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Reaction control of TiB_2 formation from titanium metal and amorphous boron

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TiB_2 powder was synthesized by a controlled formation reaction from titanium metal and amorphous boron. Precursory TiB_2 formed by the pretreatment of the mixed powder (mole ratio: B/Ti = 2.0) at 600° C for 60 min in an argon stream. Hollow TiB_2 powder with an average grain size of 15 μm was obtained by subsequent heat treatment above 900° C for more than 60 min in an argon stream. The formation reaction of TiB_2 powder was further controlled by pretreatment of the mixed powder at 600° C for 60 min in a hydrogen and argon stream and subsequent heat treatment at 1000° C for 360 min in an argon stream, when hollow-free TiB_2 powder was formed by a milder formation reaction between amorphous boron and the reformed titanium metal with hydrogen diffused lattice.

1. Introduction

Solid state reaction between elements is important as fundamental research on the formation of metal borides [1]. The direct combination of a metal or its variant metal hydride with boron is known as one of the synthetic procedures of pure metal borides, where one can control the formation reaction of the borides appropriately. In the boride formation of tungsten, for example, an activation pretreatment of the reactant species at low temperatures in a hydrogen stream was found to be effective for the promotion of boride formation in the subsequent heat treatment [2, 3]. In the solid state reaction between titanium metal and amorphous boron, it was difficult to control the rapid formation reaction of TiB_2 without any ambient pretreatment of starting powders [4]. This allowed another successful choice of titanium nitride as the titanium source in order to obtain titanium diboride powder by a milder formation reaction [5].

The difference in the formation process of TiB_2 was investigated in the present report by employing careful pretreatments of starting titanium and/or amorphous boron powders. The possibility of controlling the TiB_2 formation reaction is described in relation to the precursory TiB_2 formation or titanium hydride formation at lower temperatures. The morphology of synthesized powders is also correlated to the treatment parameters.

2. Experimental procedure

2.1. Preparation of TiB_2 powder

Fig. 1 shows the procedure for synthesis of TiB_2 powder. Commercially available titanium powder (Rare Metallic Co., purity > 99 wt %) with an average grain size of 15 μm, was used as the titanium source. Amorphous boron powder (Rare Metallic Co.), which contains volatile impurities (water, oxygen etc. 2.4 wt %) and metal impurities (magnesium, aluminium, iron, silicon etc. 1.0 wt %), was used as a boron source. Each as-received powder was first degassed in a vacuum at 600° C for 60 min, after which they are mixed at the mole ratio of B/Ti = 2.0 in an agate mortar. The volatile impurities as well as the

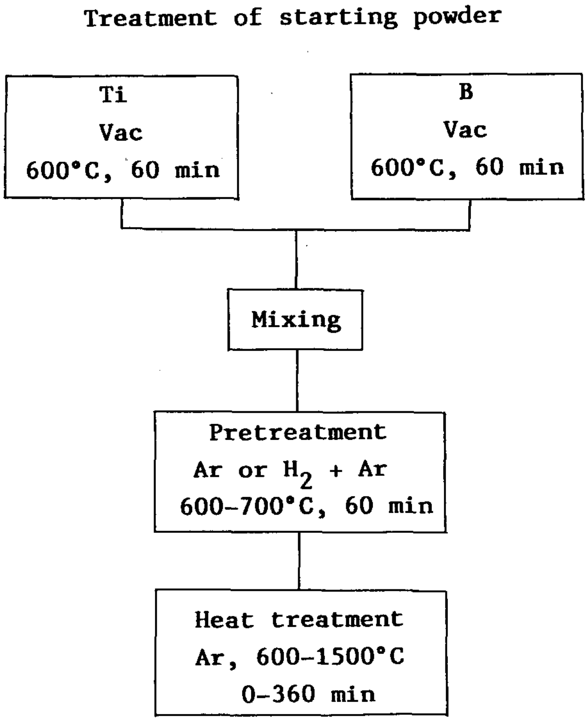

Figure 1 Procedure for synthesis of TiB_2 powder from titanium metal and amorphous boron powders.

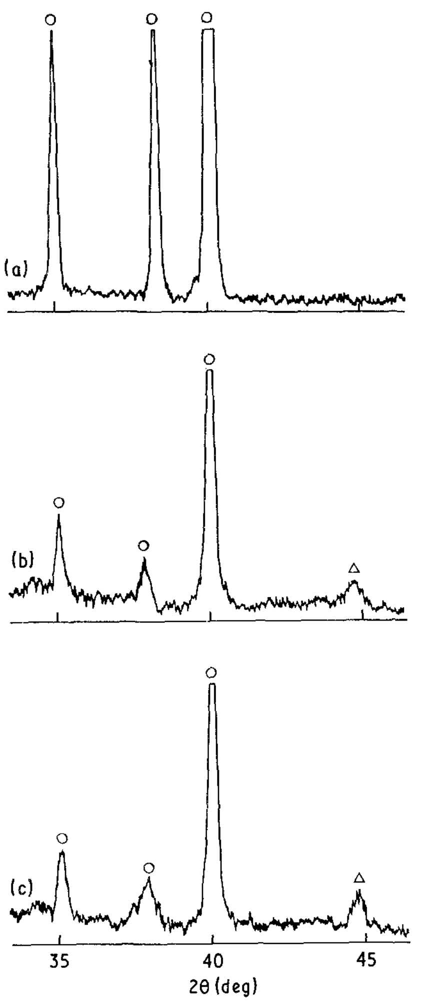

Figure 2 X-ray diffraction patterns of (a) as-mixed powder (B/Ti = 2.0), (b) pretreated powder at 600° C for 60 min in argon and (c) pretreated powder at 700° C for 60 min in argon. ○ Ti, △ TiB_2.

boron amount that will react with metal impurities were eliminated from the calculation of the net boron amount in the specimens. The mixed powder was pretreated at 600 to 700° C for 60 min in an argon stream ($50\,ml\,min^{-1}$) or in a hydrogen and argon stream ($H_2:Ar = 1:1$; $50\,ml\,min^{-1}$). The specimen was heated in 40 min to the holding temperature (600 to 1500° C), at which heat treatment was carried out for 0 to 360 min in an argon stream ($50\,ml\,min^{-1}$).

2.2. Analysis of specimens

The specimens were identified by the X-ray powder diffraction method. The relative amount and crystallinity of chemical species in the specimen were evaluated by the normalized relative intensities that were determined by the peak height ratio I/I_{Si}, where I is the intensity of the selected diffraction line of each material and I_0 is the intensity of the 2 0 0 line of the silicon internal standard. The selected lines were 0 0 1, 1 0 1 and 1 1 1 for Ti, TiB_2 and TiH_2, respectively.

The powder appearance and grain size were examined by scanning electron microscope (SEM). The cross sectional view of Ti and TiB_2 particles were observed by an optical microscope, in which the particles were embedded into the exposy resin and abraded by diamond disc.

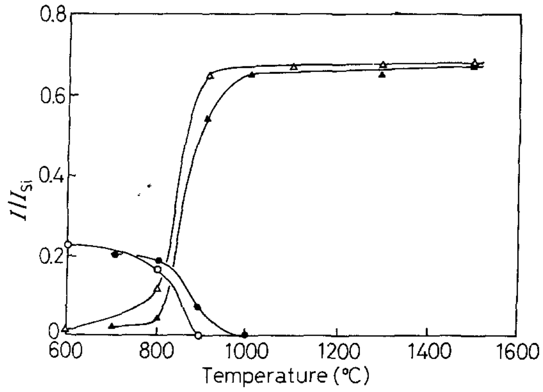

Figure 3 Relative intensity of Ti (○, ●) and TiB_2 (△, ▲) plotted against heat treatment temperature. Pretreatment atmosphere: argon. Pretreatment temperature; open symbol: 600° C [4], Solid symbol: 700° C. Heat treatment time: 60 min

3. Results and discussion

3.1. Effect of ambient pretreatment in an argon stream

Fig. 2 shows the X-ray diffraction patterns of as-mixed powder (Fig. 2a) and the pretreated powders in an argon stream (Figs 2b and c). Amorphous boron cannot be detected by X-ray diffraction. Only strong diffraction lines of titantium metal can be seen in the as-mixed (untreated) powder, as shown in Fig. 2a. In the specimen after pretreatment at 600° C for 60 min in an argon stream (see Fig. 2b), the diffraction intensity of titanium metal decreased considerably compared with that of untreated titanium (Fig. 2a). A trace amount of TiB_2 is observed in the diffraction pattern, which indicates the precursory formation of low crystalline TiB_2 at the pretreatment temperature as low as 600° C. Titanium diffraction lines are broadened and that of TiB_2 slightly increased at the pretreatment temperature of 700° C, as shown in Fig. 2c.

Fig. 3 shows the relative intensity of unreacted titanium and formed TiB_2 after the heat treatment at various temperatures for 60 min, where the ambient pretreatments were carried out at 600 and 700° C for 60 min. It was found from the plots of pretreatment temperature at 600° C [4], that the precursory TiB_2 increased the diffraction intensity slightly at the heat temperature of 800° C and a rapid formation of TiB_2 seemed to occur between 800 and 900° C. High crystalline TiB_2 powder was obtained at 900° C with no coexistence of titanium metal. The intensity of TiB_2 remained constant at 1100 to 1500° C. Analogous heat treatment dependence of the relative intensity was confirmed in the curve obtained after the pretreatment at 700° C, though the depressive effect of TiB_2 formation reaction being enhanced slightly in the temperature range of 800 to 1000° C. Pretreatment at 800° C was impossible because of the burst formation reaction of TiB_2 [4, 6].

Fig. 4 shows the variation of relative intensity of Ti and TiB_2 as a function of heat treatment time at 800 and 900° C after the pretreatment at 600° C for 60 min in an argon stream. At the heat treatment temperature of 800° C, the intensity of formed TiB_2 increased slightly in 60 min, but it remained constant even at the

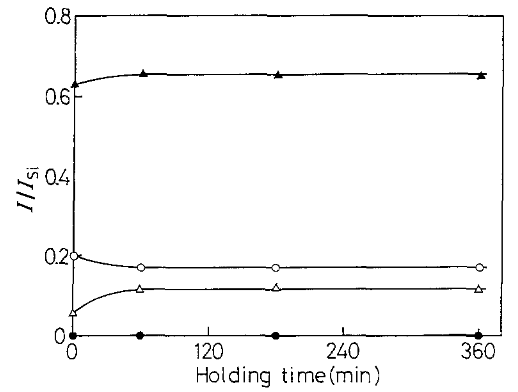

Figure 4 Relative intensity of Ti (○, ●) and TiB_2 (△, ▲) plotted against heat treatment time. Pretreatment: argon 600° C, 60 min. Heat treatment temperature; open symbol 800° C, solid symbol: 900° C.

treatment of 360 min. The formation amount or the crystallinity of TiB_2 phase is considered to be low on account of less acceleration of reaction induced by heat of formation. On the other hand, the relative intensity of TiB_2 attained a high level even at 0 min with no detection of titanium metal, which verifies that the formation reaction of TiB_2 was completed mostly in the process of raising the temperature. It is concluded that the burst formation reaction of TiB_2 would be depressed to some extent by the precursory formation of low crystalline TiB_2 phase in the pretreatment process in an argon stream, but the rapid TiB_2 formation accompanied by combustion reaction cannot be controlled in the temperature range of 800 to 900° C, as described in Section 3.3.

3.2. Effect of ambient pretreatment in a hydrogen and argon stream

Fig. 5 shows the relative intensity of coexisting species after the heat treatment at various temperatures for 60 min, where the specimens were pretreated at 600° C for 60 min in a hydrogen and argon stream. Titanium hydride (TiH_2) was identified with no residual titanium after the pretreatment in the atmosphere containing hydrogen gas, as shown by the X-ray diffraction pattern in Fig. 6a. The hydrogen in titanium hydride was found to be degassed, however, by the heat treatment at 700 to 800° C in an argon atmosphere [7]. This resulted in the formation of the reformed titanium metal having lattice constants slightly larger than those of starting titanium metal powder (compare Figs 2a and 6b). A small amount of residual hydrogen would have diffused into the reformed titanium lattice, because born atoms cannot diffuse into a titanium lattice [8]. The relative intensity and crystallinity of this reformed titanium are lower than that of starting titanium. The formation of titanium borides (TiB and TiB_2) was initiated at 900° C with the intensity of titanium metal decreased to some extent. At the treatment temperature of 1000° C, three phases of titanium, TiB and TiB_2 coexist as shown in Figs 5 and 6c. The relative intensity of TiB_2 increased greatly at 1100° C, while the diffraction line of TiB disappeared from the X-ray diffraction pattern. A single phase of TiB_2 powder was obtained above the treatment temperature of 1200° C and attained a nearly constant relative intensity up to 1500° C

Comparison of the formation curve of TiB_2 in

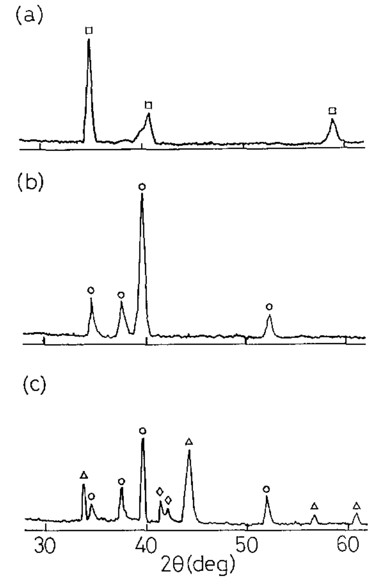

Figure 6 X-ray diffraction patterns of (a) pretreated powder at 600° C for 60 min in hydrogen and argon (b) heat-treated powder at 800° C for 60 min in argon after the pretreatment at 600° C for 60 min in hydrogen and argon (c) heat-treated powder at 1000° C for 60 min in argon after the pretreatment at 600° C for 60 min in hydrogen and argon. ○ Ti, □ TiH_2, △ TiB_2, ◇ TiB.

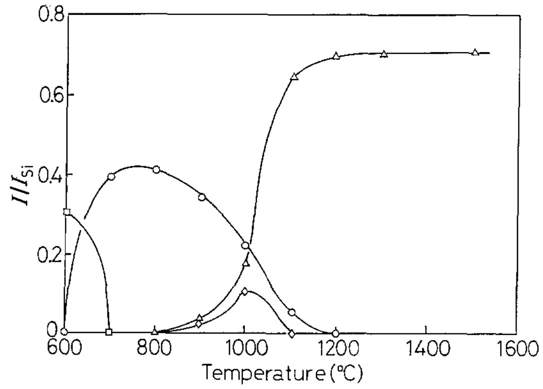

Figure 5 Relative intensity of Ti (○), TiH_2 (□), TiB_2 (△) and TiB (◇) plotted against heat treatment temperature. Pretreatment conditions: 600° C, 60 min, in hydrogen and argon. Heat treatment time: 60 min.

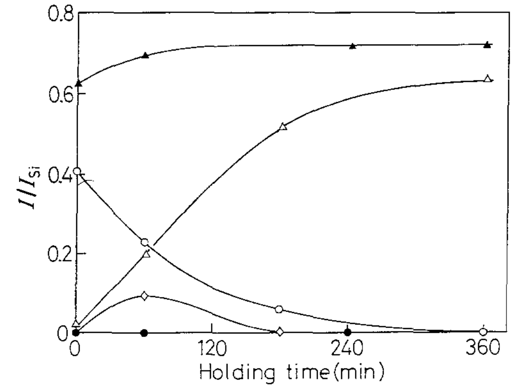

Figure 7 Relative intensity of Ti (○, ●), TiB_2 (△, ▲) and TiB (◇) plotted against heat treatment time. Pretreatment: hydrogen and argon 600° C, 60 min. Heat treatment temperature; open symbol: 1000° C, solid symbol 1300° C.

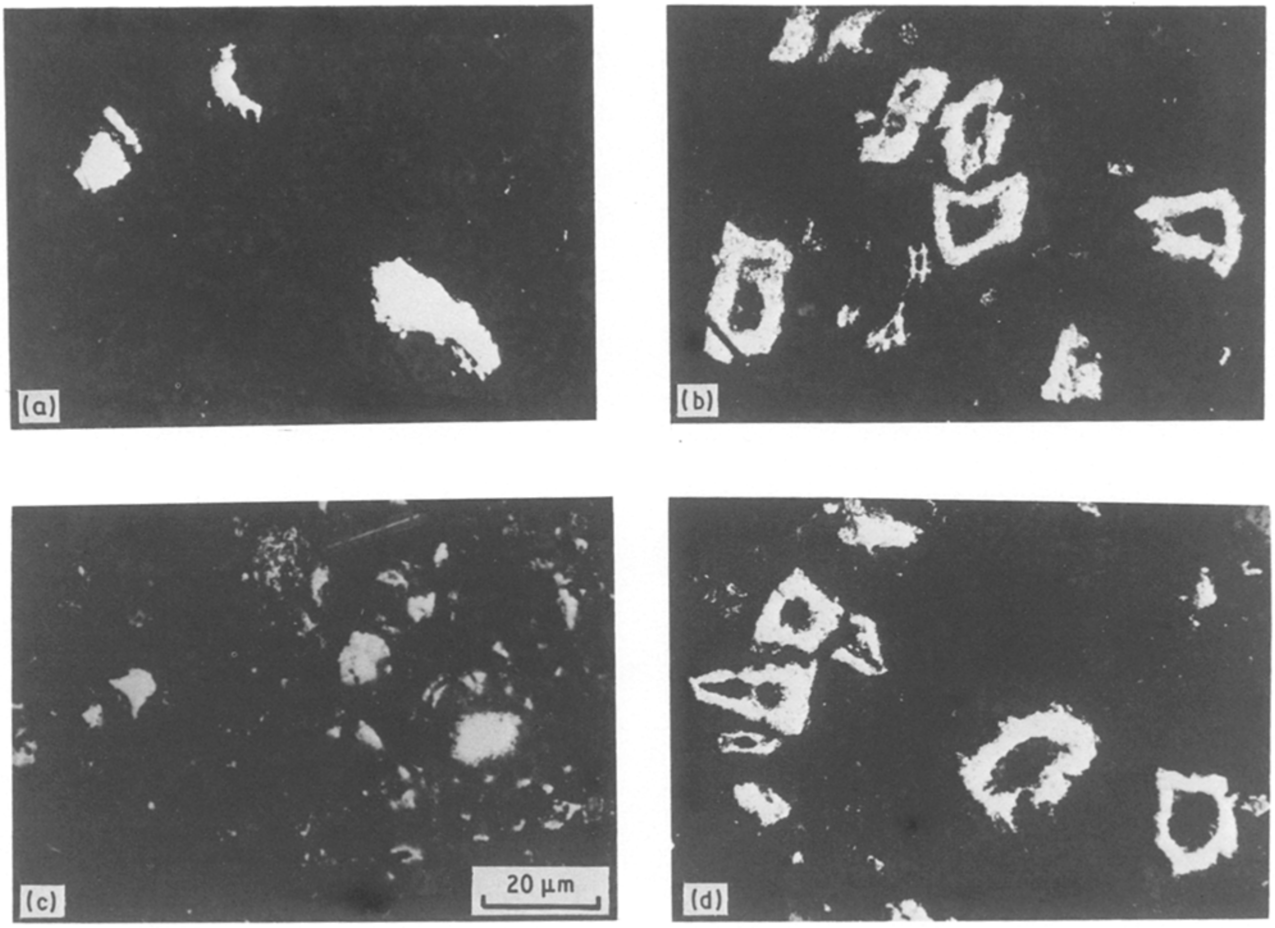

Figure 8 Micrographs of cross-sections of the treated particles. (a) Pretreatment: 600° C, 60 min, in argon; heat treatment: 800° C, 360 min, in argon. (b) Pretreatment: 600° C, 60 min, in argon; heat treatment: 900° C, 360 min, in argon. (c) Pretreatment: 600° C, 60 min, in hydrogen and argon; heat treatment: 1000° C, 360 min, in argon. (d) Pretreatment: 600° C, 60 min, in hydrogen and argon; heat treatment: 1300° C, 360 min, in argon.

Fig. 5 with that in Fig. 3 shows that the formation of TiB_2 initiates at the temperature higher by about 200° C in the case of pretreatment in a hydrogen and argon stream, and more gradual increase in the intensity of TiB_2 can be seen in the temperature range of 900 to 1200° C. Titanium hydride which decomposed at 700° C and reformed the titanium metal with hydrogen diffused lattice, would have caused the mild formation reaction of TiB_2. The temporary formation of the TiB phase at 900 to 1000° C would have also depressed the rapid formation of TiB_2.

Fig. 7 shows the variation of relative intensity of Ti, TiB_2 and/or TiB as a function of heat treatment time at 1000 and 1300° C after the pretreatment at 600° C for 60 min in a hydrogen and argon stream. At the treatment temperature of 1000° C, the intensity of TiB_2 increases linearly with treatment time up to 180 min, until when TiB was consumed by the reaction with amorphous boron to form TiB_2. The intensity of titanium decreases gradually with the treatment time, and the diffraction line disappears at 360 min, which verifies the completion of the TiB_2 formation reaction. In contrast, there can be seen no detection of titanium metal at the elevated temperature of 1300° C even at the treatment time of 0 min. Similarly to the result at 900° C in Fig. 4, this means that the TiB_2 formation reaction would be completed with the aid of the rapid exothermic reaction in the process of raising the temperature. An analogous curve was obtained at the treatment temperature of 1100° C, so that a fast exothermic formation reaction to form TiB_2 would occur at temperatures between 1000 and 1100° C (see also Fig. 5). It is suggested from the above results that the control of the formation reaction of TiB_2 would be possibly done by the heat treatment at 1000° C after the pretreatment of the starting mixed powder at 600° C for 60 min in a hydrogen and argon stream.

3.3. Particle shape of the heat-treated powder

Fig. 8 shows the SEM photographs of cross-sections of the particles which were heat-treated at selected temperatures for 360 min in an argon stream after the pretreatments at 600° C for 60 min in an argon stream (a) and (b), and a hydrogen and argon stream (c) and (d). Particles with the grain size analogous to the starting titanium powder (about 15 μm) can be observed in Fig. 8a, when the titanium powder was heat-treated at 800° C after pretreatment in an argon stream. The powder formed contains titanium metal and a small amount of precursory TiB_2 (see Fig. 4). Hollow particles with a grain size slightly larger than the starting titanium powder were formed by heat treatment at 900° C after pretreatment in an argon stream, as apparently observed in Fig. 8b. The product is a single phase of TiB_2 (see Fig. 4). These tiny balloons of TiB_2 would be formed as a result of a rapid reaction between amorphous boron surrounding a titanium particle and the molten titanium metal infiltrated from the inner part of the particle through a thin boundary TiB_2 layer. Melting of titanium metal (melting point: 1725° C) would occur by a rapid heat generation at the initial stage of TiB_2 formation reaction.

On the other hand, hollow-free TiB_2 powder was obtained by heat treatment at 1000° C for 360 min in an argon stream after pretreatment at 600° C for 60 min in hydrogen and argon stream (Fig. 8c). The grain size of initial titanium powder remains constant even after the treatment. Such a single phase of hollow-free TiB_2 powder would be formed due to the milder solid state reaction between amorphous boron and the reformed titanium metal, as described in Section 3.2. At the heat treatment temperature of 1300° C, however, hollow TiB_2 powder was formed even after the pretreatment in a hydrogen and argon stream. This verifies that molten titanium will form even after the pretreatment in a hydrogen and argon stream by rapid heat generation at a heat treatment temperature as high as 1300° C

The morphology of TiB_2 particles is highly dependent on the reaction rate, which is closely related to the accumulation of heat energy during the heat treatment and hence to the melt formation of titanium metal.

4. Conclusions

A considerable difference in the formation behaviour of TiB_2 powder from titanium and amorphous boron was found between the pretreatments (600 to 700° C, 60 min) in argon, and in hydrogen and argon. The morphology of TiB_2 particles was strongly correlated with the degree of feasibility of the reaction control.

(1) The rapid exothermic reaction to form TiB_2 was depressed considerably by the formation of precursory TiB_2 in the pretreatment at 600° C for 60 min in an argon stream. The reaction rate of TiB_2 formation was still high in the temperature range of 800 to 900° C, above which hollow TiB_2 powder was formed with the molten titanium reacted with amorphous boron.

(2) The formation reaction of TiB_2 powder was further controlled in the heat treatment at 1000° C for 360 min after the pretreatment at 600° C for 60 min in a hydrogen and argon stream. Hollow-free TiB_2 powder was formed by a milder solid state reaction between amorphous boron and the reformed titanium metal with hydrogen diffused lattice.

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