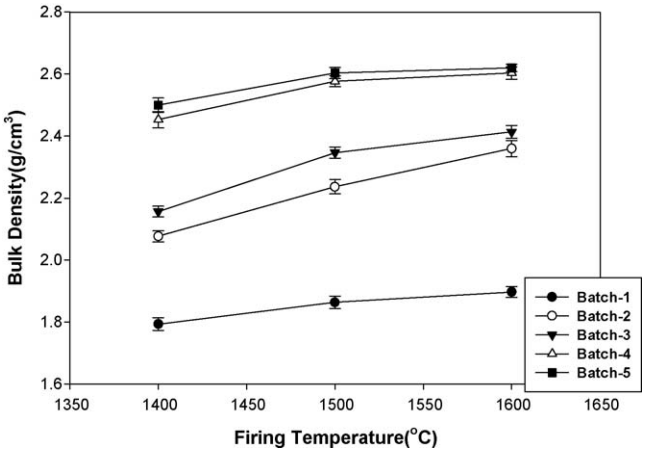

Fig. 2. Variation in bulk density with V_2O_5 content.

phase at a relatively lower temperature, which can reduce the viscosity of the SiO_2-rich liquid phase in a diphasic gel by several orders of magnitudes. Therefore, mullite formation temperature can be effectively reduced [20].

In V_2O_5 the cation V(+5) is in octahedral co-ordination. During heat treatment V_2O_5 can loose oxygen and may be converted to the corresponding tetraoxide and trioxide in the following way,

$$V_2O_5 \rightarrow V_2O_4 + (1/2)O_2 \quad (1)$$

$$V_2O_4 \rightarrow V_2O_3 + O_2 \quad (2)$$

In all the three oxides vanadium remains in octahedral co-ordination and the cationic radii of the three different oxidation states are like the following, V(+5) = 68 pm; V(+4) = 72 pm and V(+3) = 78 pm [21].

The aluminosilicate gel is basically consisted of AlO_6 octahedra and SiO_4 tetrahedra. The octahedral co-ordination of vanadium in the above mentioned oxidation states favour the substitution of Al^{3+} from the octahedral site of the mullite. The cationic sizes of vanadium in all the three mentioned oxidation states are larger than the cationic size of Al(+3), which is 53 pm. Therefore, substitution of Al^{3+} by vanadium ions results in lattice expansion Again presence of one d-electron in V(+3) also introduces a strain in the aluminosilicate structure by Jahn-Teller effect [22]. This distortion in local symmetry results in macroscopic phase transformation due to a large energetic stabilization [10,23].

The substitution of aluminum by vanadium in octahedral site could cause aluminum ion vacancies according to the following defect reaction for aluminum sub-lattice.

$$(1-x)Al_2O_3 + x'R_2O_5 \rightarrow 2(1-x)Al_{Al} + x'\ddot{R}_{Al} + \frac{2x}{3}V_{Al}^{'''} + (3-x)O_o \quad (3)$$

where R stands for vanadium ion.

This fact could enhance the mass transport and consequently, the sintering rate of the aluminosilicate gel in presence of the V_2O_5 additive was increased.

So theoretically V_2O_5 can accelerate the formation of mullite at lower temperature. From the variation in bulk density and apparent porosity (Figs. 1 and 2) of the samples with sintering temperature it is apparent that V_2O_5 exhibited a pronounced effect on the densification of the material. It may be related to the formation of more liquid phases in V_2O_5 containing batches. After sintering temperature 1500 °C, the effect was not much significant.

From the microstructures of the samples (Figs. 3 and 4) it is apparent that in the sample with V_2O_5 crystallization process was more pronounced. Mullite has a strong tendency to grow anisotropically if the grain formation occurs without constraint [20]. For samples without any additive, crystal formation was not complete. In presence of V_2O_5 the viscosity of the liquid melt is reduced, which facilitates the re-crystallization of rod-

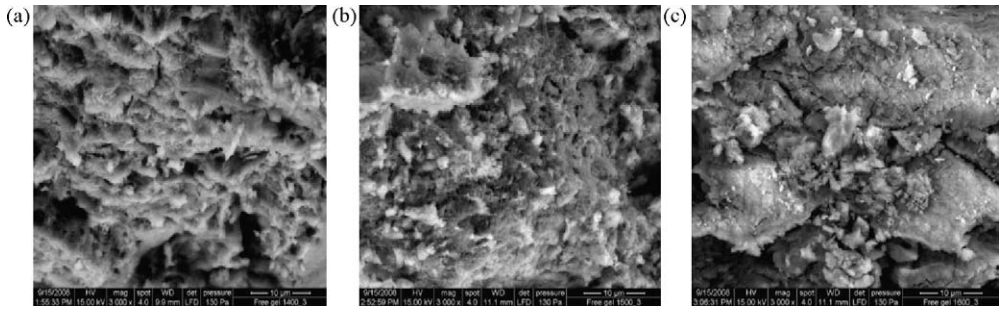

Fig. 3. Scanning electron micrograph of the sintered gel samples (no additive): (a) sintered at 1400 °C, (b) sintered at 1500 °C, and (c) sintered at 1600 °C.

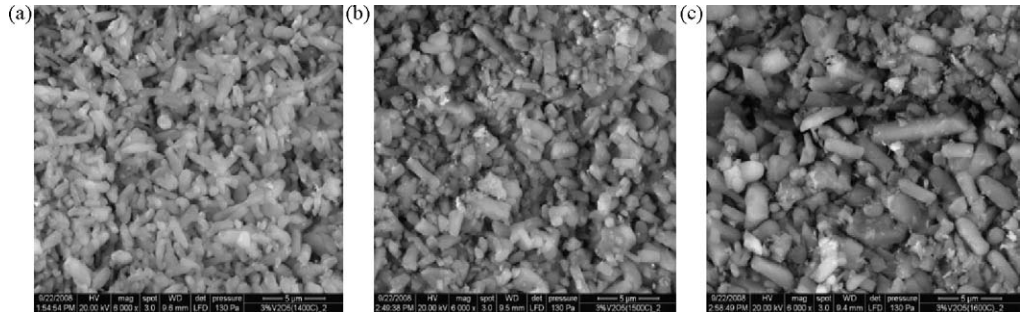

Fig. 4. Scanning electron micrograph of the sintered gel with 3% V_2O_5: (a) sintered at 1400 °C, (b) sintered at 1500 °C, and (3) sintered at 1600 °C.

Table 4
Chemical composition and lattice parameters of vanadium oxide doped mullite.

Batch no.	Composition (wt%)			Mullite unit cell			
	Al_2O_3	SiO_2	V_2O_5	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)
1	72.97	27.03	0	7.5238	7.6789	2.8671	165.6452
2	72.31	26.78	0.91	7.5239	7.6791	2.8673	165.6633
3	71.68	26.56	1.76	7.5242	7.6794	2.8678	165.7053
4	71.08	26.34	2.58	7.5246	7.6799	2.8680	165.7364
5	70.65	26.16	3.19	7.5247	7.6800	2.8682	165.7524

shaped anisotropic mullite crystals. The reduction in melt viscosity is also a function of sintering temperature. It was evident by the formation of more perfect shaped mullite at higher sintering temperature. The chemical compositions of the mullite crystals were determined by EDX analysis to determine the solubility of V_2O_5 in the crystal. The results are given in Table 4. It is apparent from the results that with the increase in its content the relative solubility of V_2O_5 in the mullite crystals reduced. The relative insolubility of V_2O_5 from 1 to 4% was found to be 0.9, 12 14 and 20% respectively. Mullite unit cell volume increased with the increase in the V_2O_5 content in the crystal and expansion took place along all the three axes. As discussed earlier, it might be related to the larger cationic size of V(+3) compared to Al(+3). With 4% V_2O_5 content the volume expansion of the lattice was about 0.65%. From the XRD pattern of the samples (Figs. 5 and 6) it was observed that the amount of mullite phase substantially increased with the addition of the additives. It was apparent from the presence of less number of alumina and cristobalite peaks in the

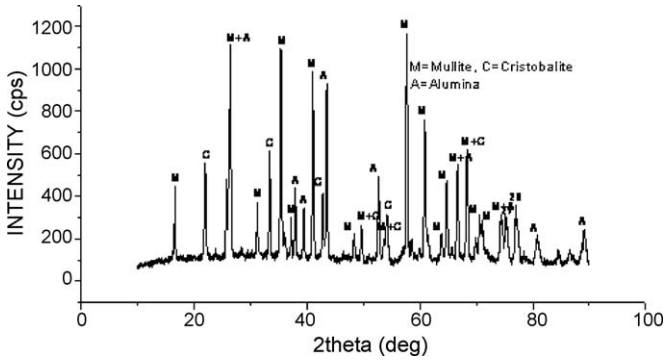

Fig. 5. XRD diagram of the gel (no additive) sintered at 1500 °C.

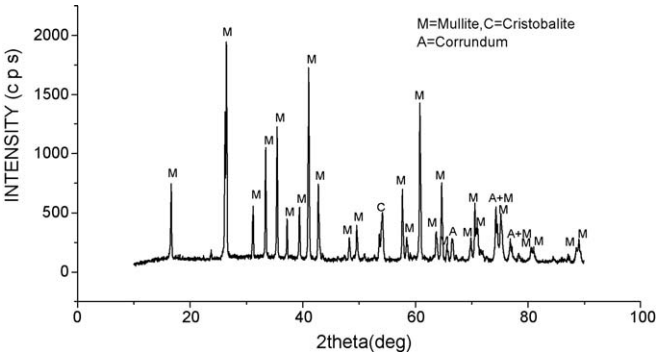

Fig. 6. XRD diagram of the sintered gel with 3% V_2O_5 at 1500 °C.

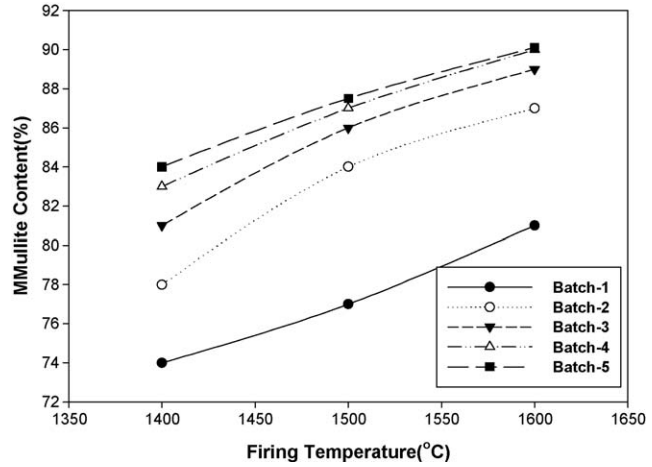

Fig. 7. Variation in mullite content with sintering temperature.

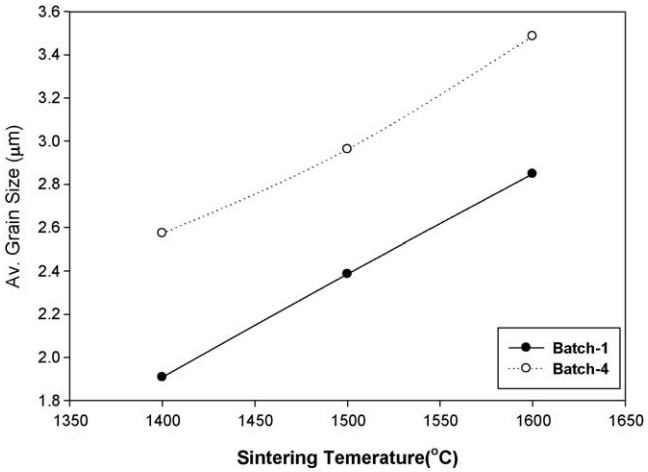

Fig. 8. Variation in average grain size with sintering temperature.

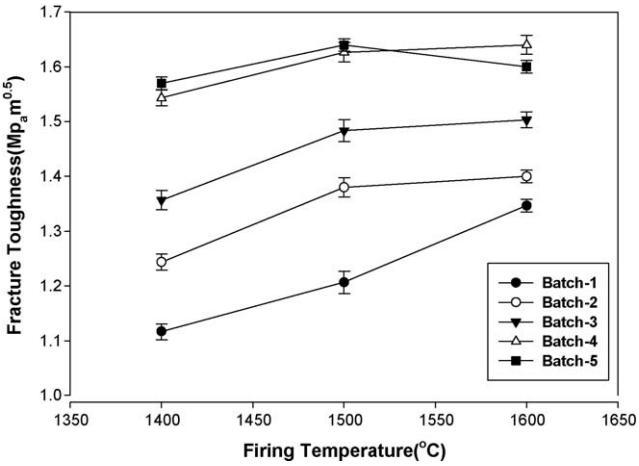

Fig. 10. Variation in fracture tougness with V_2O_5 content.

diffractogram of the samples with additive. The relative percentage of mullite increased with the increase in the both V_2O_5 content and sintering temperature. It is apparent that with the addition of 3% V_2O_5 about 15% more mullitization can be achieved at a sintering temperature of 1500 °C (Fig. 7). The average grain sizes of the sintered samples were calculated using Scherrer's formula [16]. The average grain size increased significantly with the increase in the additive content and the sintering temperature (Fig. 8).

The mechanical strength like flexural strength and fracture toughness (Figs. 9 and 10) of the samples showed much improvement in the presence of the additives. It can be related to improved densification in the batches with additives. The gas pores present in the samples disappeared with the addition of V_2O_5 and consequently the stress surrounding the pores were also eliminated [24]. Formation of more interlocked crystalline phases with the addition of the V_2O_5 additives is another reason for the improvement of the mechanical strength. From the microstructure it is apparent that most of the liquid melt has been converted to the crystalline phase in the presence of the additive. Therefore, a small amount of highly viscous silica or aluminosilicate glass may exist at the grain boundaries, which would minimize the contribution of grain boundary sliding to the fracture stress. After 3% V_2O_5 content in the batches, both the flexural strength and fracture toughness did not improve significantly. On the contrary at the highest sintering temperature under the experimental condition there was a slight drop in these mechanical properties. It might be related to the formation of excessive liquid phase with the increase in the V_2O_5 content at higher sintering temperatures for this system.

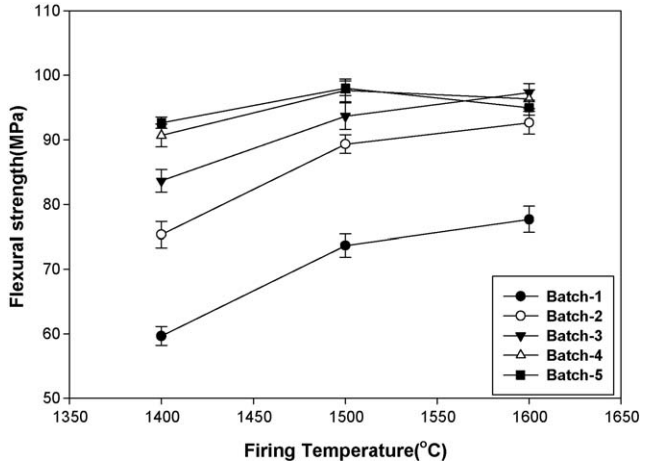

Fig. 9. Variation in flexural strength with V_2O_5 content.

4. Summary and conclusion

Aluminosilicate diphasic gel precursor of mullite was synthesized by the colloidal interaction of silicic acid and $Al(NO_3)_3$ solution. The gel powder possessed very low density and high surface area. V_2O_5 was used as sintering additive for the processing of mullite ceramics By virtue of its low melting point, Jahn-Teller effect and induced cationic vacancy in the sub-lattices, V_2O_5 promoted the formation and crystallization of mullite from the melt as a function of sintering temperature. The mechanical properties of the sintered masses were also improved considerably due to improved microstructure and favourable phase compositions. The crystal volume of mullite increased with the increase in the V_2O_5 content. After 3% V_2O_5 content the mechanical properties did not improve significantly. The average grain size was also increased significantly with the increase in the additive content and the sintering temperature.

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