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Pressure pulsed chemical vapour infiltration of SiC to two-dimensional-Tyranno/SiC–C preforms

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Preforms of two-dimensional Tyranno fibre (SiC base) of $7 \times 20 \times 1.3\,mm^3$ were chemically vapour infiltrated with SiC at 850–1050 °C from a gas mixture of CH_3SiCl_3 (6%)–H_2 using pressure pulses between below 0.3 kPa and 0.1 MPa. Above 900 °C, films grew on the macrosurface dominantly. At 850 °C, residual porosity decreased to about 10% after 10^5 pulses, and three point flexural strength reached about 200 MPa. X-ray diffractograms (XRDs) on the surface showed the deposits to be β-SiC only.

1. Introduction

The chemical vapour infiltration (CVI) process has an excellent characteristic of obtain near net-shape composites. The isothermal and isobaric CVI (ICVI) process needs long operation times because of slow diffusion into deep levels of the preforms [1–3]. Another typical process, forced CVI (FCVI), uses steep gradients of temperature and pressure which lead to short operation times; however, this process loses the characteristic of near net-shape because uniform gas flow requires that the preform shape be cylindrical or cubic [4–6]. The pressure pulsed CVI (PCVI) process operates by the sequential steps of vessel evacuation, instantaneous introduction of source gas and holding to allow deposition. During the step of gas introduction, evacuated fine spaces in the preforms are filled with fresh source gas, followed by deposition in the next step [7–12]. In this paper, PCVI of SiC to Tyranno fibre preforms will be described. Tyranno fibre is composed of Si–C–Ti–O (mainly SiC) and is a hopeful material for high temperature reinforced composites.

2. Experimental procedure

Two-dimensionally woven Tyranno cloths (Ube Kosan Co.) were piled four sheets high, immersed in polyvinylacetate emulsion (in which 5 μm diameter SiC powder was suspended), dried at 200 °C for 24 h, cut to $7 \times 20 \times 1.3\,mm^3$ pieces, and baked in a nitrogen flow at 1000 °C for 6 h. The properties of Tyranno fibre are as follows: composition (wt %) Si 48–57; C, 30–32; Ti, 2.0; O, 12–18; number of filaments per yarn, 1600; diameter of filament, 8.5 μm, density, $2.3\,g\,cm^{-3}$; and tensile strength 3.0–3.6 GPa. The average porosity of the preforms was 59–60%. The main part of the apparatus for PCVI is shown in Fig. 1. A pressure pulse was composed of gas introduction (0.1 s), hold time (0.6 s) and evacuation (1.0 s). Dead space in the reactor was narrowed to about $30\,cm^3$ for suppression of deposition on the macrosurface from the source gas in the dead space. A dual evacuation system was used here for shortening the evacuation time. From the results of previous experiments, several experimental factors were fixed as follows: CH_3SiCl_3 concentration, 6% (H_2 concentration 94%); hold time 0.6 s; and PCVI temperature, 850–1050 °C.

3. Results and discussion

3.1. Effect of temperature on XRD, weight increase and morphology of deposits

In Fig. 2, XRDs of deposits are shown, in which X-rays were diffracted on the macrosurface of the samples obtained with 10^4 pulses and at various temperatures. Diffraction peaks vary from sharp to diffuse with lowering temperature, but all peaks were assigned to β-SiC. As can be seen from Fig. 2f, XRD of Tyranno fibre showed no definite peaks, and this fact means that the Tyranno fibre is nearly amorphous. Fig. 3 shows the weight increase after 5000 pulses at various temperatures. Below 900 °C, weight increase remains 50–53 mg, however, it increases with elevation of temperature and reaches 100 mg at 1050 °C. If fresh source gas introduced in the pores of the preform reacts completely and deposits on the wall of pores during the hold time of 0.6 s, the weight increases at 850 and 1050 °C after 5000 pulses can be estimated as 22.2 and 18.9 mg, respectively. Deposition also takes place on the macrosurface of preforms, and source gas of somewhat lower temperature than that of the reaction vessel is instantaneously introduced. These two factors enlarge the weight increase compared with those of the above estimation. At least, weight increase above 900 °C is supposed to be that of deposits on the macrosurface from source gas in the dead space, and, if so, the film on the macrosurface blocks further gas penetration into deep levels.

Fig. 4 shows the morphology of deposits on the macrosurface after 5000 pulses at various temperatures. The grain size increases with increasing temperature from 2 μm at 850 °C to 6–10 μm at 1050 °C.

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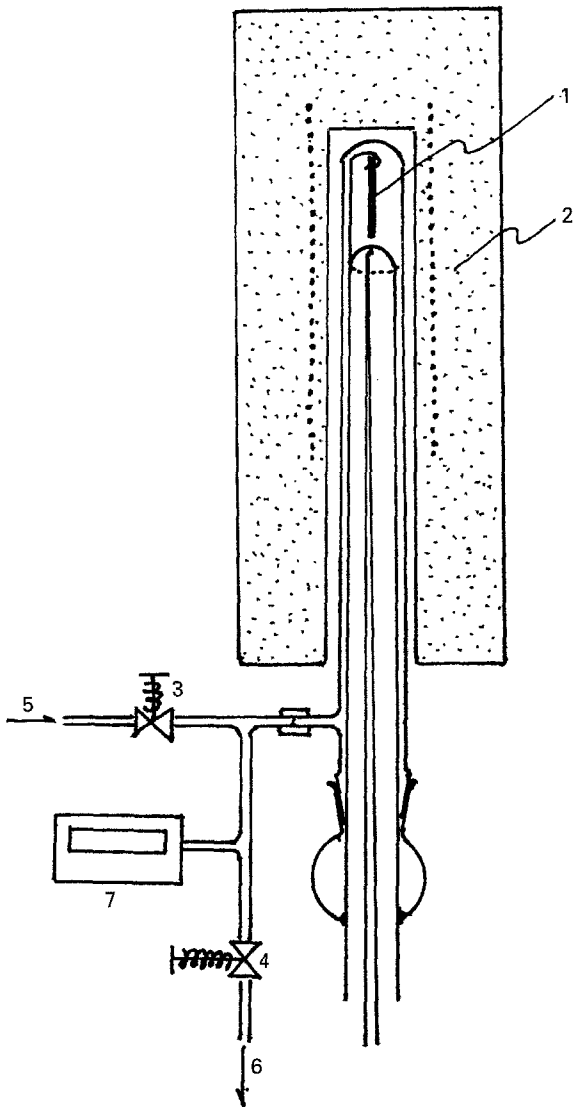

Figure 1 Main part of PCVI apparatus: (1) substrate: (2) furnace, (3) inlet magnetic valve, (4) outlet magnetic valve, (5) gas from reservoir, (6) gas to vacuum pumps, (7) pressure gauge.

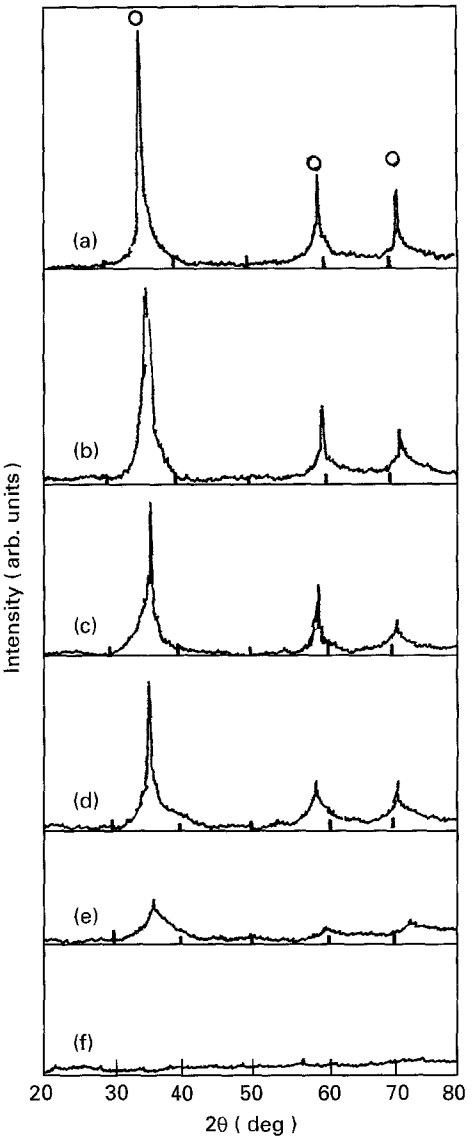

Figure 2 Effect of deposition temperature on XRDs diffracted on macrosurface (after 10000 pulses). Deposition temperature: (a) 1050 °C, (b) 1000 °C (c) 950 °C, (d) 900 °C, (e) 850 °C, and (f) original Tyranno cloths. (○) β-Sic.

Above 900 °C, grains grown on several filaments are unified. Fig. 5 shows the relation between infiltrating temperature and three point flexural strength after 10^4 and 5×10^4 pulses. After 10^4 pulses, flexural strength does not change clearly with increasing temperature. On the contrary, after 5×10^4 pulses flexural strength of the samples obtained below 875 °C increases up to 100 MPa; however, that of samples obtained above 900 °C remains as that of after 10^4 pulses. These results can be explained by two assumptions, i.e. samples after 10^4 pulses have not been rigidified, and films grown on the macrosurface contribute slightly to the flexural strength. Therefore, it is considered that the reaction temperature has to be lowered to below 875 °C for effective infiltration at a deep level.

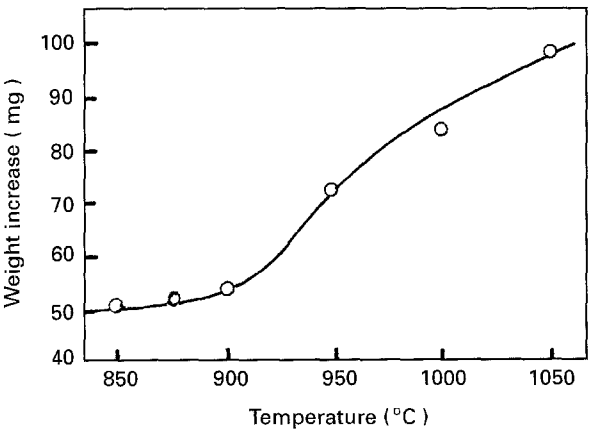

Figure 3 Effect of temperature on weight increase (after 5000 pulses).

3.2. Relation between number of pulses, flexural strength and packing ratio

Fig. 6 shows the relation between flexural strength, weight increase and number of pulses. At 900 °C, weight increase of samples increases parabolically and reaches 360 mg after 10^5 pulses, but flexural strength increases only to 30 MPa after 10^5 pulses. The second assumption, i.e. films on the macrosurface contribute slightly to the flexural strength, may act here. At 850 °C, the weight increase of samples increases also parabolically, and reaches 280 mg after 10^5 pulses,

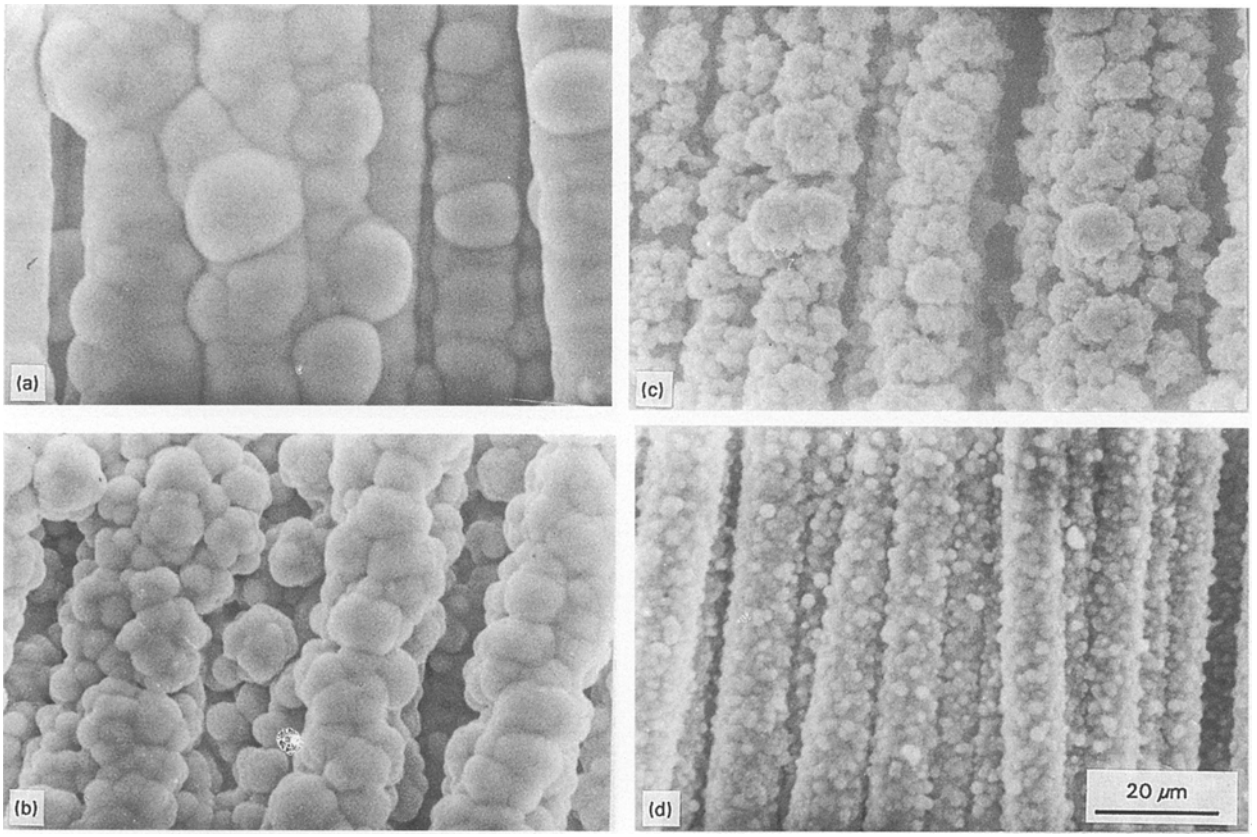

Figure 4 Surface morphology after 5000 pulses. Deposition temperature: (a) 1050 °C, (b) 950 °C, (c) 900 °C, and (d) 850 °C.

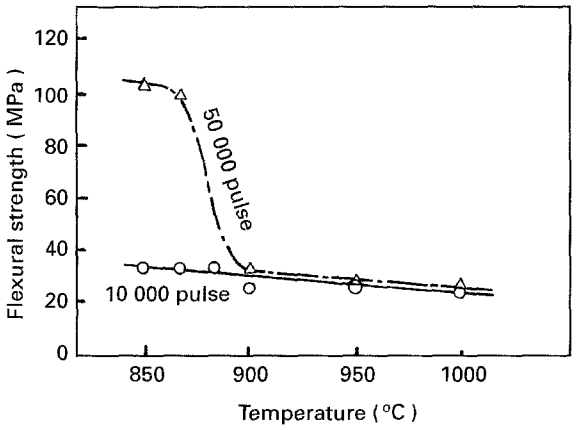

Figure 5 Relation between infiltrating temperature and flexural strength.

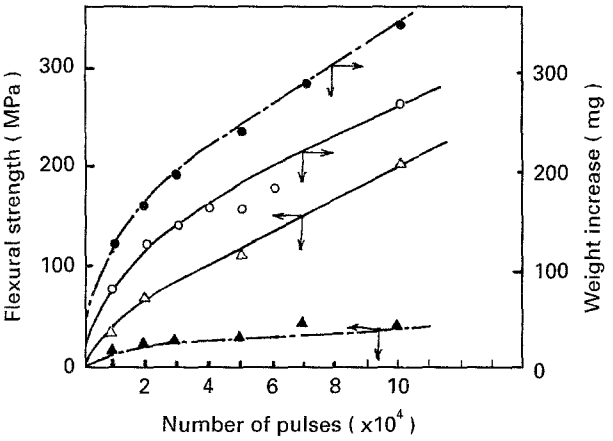

Figure 6 Relation between flexural strength, weight increase and number of pulses. Flexural strength: (▲) 900 °C, (△) 850 °C. Weight increase: (●) 900 °C, (○) 850 °C.

which is a somewhat lower value than that at 900 °C; however, flexural strength increases linearly with the number of pulses, and reaches about 200 MPa after 10^5 pulses. The linear increase of flexural strength suggests that effective infiltration is progressing even after 10^5 pulses. Fig. 7 shows the relation between porosity and number of pulses, in which the volume of macrosurface of the film was roughly subtracted by measuring the film thickness on a scanning electron microscope (SEM) image of a ruptured section. At 900 °C, porosity decreases up to 3×10^4 pulses, and a porosity of about 30% remains after 10^5 pulses. In the case of 850 °C treatment, the porosity decreases gradually to 10^5 pulses, and reaches about 10% after the same number of pulses. At 900 °C, a film of about 50 μm thickness could be seen on the surface after 3×10^4 pulses; on the contrary, at 850 °C no film on

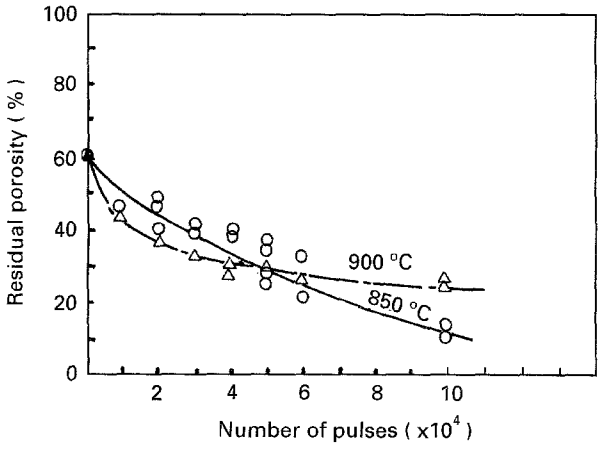

Figure 7 Relation between residual porosity and number of pulses.

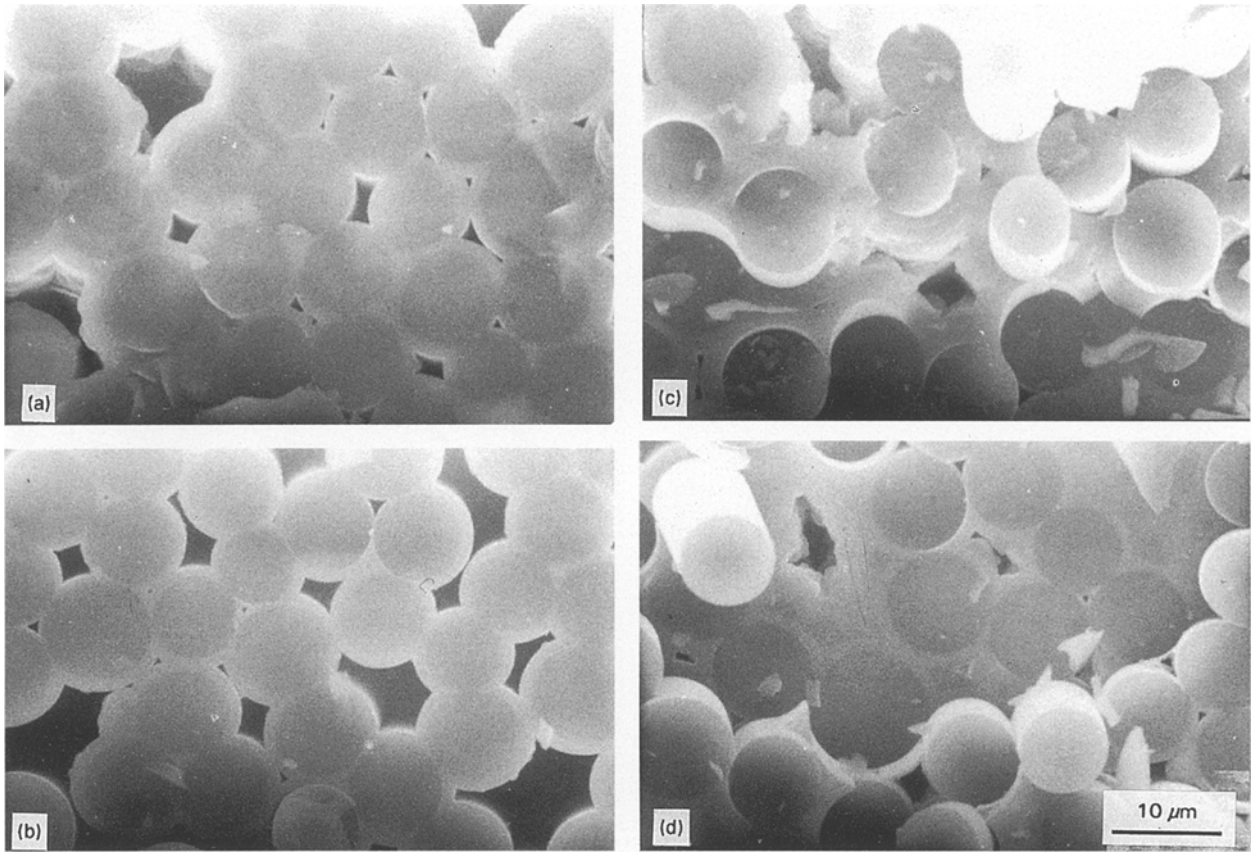

Figure 8 Ruptured sections after PCVI. Deposited at 900 °C (after 30 000 pulses): (a) near surface, (b) at the half thickness. Deposited at 850 °C (after 10^5 pulses): (c) near surface, (d) at the half thickness.

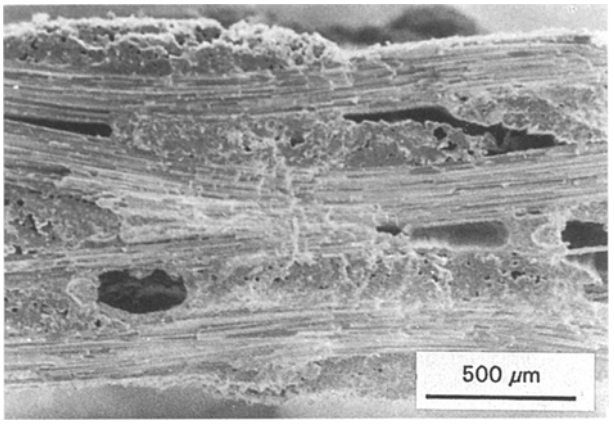

Figure 9 Ruptured section with very low magnification after 5×10^4 pulses at 850 °C.

the surface could be seen even after 10^5 pulses. Fig. 8a (near surface) and 8b (at half-thickness) show the ruptured sections of specimens infiltrated by 3×10^4 pulses at 900 °C. Due to the film formation, infiltration is insufficient not only at the half-thickness (Fig. 8b) but also near the surface (Fig. 8a). Fig. 8c, d show similar sections of specimens infiltrated by 10^5 pulses at 850 °C. Infiltration at the half-thickness (Fig. 8d) is considerably high; however, SiC matrix grips the Tyranno fibres so tightly that the pull-out of fibres is somewhat poor. Large pores of 200–300 μm in diameter can be seen on the very low magnification photograph (Fig. 9). To improve the strength, a method of preparing preforms without large pores has to be developed, because in the usual PCVI process the thickness of the deposits per pulse is as thin as 0.02 or 0.05 nm; therefore, this process is too weak to close such a large pore.

XRDs were measured on the macrosurface of the samples obtained at 850 °C. The β-SiC peaks became sharp and high with increasing number of pulses; however, peaks of elemental silicon could not be seen definitely.

4. Conclusions

The relation between the number of pulses, flexural strength and packing ratio was studied using Tyranno fibre preform as a reinforcing material and SiC as a matrix by pressure pulsed infiltration from the system CH_3SiCl_3–H_2 at various temperatures. The following results were obtained

1. Above 900 °C, films on the macrosurface grew dominantly, blocking the gas penetration path. Below 850 °C, the deposition rate was very slow, therefore, a suitable PCVI temperature was considered to be between 850–875 °C.
2. At 900 °C, macrosurface films were formed after 1×10^4–3×10^4 pulses, and a residual porosity of 30% remained after 10^5 pulses. At 850 °C, infiltration into deep levels continued up to 10^5 pulses without formation of macrosurface films, and residual porosity decreased to about 10%.
3. Three point flexural strength after 10^5 pulses reached about 30 and 200 MPa at 900 and 850 °C,

respectively. It was supposed that macrosurface films contributed slightly to the strength.

4. From XRDs diffracted on the macrosurface, only β-SiC was assigned, and Si peaks could not be seen definitely.

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