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A Study of the Photo-Catalytic Character of Plasma Sprayed TiO_2 Coatings †

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Abstract

Two types of rutile and anatase powders are used for the deposition of TiO_2 *coatings. The effects of plasma spraying conditions on the structure of* TiO_2 *coatings are investigated in order to clarify controlling factors of the phase formation and to aim at the development of effective photo-catalyst* TiO_2*. It is found that the amount of anatase* TiO_2 *in the coating is influenced by spray parameters. The decrease of the heat input to spray droplet and an increase in the cooling speed during droplet deposition will increase the amount of the anatase* TiO_2 *in the coating. As a photo-catalyst, the coating deposited under limited plasma power using anatase powder is effective for the decomposition of acetaldehyde gas.*

KEYWORDS : (Plasma Spray) (Photo-Catalyst) (TiO_2 Coating) (Acetaldehyde) (Decomposition)

1. Introduction

Owing to its unique semi-conductor characteristics, TiO_2 oxide is increasingly of interest as a promising photo functional material, which can be applied to solar cells, water decomposition, photo assisted decomposition of harmful organic substances and removal of harmful foul gases by decomposition, especially with increasing attention concerning environment protection[1]. TiO_2 presents three different types of crystal structures. These are rutile type, anatase type and brookite type. Generally, the rutile type of TiO_2 is thermally stable. The anatase TiO_2 is metal-stable, which will be transformed to rutile structure after an annealing treatment[2]. As a photo-catalyst, anatase TiO_2 is more effective[3]. Therefore, TiO_2 photo-catalyst is generally prepared by low temperature processes such as dipping and spraying using the microfine powders of anatase structure, and sol-gel method as well.

Plasma spraying has been used effectively to produce ceramic coatings. Generally, the meta-stable phase can be deposited because of the inequilibrium characteristics of rapid cooling after a droplet impacts on a surface[4]. Therefore, despite the high temperature characteristics of thermal plasma as a heat source, it was found that the anatase TiO_2 can be formed in plasma-sprayed TiO_2 coatings although the amount of the anatase phase in the coating is much limited[5].

The present study aims to clarify controlling factors of the phase transformation in the deposition of TiO_2 coating and the development of anatase-TiO_2 dominant coatings. TiO_2 coatings are sprayed using two TiO_2 powders with rutile and anatase structures, and the effects of plasma spraying conditions on the TiO_2 coating structure are investigated.

2. Materials and experimental procedures

2.1 Materials

Two types of TiO_2 powders with rutile and anatase crystal structures were used in the experiments for plasma spraying. The commercial rutile TiO_2 powder of a mean grain size of 27μm consisted of a fraction of magneli phases besides the main rutile phase. Therefore, the powder was annealed at 1270K for 10.8ks in the ambient atmosphere before spraying. After the annealing treatment, the structure of the powder became the single rutile phase. The anatase

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(a) (b)

Fig. 1 The morphologies of powders of rutile TiO_2 (a) and anatase TiO_2 (b).

TiO_2 powder, which has a mean grain size of 34μm, was an agglomerated powder with the fine TiO_2 powders of 0.2μm in original grain size. The morphologies of two powders were illustrated in Fig. 1. Stainless steel was used as a substrate.

2.2 Plasma spraying

The TiO_2 coatings were deposited by a Metco 9MB plasma spray system. Argon was used as a primary plasma gas and hydrogen was used as the secondary gas. Table 1 illustrates the primary spray conditions. During the spraying, the flow of hydrogen gas and arc current were changed to investigate the effect of spray conditions on the structure of deposited TiO_2 coatings.

2.3 Characterization of the coating

The structure of the coating was characterized by X-ray diffraction analysis. The relative content of anatase TiO_2 in the coating was estimated from the ratio of diffraction intensity of the anatase (101) peak with the total intensity of the anatase (101) and rutile (101) peaks. Regarding the orientation of the rutile TiO_2 in the coating, the above estimation utilized the intensity of the (101) peak of rutile TiO_2 instead of the main peak (110).

The microstructure of the TiO_2 coating was examined by optical microscopy and electron scanning microscopy.

Table 1 Plasma spray conditions

Primary plasma gas (Ar) Pressure Flow rate	 0.7 MPa 7.88×10^{-4} m^3/s
Secondary plasma gas (H_2) Pressure Flow rate	 0.4 MPa 0 - 1.97×10^{-4} m^3/s
Spray distance	100 mm
Arc current	400 - 900 A
Arc voltage	37 -72 V

2.4 Characterization of the acetaldehyde gas decomposition by TiO_2 coating

The TiO_2 coating as a semi-conductor photo-catalyst was characterized through the decomposition test of acetaldehyde. Fig. 2 shows schematically the experimental set-up. The volume of the container is about 2l. After the container was filled with a certain concentration of the acetaldehyde, the ultraviolet lamp was switched on to generate the light of 360nm wave length towards the sample surface at an intensity of $1mW/cm^2$. Afterward, the decay in the concentration of the acetaldehyde was measured with a gas detector after a certain time interval.

The experiment results showed that the decay of the concentration of the acetaldehyde follows the exponential rule, e.g. :

$$N = N_0 \exp(-t / t_0)$$

Where, N and N_0 is the concentration at time t and initial concentration, respectively; t_0 is a constant related to the decay speed. The lower the value t_0, the more rapid the decomposition of acetaldehyde. Therefore, the t_0 was used as the characteristic decay time to evaluate the effectiveness of the coating for decomposition.

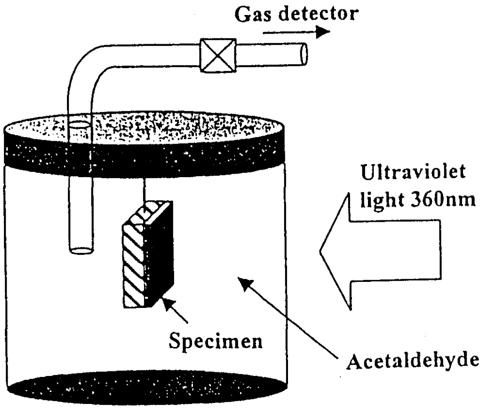


Fig. 2 Schematic diagram of photo-catalytic experimental set-up.

3. Results and discussion

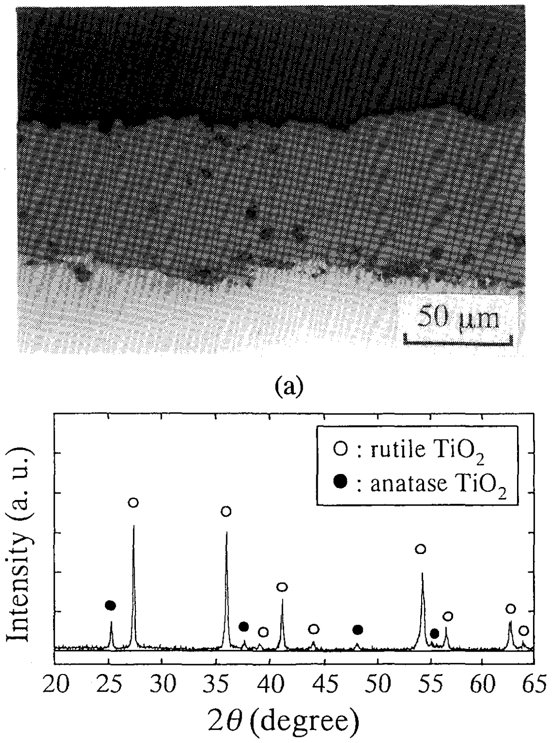
3.1 The structure of the TiO_2 coating deposited by rutile powder

Fig. 3 shows the typical cross-sectional microstructure and X-ray diffraction pattern of a TiO_2 coating sprayed by rutile powder under an arc current of 600A and H_2 flow of 7.88×10^{-4} m^3/s.

From the X-ray diffraction pattern it is clearly recognized that the coating consists of rutile TiO_2 and anatase TiO_2. Regarding the rutile structure of the starting powder and the thermal stability of rutile TiO_2 at high temperature, it can be considered that the formation of the anatase TiO_2 is related to the rapid cooling of spray droplets inherent to the thermal spray process. In order to clarify the forming process of anatase TiO_2 in the coating, the effects of spray parameters on the anatase TiO_2 in the deposited coating were investigated.

3.2 Effect of H_2 flow rate on the formation of anatase-TiO_2 in the deposited coating

Fig. 4 shows the X-ray diffraction patterns of the TiO_2 coatings deposited under different H_2 flow rates. It is evident that with an increase in H_2 flow rate the intensity of the anatase TiO_2 decreases. Fig. 5 illustrates the anatase ratio in TiO_2 coatings estimated from the relative intensity of the X-ray diffraction peaks. The result clearly shows that the increase in H_2 gas flow has the effect of suppressing the formation of the anatase phase in the TiO_2 coatings. This may be because an increase of the H_2 gas flow into the plasma improves the heating of plasma jet to the spray powder, and subsequently raises the temperature of droplet solidification. Therefore, the result suggests that a decrease in the droplet temperature during plasma spraying enhances the formation of the anatase TiO_2.



(a)

(b)

Fig. 3 Microstructure (a) and X-ray diffraction pattern (b) of plasma-sprayed TiO_2 coating.

3.3 Effect of plasma arc current on the formation of anatase-TiO_2 in the TiO_2 coating

The effect of H_2 addition into the plasma gas on the X-ray diffraction results of the sprayed coatings implies that the high heat input into spray powder will suppress the formation of the anatase TiO_2 in the coating. Regarding the

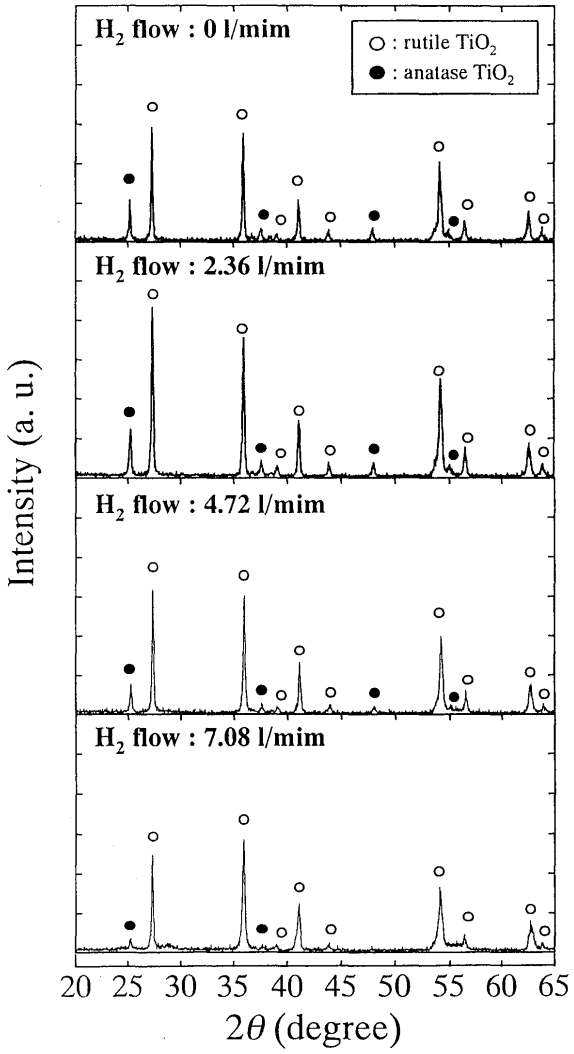


Fig. 4 X-ray diffraction patterns of TiO2 coatings sprayed at different H_2 flow rates (Arc current : 600A).

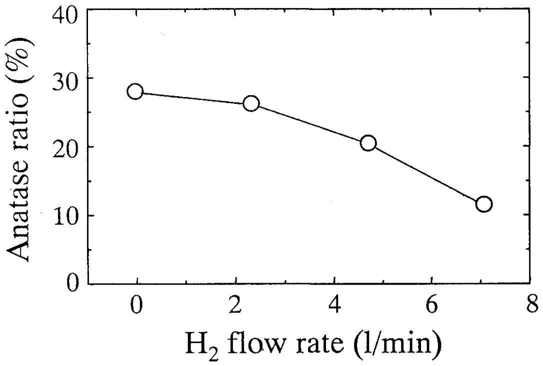


Fig. 5 Effect of H_2 flow rates on the anatase ratio in the TiO_2 coating (Arc current : 600A).

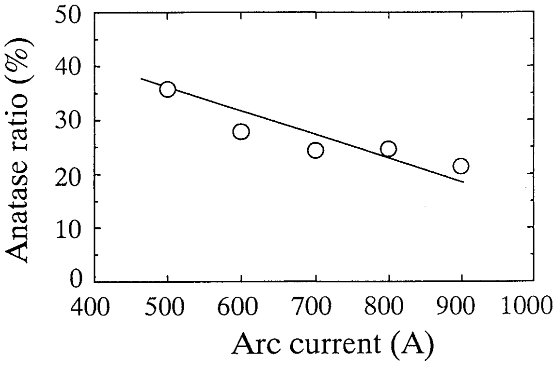


Fig. 6 Effect of arc current on the anatase ratio in the TiO_2 coating.

heating of the powders by the plasma jet, the plasma power is one of the important parameters. Fig. 6 illustrates the effect of the plasma arc current on the relative anatase ratio in the TiO_2 coating. During the deposition the argon plasma was used without H_2 addition. It is seen that with an increase in plasma arc current (e.g. plasma power) the content of the anatase phase in the coating decreases.

3.4 Effect of substrate cooling on the formation of anatase-TiO_2 in the TiO_2 coating

The effect of the power and H_2 addition into plasma gas revealed that the formation of the anatase phase is closely related to the heating of the droplet and subsequent cooling processes. A lower heat input to the spray powder and rapid cooling of the droplet will enhance the formation of the anatase phase in the TiO_2 coating. To confirm the effect of the cooling of the droplet on the formation of anatase TiO_2, a TiO_2 coating was deposited onto a copper substrate of 3mm in thickness and the effect of the cooling from the back of the substrate by running water was examined.

Fig. 7 illustrates the X-ray diffraction patterns of TiO_2 coatings deposited on the copper substrate both with, and without water cooling compared with that of the coating deposited on the stainless steel. It can be seen that the coatings sprayed on the copper substrate contain a little more anatase phase and the cooling of the copper substrate tends to increase the anatase ratio in the TiO_2 coating.

Therefore, it is clear that an increase in the cooling speed of the droplet after it impacts on a substrate lead to an increase of the anatase phase in the coating. On the other hand, it is also evident that the maximum relative content of the anatase TiO_2 phase in a plasma-sprayed TiO_2 coating is around 30 to 35% by using rutile powder.

3.5 Effect of powder types on the formation of anatase-TiO_2 in the deposited coating

Fig. 8 illustrates the X-ray diffraction patterns of TiO_2 coatings sprayed with Ar plasma at different arc currents using agglomerated anatase powder. The estimation of the anatase ratios of the coatings deposited at the arc currents of 400, 500 and 600A yielded about 32%, 18% and 16%, respectively. It is clear that the arc current exerts the same effect on the anatase ratio as in the coatings deposited with rutile powder. The maximum anatase ratio yielded a similar value to that using rutile powder. An annealing treatment of the anatase powder above 1223K revealed that after annealing the anatase phase in the original powder is changed to rutile phase. Therefore, it can be considered that the anatase phase in the coating deposited using the anatase powder is primarily formed through the same process as with rutile powder when the powder is completely melted during the spraying, because the heating and subsequent melting of the powder leads to the formation of liquid droplets of the same structure despite original structure of the powders.

3.6 The decomposition characteristics of acetaldehyde by plasma-sprayed TiO_2 coating

Fig. 9 illustrates the decay characteristics of the acetaldehyde concentration by TiO_2 coating catalyst-assisted decomposition. The coatings were deposited under different arc currents using anatase powder. It was found that using the coating deposited under low arc current (which contains a little more anatase TiO_2) the decomposition of the acetaldehyde is much more rapid compared with the coating deposited under a high arc current. The relationship between the anatase ratio, arc current and decay time of

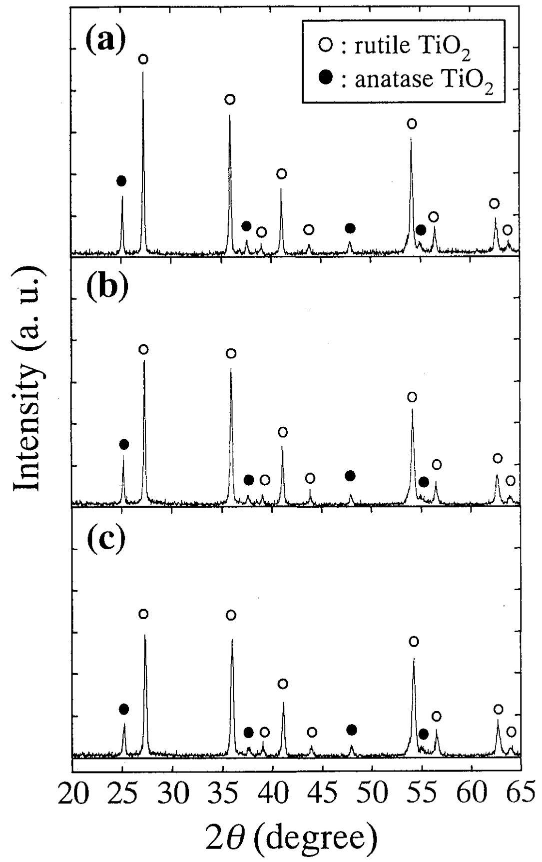


Fig. 7 X-ray diffraction patterns of TiO_2 coatings.
(a) Cu substrate with water cooling,
(b) Cu substrate without water cooling,
(c) Stainless steel substrate.

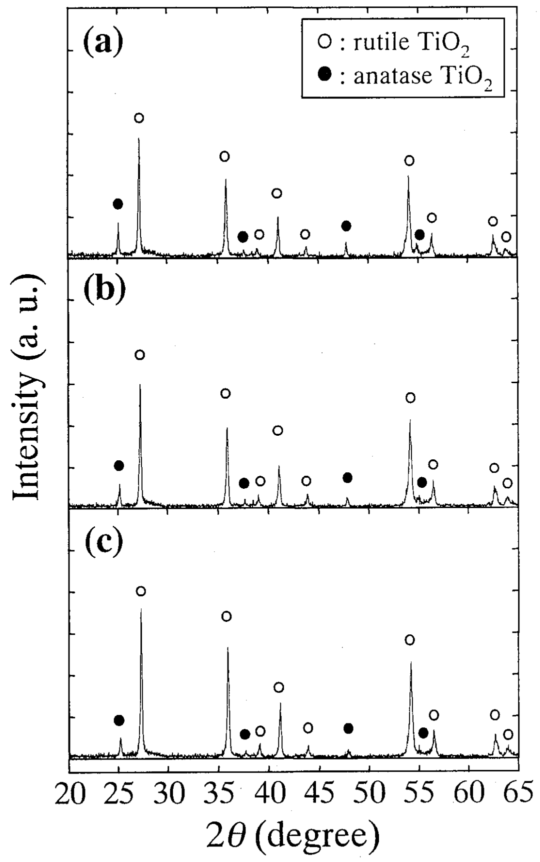


Fig. 8 X-ray diffraction patterns of TiO_2 coatings sprayed under different arc currents using the anatase powder.
(a) 400 A, (b) 500 A, (c) 600 A.

acetaldehyde gas, shown in Fig. 10, clearly revealsed that the decay time of the acetaldehyde gas by the coatings deposited under low arc currents of 400A and 500A is less by one order than that using the coating deposited under the current of 600A.

It was also noticed that although the anatase ratios in the above mentioned three coatings have no significant difference, the decay time is much different. The examination of the surface morphology of the coatings as shown in Fig. 11 clearly shows that under low arc current the surface of the coating has a similar morphology with that of the powder, which evidently shows that the powder is only partially melted. However, the surface of the coating deposited under a high arc current (plasma power) presents a more typical thermally sprayed coating morphology which suggests the significant melting of the spray powder. From these results it can be suggested that, under partially melting, although the anatase phase is still formed during droplet cooling, the subsequent anatase phase will be distributed preferably near the particle surface. As the result, the anatase phase can directly act as the catalyst to promote the decomposition of acetaldehyde.

4. Conclusions

TiO_2 coatings deposited by plasma spraying using two powders of rutile and anatase structures, the effects of plasma arc current and the addition of H_2 gas into the plasma on the formation of the anatase TiO_2 in the coating are investigated.

The experimental results clearly show that the plasma spraying process prefers to deposit a TiO_2 coating with rutile dominant structure despite the structure of the starting powder. The amount of the anatase TiO_2 in the coating is influenced by spray conditions. An increase in plasma arc current and the addition of H_2 gas into the plasma tend to suppress the formation of the anatase-TiO_2 through the increase of heat input to the spray droplets. Moreover, an increase in the cooling speed during droplet deposition will increase the amount of the anatase-TiO_2 in the coating. The photocatalytic characteristics of the TiO_2 depend on the amount

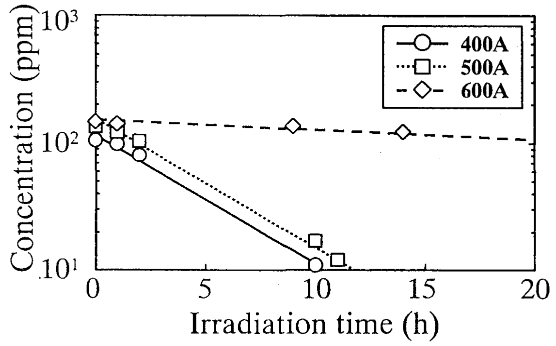


Fig. 9 The decay charasteristic of the acetaldehyde concentration by TiO_2 photo-catalyst coatings sprayed under different arc currents.

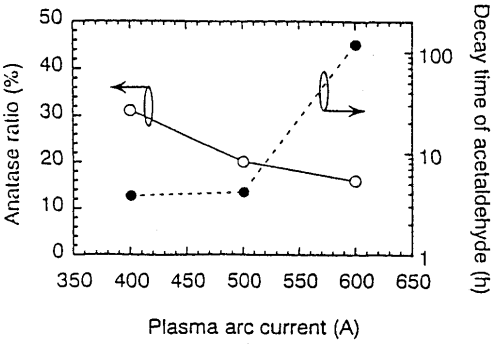
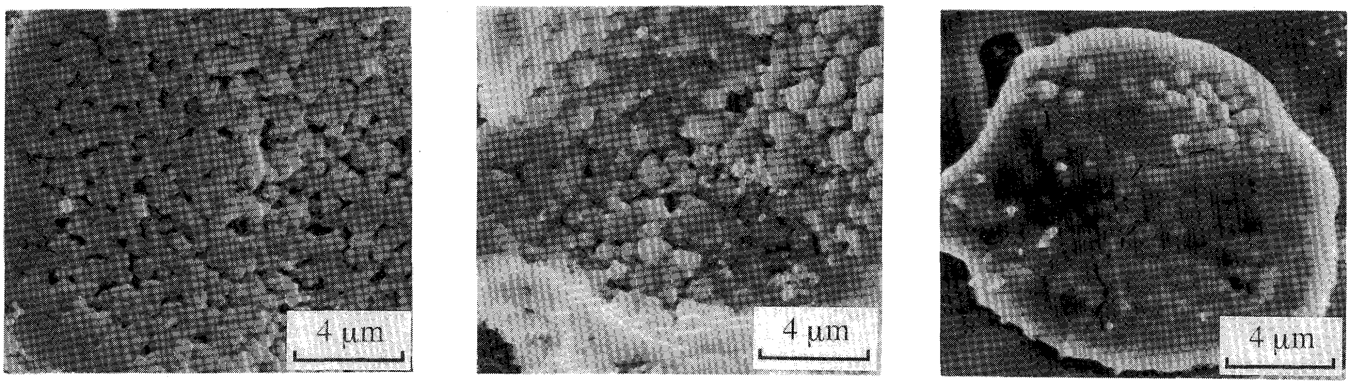


Fig. 10 Effect of plasma arc current on the anatase ratio in TiO_2 coatings and decay time of acetaldehyde irradiated by ultra violet light.



(a) (b) (c)

Fig. 11 Surface morphologies of TiO_2 coatings sprayed at different arc current. (a) 400 A, (b) 500 A, (c) 600 A.

of anatase-TiO_2 and also the surface morphology of the coating. It is found that the decay time of acetaldehyde concentration using the coating deposited with partially melted agglomerated anatase powder is one order less than that of the coating deposited with well-melted droplets.

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