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A new polymorph phase of $LiAlSiO_4$ in β-$LiAlSiO_4$/Cu composite

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β-eucryptite ($LiAlSiO_4$) with a negative thermal expansion coefficient can be used as reinforcement in metal matrix composites to reduce the coefficient of thermal expansion (CTE) of the composites. It is necessary to clarify the phase transformation of β-eucryptite ($LiAlSiO_4$) which influences the CTE of the composite. A copper matrix composite reinforced by β-$LiAlSiO_4$ was fabricated by spark plasma sintering. The composite was characterized using X-ray diffraction and transmission electronic microscope. A new phase of eucryptite has been found, which is a polymorph phase and has primary cubic structure with the lattice constant of 0.435 nm. The reason for the phase transition from β-$LiAlSiO_4$ to the new phase was discussed which may result from the large anisotropic stress in the β-$LiAlSiO_4$ particles of β-$LiAlSiO_4$/Cu composite. The discovery of the new polymorph of $LiAlSiO_4$ in β-$LiAlSiO_4$/Cu composite indicates that the phase transformation caused by thermal mismatch stress may be easier than that caused by hydrostatic pressure.

Keywords: β-$LiAlSiO_4$; metal matrix composites; spark plasma sintering; phase transition

1. Introduction

β-$LiAlSiO_4$ (β-eucryptite) has attracted attentions over the last several decades due to its unusual properties, such as special thermal expansion, one-dimensional superionic conductivity of Li^+ ions, and good chemical and thermal stability.[1] For thermal expansion, β-eucryptite has highly anisotropic coefficient of thermal expansion (CTE),[2,3] CTEs perpendicular and parallel to the *c*-axis are 7.26×10^{-6} and $-16.35 \times 10^{-6}\,K^{-1}$, respectively, which results in a negative volume CTE.[4] The negative CTE of β-$LiAlSiO_4$ has been used to reduce the CTEs of both ceramics [5] and metal matrix composites (MMCs).[6]

In the early years, the crystal structure of β-eucryptite was intensely studied by Winkler, Buerger, Hornyak, and Laves.[7–11] Later, researchers found that temperature and pressures affected the crystal structure of β-$LiAlSiO_4$. The Li^+ order-disordering transition in the β-$LiAlSiO_4$ at 460 °C on heating has been proved by numerous researches.[12,13] Zhang et al. [14] have carried out comprehensive experiments for phase transformation of β-$LiAlSiO_4$ at different temperatures and hydrostatic pressures. Two kinds of reversible phase transformations of β-$LiAlSiO_4$ at room temperature were reported in the research of Zhang et al.,[15] one is the phase transformation of

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β-$LiAlSiO_4$ to ε-$LiAlSiO_4$ at the hydrostatic pressure between 0.83 and 1.12 GPa; another is amorphization of β-$LiAlSiO_4$ with hydrostatic pressure increasing from 4.5 to 17.0 GPa. With temperature and pressures increasing, some irreversible phase transformations can happen and form other phases, such as α-$LiAlSiO_4$, $LiAlSi_2O_6$, $LiAlO_2$, and a new phase with spinel structure.[14]

The previous researches have given a general understanding on the transformation of β-$LiAlSiO_4$ under hydrostatic pressure condition. It was also found that phase transformation of β-eucryptite ($LiAlSiO_4$) has complex effect on the CTE of Al matrix composites.[16,17] However, our understanding of this material is far from complete, the phase transition of β-$LiAlSiO_4$ under complex stress condition in composites has not been clarified. In this study, we have found that a new polymorph phase transition of $LiAlSiO_4$ in β-$LiAlSiO_4$/Cu composite, which is caused by residual stress due to the large CTE mismatch between β-$LiAlSiO_4$ and Cu matrix.

2. Experiments

β-$LiAlSiO_4$ powder used in this work was produced by the method developed in our laboratory.[18] Pure copper powder (500 mesh) was supplied by Harbin Dong Da High-Tech Materials (Group) Corp. Ltd. β-$LiAlSiO_4$ particles were firstly coated with Ag coating by an electroless plating method for improving the wetability.[6] Then, pure Cu powder and Ag-coated β-$LiAlSiO_4$ particles were mechanically blended in a planetary mill for 4 h. Finally, β-$LiAlSiO_4$/Cu composites were fabricated by spark plasma sintering (SPS) at 750 °C in a graphite die under the pressure of 50 MPa for 5 min.

Phase composition of the composite was analyzed by using X-ray diffraction (XRD) on a Philips X'Pert X-ray diffractometer with Cu K_α radiation. Microstructures were investigated on an H3000 type scanning electron microscopy (SEM) and a FEI G^2 Tecnai transmission electronic microscope (TEM). The specimens for TEM observations were thinned by ion milling.

3. Results and discussion

The SEM microstructure image of the β-$LiAlSiO_4$/Cu composites is shown in Figure 1. It can be seen that β-$LiAlSiO_4$ particles are distributed uniformly in the Cu matrix of the composite, and no crack can be found.

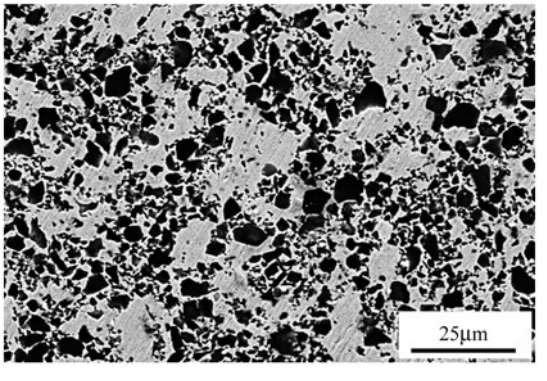

Figure 1. SEM micrograph of β-$LiAlSiO_4$/Cu composite.

Figure 2 shows the wide angle scan XRD of β-$LiAlSiO_4$/Cu composite and fine scan XRD peaks of (2 0 2) diffractions of β-$LiAlSiO_4$ as powder and in composite. The diffraction peaks in Figure 2(a) can be indexed as Cu, Ag, and β-$LiAlSiO_4$. Ag phase results from the surface coating of β-$LiAlSiO_4$ particles. The result suggests that the interfacial reaction between β-$LiAlSiO_4$ and Cu is very light, and the main phase components in the composite are not changed during SPS process. In Figure 2(b), it can be found that the diffraction peak position of β-$LiAlSiO_4$ (2 0 2) in the composites is higher than that of β-$LiAlSiO_4$ powder, which implies that compressive residual stress exists in the β-$LiAlSiO_4$ particles in the composite. The compressive residual stress in the composite is caused by the mismatch of CTE between β-$LiAlSiO_4$ particle and Cu matrix, so it is called as thermal mismatch stress (TMS) and has generally been found in MMCs.[19]

The TEM morphologies of β-$LiAlSiO_4$/Cu composite are shown in Figure 3. Firstly, no reaction between β-$LiAlSiO_4$ and Cu can be found at the interface. Meanwhile, some black spots with the size of 200–400 nm in the β-$LiAlSiO_4$ particles can be clearly found in Figure 3(a) and (b) but not in Figure 3(c). The selected area electronic diffraction pattern (SADP) (see Figure 3(d)) shows that the white regions in the particle

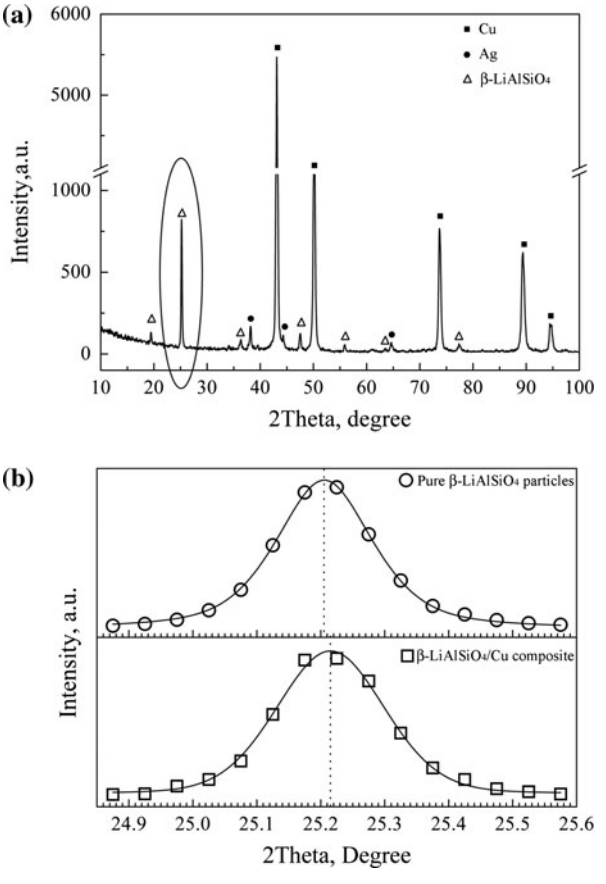

Figure 2. Wide angle scan XRD of β-$LiAlSiO_4$/Cu composite (a) and fine scan XRD peaks of (2 0 2) diffractions of pure β-$LiAlSiO_4$ and β-$LiAlSiO_4$ particles in β-$LiAlSiO_4$/Cu composite (b).

is β-$LiAlSiO_4$, but the black spots are not β-$LiAlSiO_4$ according to their SADPs which are analyzed in Figure 4. Therefore, it can be concluded that a phase transition takes place in some β-$LiAlSiO_4$ particles of the β-$LiAlSiO_4$/Cu composite. In addition, there are a lot of dislocations in the Cu matrix near the interface of the composite as shown in Figure 3(c), which indicates that large TMS exist in the composite.[20]

To determine the structure of the small black spots in β-$LiAlSiO_4$ particles, the SADPs with different orientations of the black spots in β-$LiAlSiO_4$ particles were taken from the composite, and the typical SADPs are shown in Figure 4. It is found that the SADPs cannot be indexed by $LiAlSiO_4$ compounds found in the previous studies, so the result suggests that the black spot in Figure 3(a) and (b) is a new polymorph phase of $LiAlSiO_4$. The new phase is called as 'C-phase' for the convenient of discussion. On the basis of analysis of SADPs from the C-phase, some values of d (interplanar spacing) and $1/d^2$ of the different SADPs for new polymorph phase of $LiAlSiO_4$ are listed in Table 1.

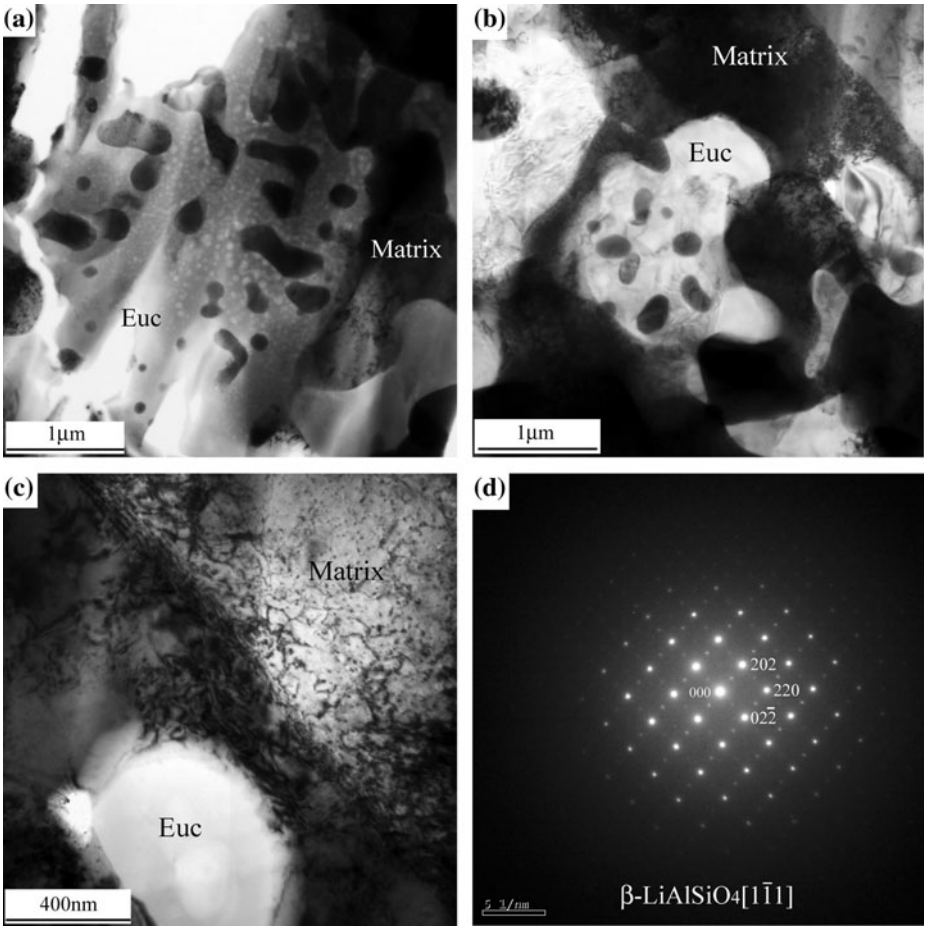

Figure 3. TEM morphologies of β-$LiAlSiO_4$/Cu composite, (a) and (b) β-$LiAlSiO_4$ particles with new phase particles in them, (c) β-$LiAlSiO_4$ particle without new phase in it, (d) typical SADP and indexes of white regions in (a) and (b), and the weak spots in (d) result from secondary electron diffractions.

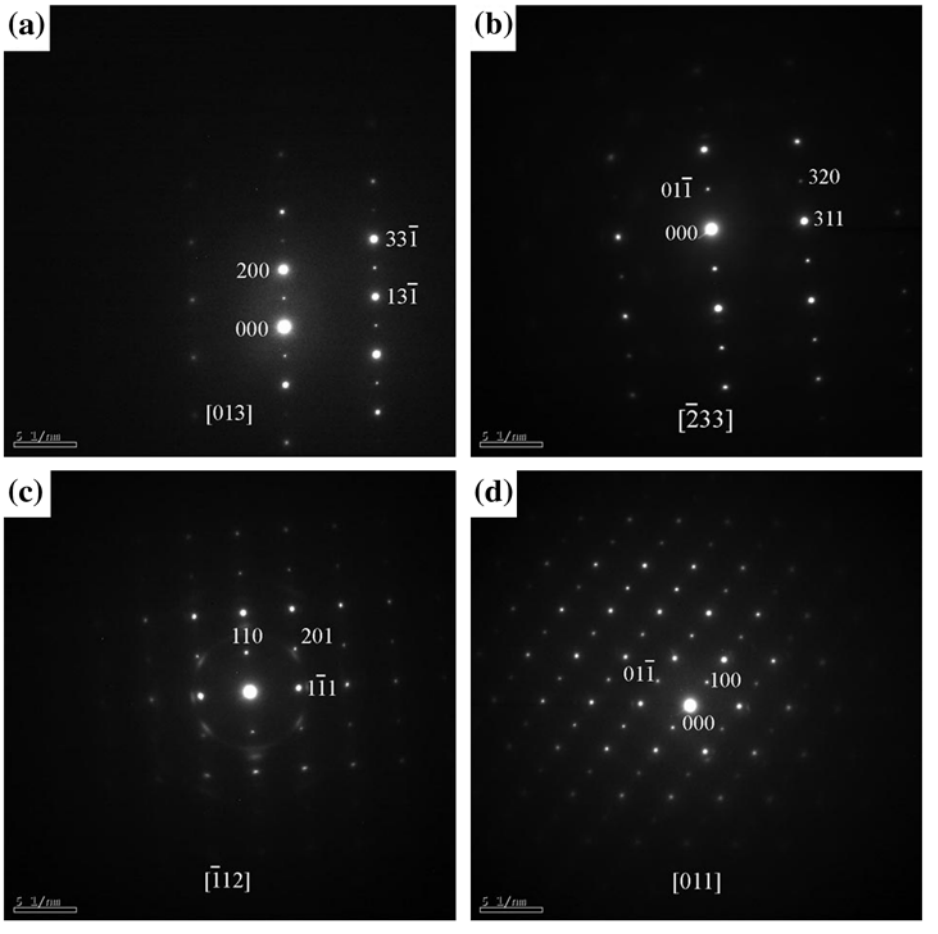

Figure 4. Different orientation SADP of the new polymorph phase in β-$LiAlSiO_4$ of the composite, and the SADPs are indexed using primary cubic structure.

From the results in Table 1, it can be found that the $1/d^2$ values of the new polymorph of β-$LiAlSiO_4$ are fulfilled the following relationship:

$$\frac{1}{d_1^2} : \frac{1}{d_2^2} : \frac{1}{d_3^2} : \cdots : \frac{1}{d_{10}^2} : \cdots \approx 1 : 2 : 3 : 4 : 5 : 9 : 11 : 13 : 19 : \cdots \quad (1)$$

Equation (1) suggests that C-phase of $LiAlSiO_4$ is primary cubic according to the formula of interplanar spacing.[21] The SADPs of C-phase are indexed using primary cubic structure with the lattice constant (a) of 0.435 nm, and some of index results are also shown in Figure 4. It is found that all SADPs obtained of the C-phase can be indexed as cubic structure.

SADPs were also taken *in situ* for one C-phase particle with different tilt angles to further determine the C-phase structure. Figure 5(a) shows a SADP of a C-phase particle, the sample was then tilted 26.2° and a new SADP was taken as shown in Figure 5(b). Using cubic structure with a = 0.435 nm, Figure 5(a) and (b) can be indexed as $[\bar{2}\,3\,3]$ and $[0\,1\,1]$ zone diffraction patterns, respectively. It is easy to

Table 1. d and $1/d^2$ values of the different SADP for C-phase of $LiAlSiO_4$.

Number	d (nm)	$1/d^2$ (nm^{-2})
1	0.4354	5.2750
2	0.3091	10.4665
3	0.2501	15.9872
4	0.2175	21.1388
5	0.1946	26.4067
6	0.1781	31.5262
7	0.1452	47.4315
8	0.1324	57.0459
9	0.1210	68.3014
10	0.1003	99.4027

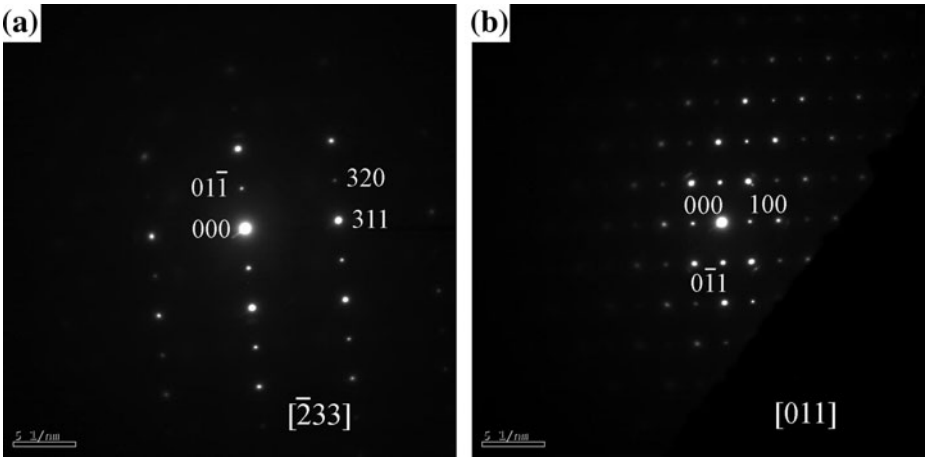

Figure 5. Different orientation SADPs before and after TEM sample tilting with the angle of 26.2° (a) before tilting, (b) after tilting.

calculate that the angle between $[\bar{2}\,3\,3]$ and $[0\,1\,1]$ zones is 25.2° which is approximately equal to the sample tilting angle of 26.2°. This result further demonstrates the validity that the C-phase of $LiAlSiO_4$ can be indexed as cubic structure. The similar observation of SADPs is shown in Figure 6(a) and (b). The angles obtained from tilting specimen and calculated from zone axis indexed using primary cubic structure are shown in Table 2. A little difference of the angles between the titled and calculated can be found in Table 2 which is due to that the reciprocal plane corresponding to the SADP is not accurately perpendicular to the incidence electron beam.

On the basis of above analysis, a new polymorph of $LiAlSiO_4$ (C-phase), can be determined as primary cubic structure with the lattice constant of 0.435 nm, which has never been found in the previous study, although the phase transition of β-$LiAlSiO_4$ in pressure has been systematically studied.

In our opinion, the phase transition of β-$LiAlSiO_4$ is caused by the large anisotropic TMS in composites. In previous studies on the phase transition of β-$LiAlSiO_4$, some of polymorph phase of $LiAlSiO_4$ were formed at high hydrostatic pressure of several GPa, [14] however, the level of TMS in β-$LiAlSiO_4$ particles of the MMCs may be much

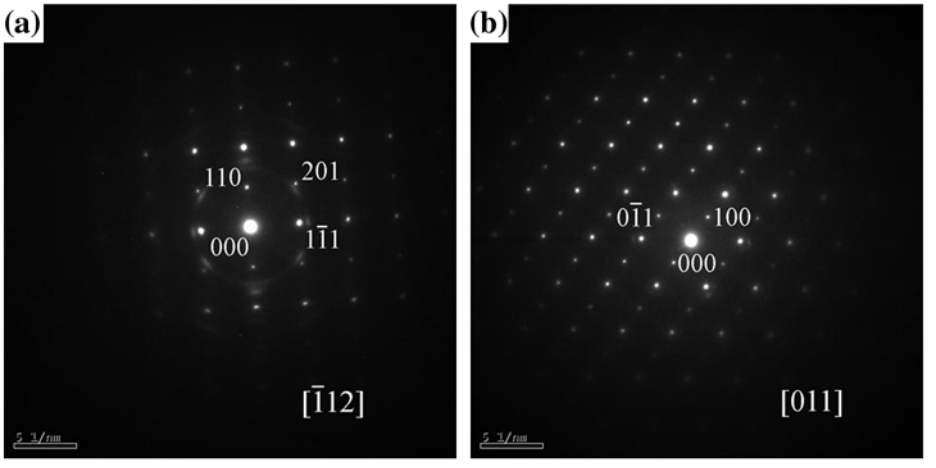

Figure 6. Different orientation SADPs before and after TEM sample tilting with the angle of 27.2° (a) before tilting, (b) after tilting.

Table 2. Angles of sample tilt and crystal zone axes determined from SADP analysis.

SADPs	Tilting angle of TEM sample (°)	Angles between the zone axes calculated from SADPs before and after sample tilting (°)
Figure 5(a) and (b)	26.2	25.2
Figure 6(a) and (b)	27.2	30

smaller than that in the previous study.[15] The main difference of the stress state in the β-$LiAlSiO_4$ particles of β-$LiAlSiO_4$/Cu composite from hydrostatic pressure is that large anisotropic TMS exists in the composite, which results from the highly anisotropic CTE of β-$LiAlSiO_4$. The CTE of β-$LiAlSiO_4$ along *c*-axis is $-16.35 \times 10^{-6}\,K^{-1}$ and much smaller than that along *a*-axis ($7.26 \times 10^{-6}\,K^{-1}$) and that of Cu matrix ($16.5 \times 10^{-6}\,K^{-1}$), so it can be expected that the highly anisotropic TMS is induced when the composite is cooled from SPS temperature. As a result, the phase transition from β-$LiAlSiO_4$ to C-phase $LiAlSiO_4$ with primary cubic structure is caused by the large anisotropic TMS.

The discovery of the new polymorph of $LiAlSiO_4$ in β-$LiAlSiO_4$/Cu composite indicates that the phase transformation caused by anisotropic TMS may be easier than that caused by hydrostatic pressure since the anisotropic TMS in β-$LiAlSiO_4$/Cu composite must be lower according to the lower yield stress of copper.

4. Conclusions

In order to clarify the phase transformation of β-eucryptite in β-$LiAlSiO_4$/Cu composite, a copper matrix composite reinforced by β-$LiAlSiO_4$ was fabricated by SPS. The composite was characterized using XRD and TEM. The following conclusions were drawn from the results of this study:

(1) A new polymorph phase (C-phase) is first found in β-$LiAlSiO_4$ particle of β-$LiAlSiO_4$/Cu composite.
(2) The crystal structure of the new phase can be determined as primary cubic with the lattice constant of 0.435 nm according to SADP analysis.
(3) The discovery of the new polymorph of $LiAlSiO_4$ in β-$LiAlSiO_4$/Cu composite suggests that the phase transformation caused by TMS may be easier than that caused by hydrostatic pressure.

Acknowledgements

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