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A new synthesis reaction of Ti_3SiC_2 from Ti/$TiSi_2$/TiC powder mixtures through pulse discharge sintering (PDS) technique

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Abstract Ti/$TiSi_2$/TiC powder mixtures with molar ratios of 1:1:4 (M1) and 1:1:3 (M2) were first employed for the synthesis of Ti_3SiC_2 through pulse discharge sintering (PDS) technique in a temperature range of 1100–1325 °C. It was found that Ti_3SiC_2 phase began to form at the temperature above 1200 °C and its purity did not show obvious dependence on the sintering temperature at 1225–1325 °C. The TiC contents in M2 samples is always lower than that of the M1 samples, and the lowest TiC contents in the M1 and M2 samples were calculated to be about 7 wt% and 5 wt% when the sintering was conducted at the temperature near 1300 °C for 15 minutes. The relative density of the M1 samples is always higher than 99% at sintering temperature above 1225 °C, indicating a good densification effect produced by the PDS technique. A solid-liquid reaction mechanism between Ti-Si liquid phase and TiC particles was proposed to explain the rapid formation of Ti_3SiC_2. Furthermore, it is suggested that Ti/$TiSi_2$/TiC powder can be regarded as a new mixture to fabricate ternary carbide Ti_3SiC_2.

Keywords Ti/$TiSi_2$/TiC powder · Ti_3SiC_2 · Pulse discharge sintering (PDS) · X-ray diffraction (XRD) · Synthesis · Solid-liquid reaction

Introduction

Recently, ternary carbide Ti_3SiC_2 was found to be a novel material which possesses many best attributes of both metals and ceramics. The early synthesis work of this material was first reported by Jeitschko and Nowotny [1] in 1967 via chemical reaction, followed by Goto and Hirai [2] through the VCD method in 1987. To fabricate bulk Ti_3SiC_2 products, sintering technique should be a superior and practicable method for rapid densification at high temperature. From the reports available on the synthesis of Ti_3SiC_2 samples, in general, there are mainly two kinds of powder mixtures, i.e. Ti/Si/C [3–12] and Ti/SiC/C [13–15] with different molar ratios. The synthesis processes above were often conducted by hot-isolated-pressing (HIP) technique at the temperature higher than 1400 °C. Recently, a new technique, i.e. pulse discharge sintering (PDS) or spark plasma sintering (SPS) was developed for rapid densification of metals and ceramics. The sintering processes consist of a pulse electrical discharge step when plasma is generated between powder particles, followed by resistance heating while a uniaxilal pressure is applied. Therefore, the parts prepared by the PDS technique often represent better mechanical properties than those prepared by existing sintering methods. It has been proved that the PDS technique could be used to sinter both ceramics and metallic materials, for example: Ti-Al [16], Fe-Al [17], Al_2O_3 [18], nano-materials [19] etc, at relatively low temperature.

Relation to previous work

In our previous work, except for using the staring powders of Ti/Si/C [20] and Ti/SiC/C [21], new powder mixtures of Ti/Si/TiC [22–24] and Ti/SiC/TiC [25] were developed for the synthesis of Ti_3SiC_2 samples through the PDS technique. It was confirmed that the optimized sintering temperature could be efficiently decreased to 1250–1300 °C with a short sintering time of 15 minutes. Another new finding is that TiC and $TiSi_2$ were frequently observed to be the impurity phases in the Ti_3SiC_2 samples synthesized from the four groups of powder mixtures [20–25]. Furthermore, it was proposed

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that there existed a solid-liquid reaction between TiC particles and Ti-$TiSi_2$ liquid phase for the formation of Ti_3SiC_2 phase during sintering. Therefore, the main purpose of the present research is to further identify the proposed solid-liquid reaction mechanism of Ti_3SiC_2 by using the starting powders of Ti/$TiSi_2$/TiC through the PDS technique.

Experimental procedure

Commercially available Ti, $TiSi_2$ and TiC with the sizes and purities of 10 µm and 99.9% (Ti), 5 µm and 99.9% ($TiSi_2$), 2–5 µm and 99% (TiC) were selected as the starting powders in the present study. The Ti/$TiSi_2$/TiC powder mixtures with molar ratios of 1:1:4 (M1) and 1:1:3 (M2) were mixed in a Turbula shaker mixer in Ar atmosphere for 24 hours. The sintering process of the mixed powders was performed in a graphite mold (20 mm in diameter) under the vacuum condition of about 10^{-4} Pa in a PDS apparatus. The heating rate was controlled in the range of 50–60 °C/min and the holding temperature was in the range of 1100–1325 °C for 0–60 minutes under a pressure of 50 MPa. After sintering, the surfaces of samples were ground to remove the graphite layer and analyzed by X-ray diffractometry (XRD) with CuKα radiation at 30 KV and 40 mA to determine the constituent phases. The contents of TiC and Ti_3SiC_2 in the sintered samples were calculated by means of standard additive method [24]. The samples were mechanically polished and etched in a solution of H_2O:HNO_3:HF (2:1:1) for 5–10 seconds to expose the Ti_3SiC_2 grains, then were observed by scanning electron microscopy (SEM). In the end, the densities of the samples were measured to show the degree of densification by means of the Archimedes principle.

Results and discussion

Figure 1 shows the X-ray diffraction profiles of the Ti/$TiSi_2$/3TiC powder and the as-sintered samples in the temperature range of 1100–1300 °C. It is seen that Ti, $TiSi_2$ and TiC peaks can be examined from the XRD pattern of the mixture powder. When the powder was sintered at 1100 °C, $TiSi_2$ and TiC peaks are still in the XRD pattern, whereas, Ti peak disappeared. Besides, Ti_5Si_3 peaks can be seen at 2θ=36.8 °, 37.5 °, 41 ° and 42.7 °, respectively, however, there is no Ti_3SiC_2 peak in the XRD pattern. With increasing sintering temperature to 1200° C, it is seen that Ti_3SiC_2 peak with low intensity began to appear in the XRD pattern. At 1100 °C and 1200 °C, apparently, TiC is always the main phase, however, at 1300 °C, Ti_3SiC_2 became the main phase and the intensity of TiC and $TiSi_2$ peaks were decreased to a low level. With extending sintering time to 30 minutes at 1300 °C, both of the relative intensities of TiC and $TiSi_2$ peaks were obviously reduced. From this figure, it is indicated that Ti_3SiC_2 began to form at the temperature above 1200 °C and became the main phase near 1300 °C from the Ti/$TiSi_2$/TiC powder through the PDS technique.

Figure 2 demonstrates the effect of sintering time on the formation of Ti_3SiC_2 synthesized from Ti/$TiSi_2$/4TiC powder at 1250 °C and 1300 °C. It can be seen that $TiSi_2$ peak still existed in the XRD patterns of the M1 samples sintered at the two temperatures for 0 minutes, and became undectable when the sintering time was extended to 60 minutes. Meanwhile, TiC peak was also decreased in the sample sintered at 1250 °C for 60 minutes. It is indicated that extending sintering time would further purify the samples. Figure 3 and Fig. 4 show the XRD patterns of the M1 and M2 samples sintered at 1225–1325 °C for 15 minutes, and the following features can be seen. (1) Ti_3SiC_2 is always the main phase and the relative intensity of TiC peak is decreased to a low value. (2) For the M1 samples, $TiSi_2$ peak can not be seen except for at 1225 °C and 1250 °C, however, for the M2 samples, $TiSi_2$ peak always exists in their XRD patterns. (3) The relative intensity of TiC peaks in the M2 samples is slightly lower than that of the M1 samples. The present XRD results in Figs. 1–4 indicate that the Ti/$TiSi_2$/TiC powders can be used to synthesize Ti_3SiC_2 with low peak intensity of TiC and $TiSi_2$ impurity phases in a low sintering temperature range of 1225–1325 °C by using the PDS technique.

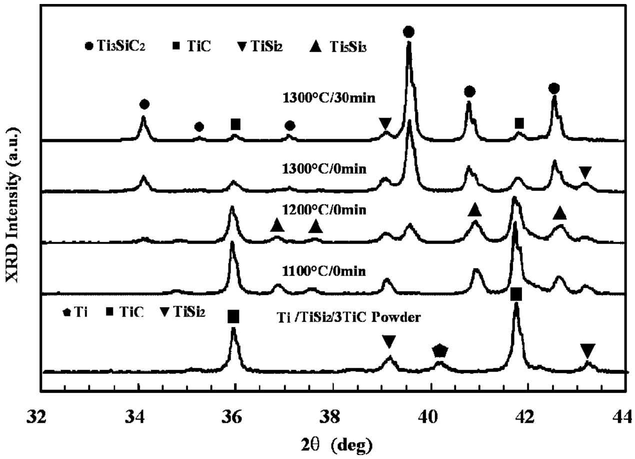

Fig. 1 X-ray diffraction profiles of Ti/$TiSi_2$/3TiC powder and the as-sintered samples at 1100–1300 °C

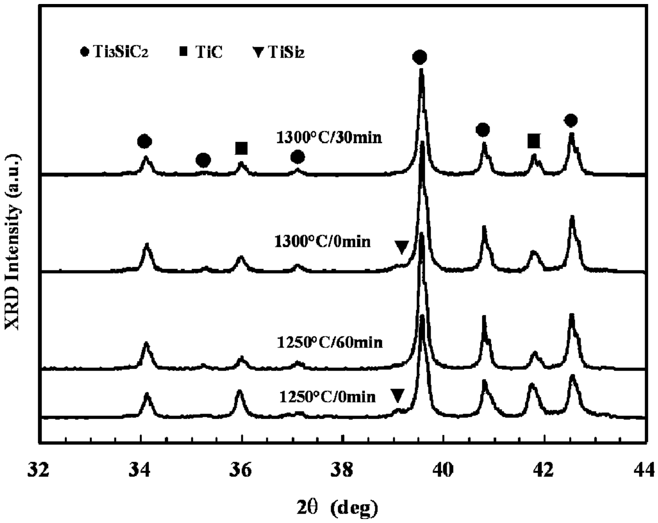

Fig. 2 X-ray diffraction profiles of the M1 samples sintered from Ti/$TiSi_2$/4TiC powder at 1250 °C and 1300 °C for 0 and 60 minutes

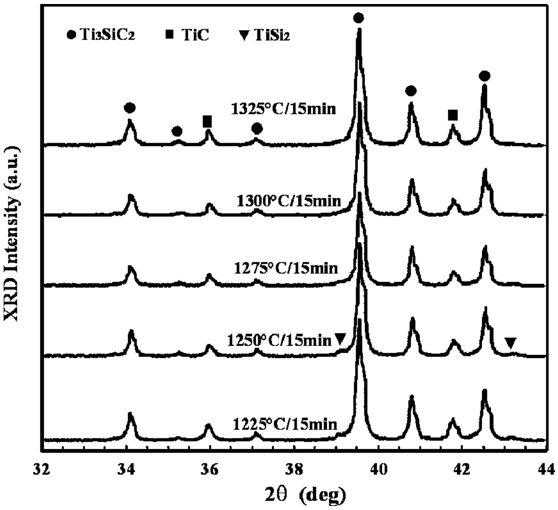

Fig. 3 X-ray diffraction profiles of the M1 samples sintered from Ti/$TiSi_2$/4TiC powder at 1225–1325 °C for 15 minutes

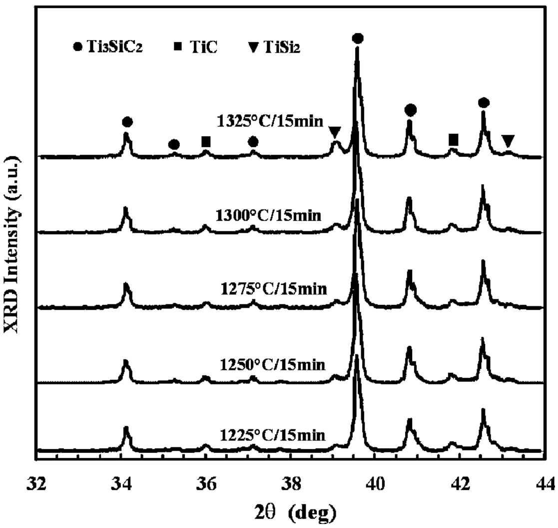

Fig. 4 X-ray diffraction profiles of M2 samples sintered from Ti/$TiSi_2$/3TiC powder at 1225–1325 °C for 15 minutes

To calculate the purity of Ti_3SiC_2, we had calibrated the dependence of relative intensity I_{TC}/I_{TSC} of TiC peak to Ti_3SiC_2 main peak. For a two-phase mixture of Ti_3SiC_2 and TiC, the following two equations were obtained [24]:

$$W_{TSC} = \frac{1.80}{1.80 + I_{TC}/I_{TSC}} \text{ and } W_{TC} = \frac{I_{TC}/I_{TSC}}{1.80 + I_{TC}/I_{TSC}} \quad \text{(a)}$$

Wherein, W_{TSC} and W_{TC} are the weight percentages of Ti_3SiC_2 and TiC phases, respectively. I_{TC}/I_{TSC} is the integrated intensity ratio of TiC to Ti_3SiC_2 main peak and can be obtained from the XRD results of the examined samples. For the M1 samples sintered at 1225–1325 °C for 15 minutes, from their XRD patterns in Fig. 3, we can regard it as a two-phase mixture of Ti_3SiC_2 and TiC. Therefore, the content of TiC (or Ti_3SiC_2) can be calculated by means of the two equations, and the results are shown in Fig. 5. It is seen that the TiC content in the M1 samples nearly maintains constant value of 7–9wt% when sintered at 1225–1325 °C. However, there are three phases, i.e. Ti_3SiC_2, $TiSi_2$ and TiC, in the M2 samples sintered at 1225–1325 °C for 15 minutes. For comparing the TiC content with that in M1 samples, the equations above can only be used to calculate the relative percentage of TiC existing in the part of Ti_3SiC_2 and TiC in the M2 samples if regardless of the $TiSi_2$ phase. From Fig. 5, it can be seen that the TiC content in the M2 samples also shows a weak dependence on the sintering temperature and varies from 5 to 7 wt%. If taking $TiSi_2$ impurity in the M2 samples into account, the purity of Ti_3SiC_2 in the M1 and M2 samples should be approximately same. It is indicated that the purity of Ti_3SiC_2 synthesized from the two groups of Ti/$TiSi_2$/TiC powders can be improved to about 93 wt% when the sintering time is 15 minutes. On the other hand, it is noted that both TiC and $TiSi_2$ co-exist in the synthesized M2 samples, it should be possible that the purity of Ti_3SiC_2 can be further improved either by adding more Ti powder into the Ti/$TiSi_2$/3TiC mixture or by extending sintering time.

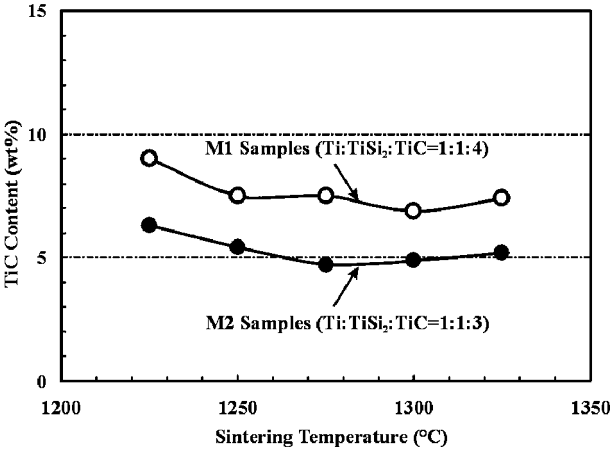

Fig. 5 TiC content in the M1 and M2 samples sintered at 1225–1325 °C for 15 minutes

Figure 6 shows the typical microstructure of the M1 samples sintered at different temperatures for 15 minutes observed by SEM. When the sample was sintered at 1225 °C, its microstructure consists of homogenous fine grains, as shown in Fig. 6(a). These grains have the shape of plate-like with an average size of about 5–10 μm in length and 2–3 μm in width. The plate-like Ti_3SiC_2 grains are in good agreement with those identified by many investigators. At 1300 °C, as shown in Fig. 6(b), the microstructure becomes coarse and has a average grain size of 20 μm in length. For the M2 samples, its microstructure displays the similar feature with the M1 samples. Figure 7 shows the dependence of the densities of M1 and M2 samples on the sintering temperature. We can see that, at 1225–1325 °C, the measured density (ρ_M) of M1 samples is always higher than 4.50 g/cm^3, which is quite close to the theoretical density

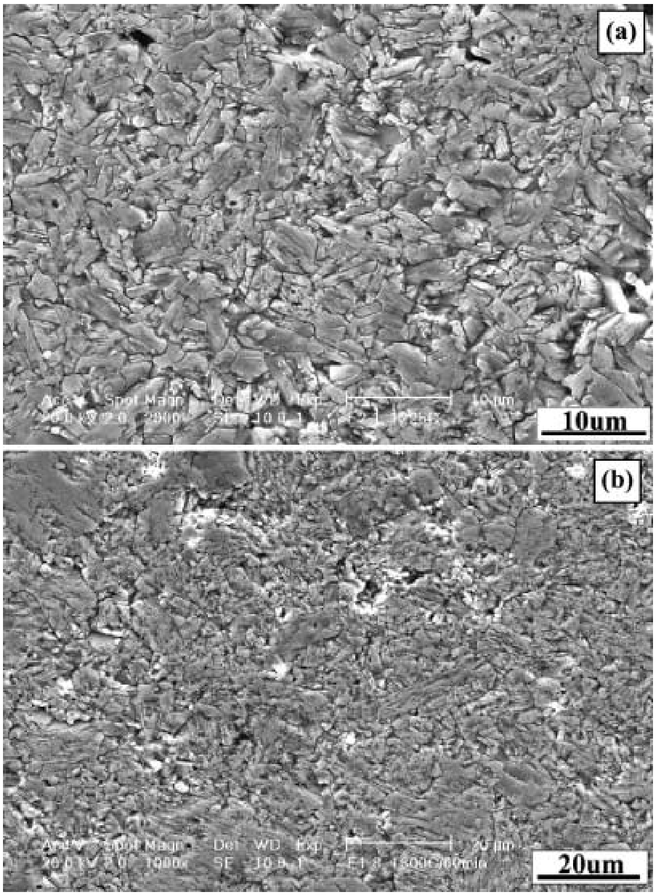

Fig. 6 Microstructure of the M1 samples sintered at various temperatures observed by SEM. **(a)** T=1225 °C, t=15 minutes; **(b)** T=1300 °C, t=60 minutes

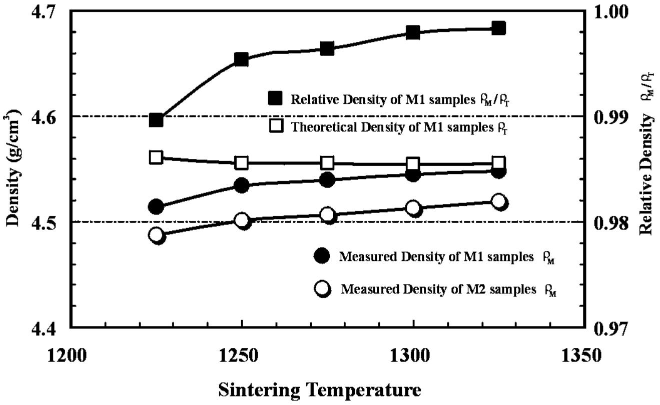

Fig. 7 Dependence of the measured density, theoretical density and relative density of the M1 samples along with the measured density of the M2 samples on the sintering temperature

4.53 g/cm^3 of pure Ti_3SiC_2. For M2 samples, its density is slightly lower than that of M1 samples, but still reaches to 4.50 g/cm^3 at the sintering temperature above 1250 °C. Since the theoretical densities of pure Ti_3SiC_2 and TiC are equal to 4.53 g/cm^3 and 4.94 g/cm^3 [11], the theoretical densities (ρ_T) of the synthesized samples can be calculated by taking the purity of Ti_3SiC_2 in Fig. 5 into account. Furthermore, the relative density of the samples will be easily deduced from the ratio ρ_M/ρ_T of the measured density (ρ_M) to the theoretical density (ρ_T). As shown in Fig. 7, apparently, the relative density of the M1 samples is sufficiently high (more than 99%) at the sintering temperature above 1225 °C. It is indicated that the synthesized samples from Ti/$TiSi_2$/3TiC powder at relatively low temperature for short time have a good densification effect produced by the PDS technique under a pressure of 50 MPa.

Prior to the present work, Ti/Si/C [3–12, 20] and Ti/SiC/C [13–15, 21] powders have been widely employed for the synthesis of Ti_3SiC_2 samples by different methods. Besides, Ti/Si/TiC [22–24, 26] and Ti/SiC/TiC [25] powders were also tried to fabricate this novel material. From the synthesized samples available, it has been widely recognized that TiC is one of important impurity phases during sintering various powder mixtures, however, another impurity, i.e. $TiSi_2$, was not paid much attention. To reveal the synthesis mechanism of Ti_3SiC_2, we compared and summarized all the results from the recent synthesis work of Ti_3SiC_2 samples. It is found that the formation of $TiSi_2$ phase is also a common phenomenon in the Ti_3SiC_2 products, which were synthesized by distinctly different methods, such as solid-state-reaction [3, 4], spark-plasma-sintering [5], hot-pressing (HP) [6, 7], hot-isostatic-pressing (HIP) [8, 9], solid-liquid-reaction [11, 12] and arc-melting [27]. From our recent work, the $TiSi_2$ phase was also frequently observed in the Ti_3SiC_2 samples synthesized from Ti/Si/C [20], Ti/SiC/C [21] and Ti/Si/TiC [24] powder mixtures through the PDS technique. Therefore, it can be concluded that except for the TiC impurity, $TiSi_2$ should be regarded as another important intermediate phase companying with the formation of Ti_3SiC_2. From the present results, it has been confirmed that Ti_3SiC_2 is easily formed from the Ti/$TiSi_2$/TiC powders at 1225–1325 °C. Therefore, as follows, we propose a solid-liquid reaction mechanism for the formation of Ti_3SiC_2, i.e.

$$Ti + TiSi_2\ (liquid) + 4TiC \Rightarrow 2Ti_3SiC_2 \qquad (b)$$

This reaction mechanism should be reasonable if we consider the following three factors. First of all, As we know, TiC has an octahedral structure; meanwhile, Ti_3SiC_2 is a layered hexagonal structure, in which two TiC are connected by Ti and Si layers [28, 29]. Therefore, the octahedral TiC can be regarded as a unit cell of Ti_3SiC_2 in structure. Secondly, it was reported that there are two eutectic reactions, i.e. Ti-Ti_5Si_3 and Si-$TiSi_2$, in Ti-Si system at 1330 °C [30]. When the eutectic liquid phase of Ti-Si system appeared in the mixture powder, Ti_3SiC_2 would be easily formed at the interfaces between the Ti-Si liquid phase and the existed TiC particles due to the wetting effect and the similarity between TiC and Ti_3SiC_2 in structure. From the XRD results in Figs 1–4, except for the starting powder of $TiSi_2$, another eutectic liquid phase of Ti-Si system, i.e. Ti_5Si_3, can also been observed in Fig. 1. Therefore, it is possible for the formation of Ti_3SiC_2 by the solid-liquid reaction. Finally, in a PDS process, it is assumed that pulse electric filed may activate the surface of the powder particles which enable an easy sintering process, and possible plasma occurred between the particles may locally increase the temperature to much higher a level than the controlled average temperature, which could effectively promote the synthesis reaction of Ti_3SiC_2 [16–19].

Conclusions

$Ti/TiSi_2/TiC$ powder can be regarded as a new mixture for the synthesis of Ti_3SiC_2 samples through the pulse discharge sintering (PDS) technique at 1225–1325 °C. When the molar ratios of $Ti:TiSi_2:TiC$ were adjusted into 1:1:4 and 1:1:3, the purity of Ti_3SiC_2 in the synthesized samples was improved to about 93 wt%. It is expected that the purity of Ti_3SiC_2 can be further improved either by adding more Ti powder into the $Ti/TiSi_2/3TiC$ powder or extending sintering time. With the PDS technique, the relative density of the synthesized sample was higher than 99% at the sintering temperature above 1225 °C, showing a good densification effect. Based on the present results, a solid-liquid reaction mechanism between Ti-Si liquid phase and TiC particles was proposed to explain the rapid formation of Ti_3SiC_2, i.e. $Ti+TiSi_2$ (liquid) $+4TiC \Rightarrow 2Ti_3SiC_2$.

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