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The influence of deposition mechanism on the microstructure of pyrolytic carbon deposited in a tumbling bed

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The factors influencing the size of the microstructure of isotropic carbon are suggested. Scanning electron micrographs of pyrolytic carbons deposited in a low RPM (below 2.4 rpm) tumbling bed are examined. The growth of surface carbon on the deposited droplets, which causes the increase in the size of the microstructure, occurs in two ways: (1) an increase in the period of static state of the substrate and a decrease in the tumbling factor (e.g. by decreasing the rpm) after the gas-borne droplets are deposited on the substrate; (2) the gas-recirculation existing in a dynamic bed before the gas-borne droplets are deposited onto the substrate.

1. Introduction

Pyrolytic carbon is a quasi-crystalline material which is deposited onto a substrate by the thermal pyrolysis of a carbon-bearing vapour [1]. The pyrolytic carbon coatings have been used as resistors [2], rocket nose cones and nozzles [3], a coating for nuclear fuel particles [4], matrices of carbon fibre composite materials [5], and biomaterials [6]. A stationary bed or fluidized bed is usually used to deposit the pyrolytic carbons. Bokros and coworkers developed a fluidized bed process to produce LTI-pyrolytic carbon for biomaterials and nuclear fuel particle coatings for the high-temperature gas-cooled reactors. The microstructures of pyrolytic carbon deposited in a fluidized bed are made up of isotropic, laminar, columnar and granular structures, depending upon the deposition conditions [7]. Recently, Lee *et al.* developed a new tumbling bed process to deposit the pyrolytic carbons [8]. Kaae [9] and Pollmann *et al.* [10] observed the isotropic carbon using transmission electron microscopy and showed that it consisted of spherical or polyhedral shaped microstructures. However, how and why the size of the microstructures varies with deposition conditions has not been studied. Therefore, the purpose of this study is to observe the microstructures of isotropic carbon using scanning electron micrographs of the fracture surface of cross-sections of pyrolytic carbons deposited in a low rpm (below 2.4 rpm) tumbling bed [11] and to suggest the factors influencing the size of the growths. The role of gas-recirculation existing in a tumbling bed is demonstrated, and the size of the microstructures grown in the isotropic carbon deposited in a low rpm tumbling bed is compared with that obtained from the fluidized bed.

2. Experimental details

The tumbling bed apparatus [8, 11], used to deposit the pyrolytic carbon on graphite substrates is shown schematically in Fig. 1. The reaction tube was rotated by a variable speed motor. The inside diameter of the reaction tube was 3 cm, the inlet and outlet cone was 15°, and the length of the tumbling bed was 5 cm. Five grooves were cut on the inner wall of the tumbling bed, parallel with the tube axis, to promote the tumbling action of the substrate. Deposits were mainly formed on a graphite disc 18 mm diameter and 2.5 mm thick. Four discs were used in one coating run and the bed particle was not used. Propane or methane were used as the carbon source, with argon as the carrier gas. A total pressure was 1 atm was used and the deposition temperature was 1200°C in all

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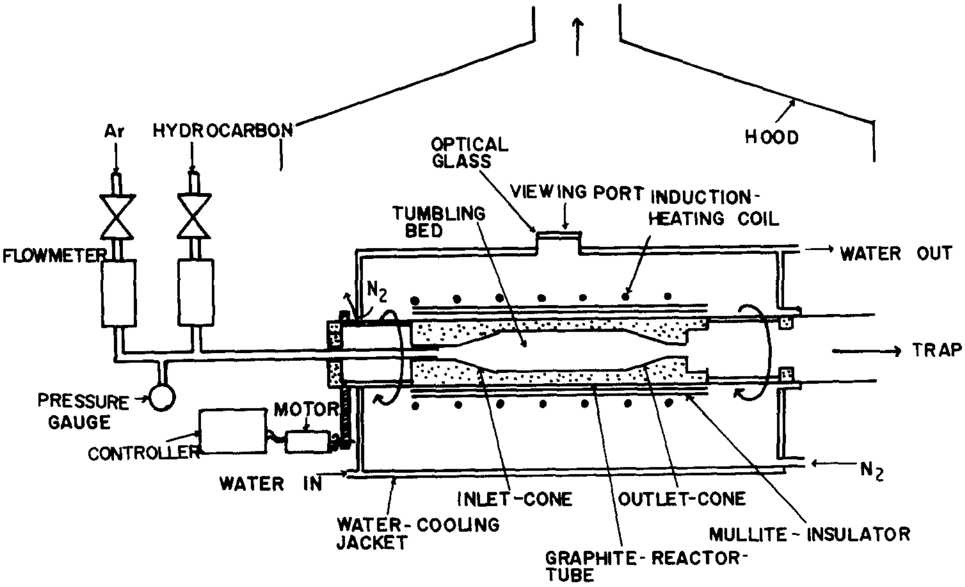

Figure 1 Schematic diagram of the coating apparatus.

experiments. The rpm of the reaction tube varied between 0.2 and 2.4. The scanning electron micrographs of the deposits were examined using an ETEC Auto Scan 149-10.

3. Results

The scanning electron micrographs of Fig. 2 show the variation of the fracture surfaces of cross-sections of pyrolytic carbons with decreasing rpm of reaction at a propane concentration of 23%, no bed particle, a total flow rate of 1.4 l min^{-1}, and a deposition temperature of 1200°C. Except in the case of 0.2 rpm, the microstructures of isotropic carbon are shown in all cases. These features are formed by deposition of the gas-borne droplet onto the substrate and its subsequent growth from the surface carbon [9, 12]. As the rpm decreases, the size of the microstructures increase from 0.5 to 0.7 μm at 2.4 rpm to 1.0 to 1.2 μm at 0.3 rpm. At a low rpm (0.2), the disc substrate became stuck on the bed wall by the deposition of pyrolytic carbon on the wall, therefore, columnar carbon was deposited on the disc which faces the centre of the reactor despite of the rotation of the reactor, as shown in Fig. 2f. At an rpm of 0.3, open pores were found in the deposit and the bonding force between the growth features seemed weak. The scanning electron micrographs showing a closed macro-pore among the representative deposits from Figs. 2a to d are shown in Fig. 3. The growth features of the inner surface of these pores are extremely large compared to those in other positions, reaching a size of 3.5 μm at 0.5 rpm. The growth direction of the microstructures is normal to the inner surface of the pore and not to the substrate. The size of these features increases with decreasing rpm. At 0.3 rpm there is no macro-closed pore throughout the deposit.

Fig. 4 shows a scanning electron micrograph of the fracture surface of a cross-section of the isotropic carbon deposited on the right-hand side of a graphite substrate of 22 mm × 22 mm × 7 mm, which is placed as shown in Fig. 5, at 0 rpm, a propane concentration of 23%, total flow rate 1.4 l min^{-1}, and a deposition temperature of 1200°C. The particles were about 0.8 μm in size, the microstructure is relatively porous, and the bonding force between the particles seemed weak.

Fig. 6 shows a scanning electron of the fracture surface of a cross section of isotropic carbon deposited from methane at 1.0 rpm. a methane concentration of 100%, a total flow rate of 1.4 litre min^{-1}, a deposition temperature of 1200°C, and no bed particle. The size of the particles was about 1.5 μm, larger than those of the isotropic carbon deposited from propane.

4. Discussion

Because the disc substrate experiences a static state and a tumbling state, operating in the tumbling bed without any bed particle [13], carbon continues to be deposited on the gas-borne droplet during the

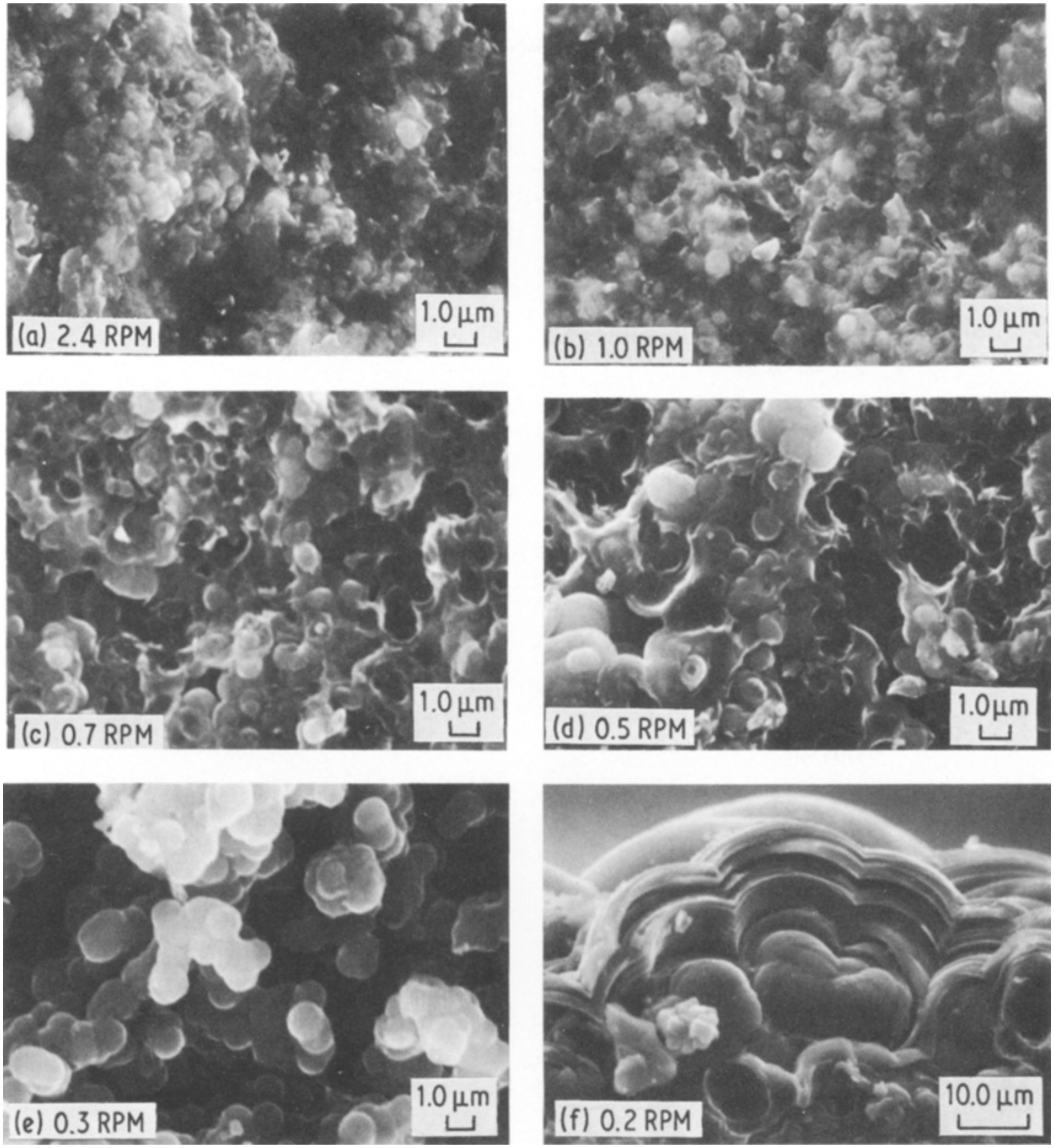

Figure 2 Variation in the scanning electron micrographs of the fracture surface of cross-sections of pyrolytic carbons with decreasing rpm of the reactor at a propane concentration of 23%, no bed particle, a total flow rate of $1.4\,\mathrm{l\,min^{-1}}$, and a deposition temperature of 1200° C.

static state of the substrate after the gas-borne droplet is deposited onto the substrate. Therefore, as the rpm decreases, the period of the static state increases [13], which increases the size of the particles as shown in Table I. The other factor which increases the particle size with decreasing rpm is the decrease in the tumbling factor, f, which is defined as [13]:

the actual tumbling number of the substrate per unit rotation of reactor $= 5f$.

Five parallel grooves on the inner wall of tumbling bed induce the disc substrate to tumble 5 times unit rotation of the reactor. However, at low rpm (below 1.0), the grooves are filled with plume [14, 15] or filamentous carbon [8] during deposition of pyrolytic carbon, thus hindering the tumbling action of the disc substrate. Thus, as the rpm decrease, the tumbling factor decreases and the static state period of the substrate increases, increasing the size of the microstructures. At 0.3 rpm, in

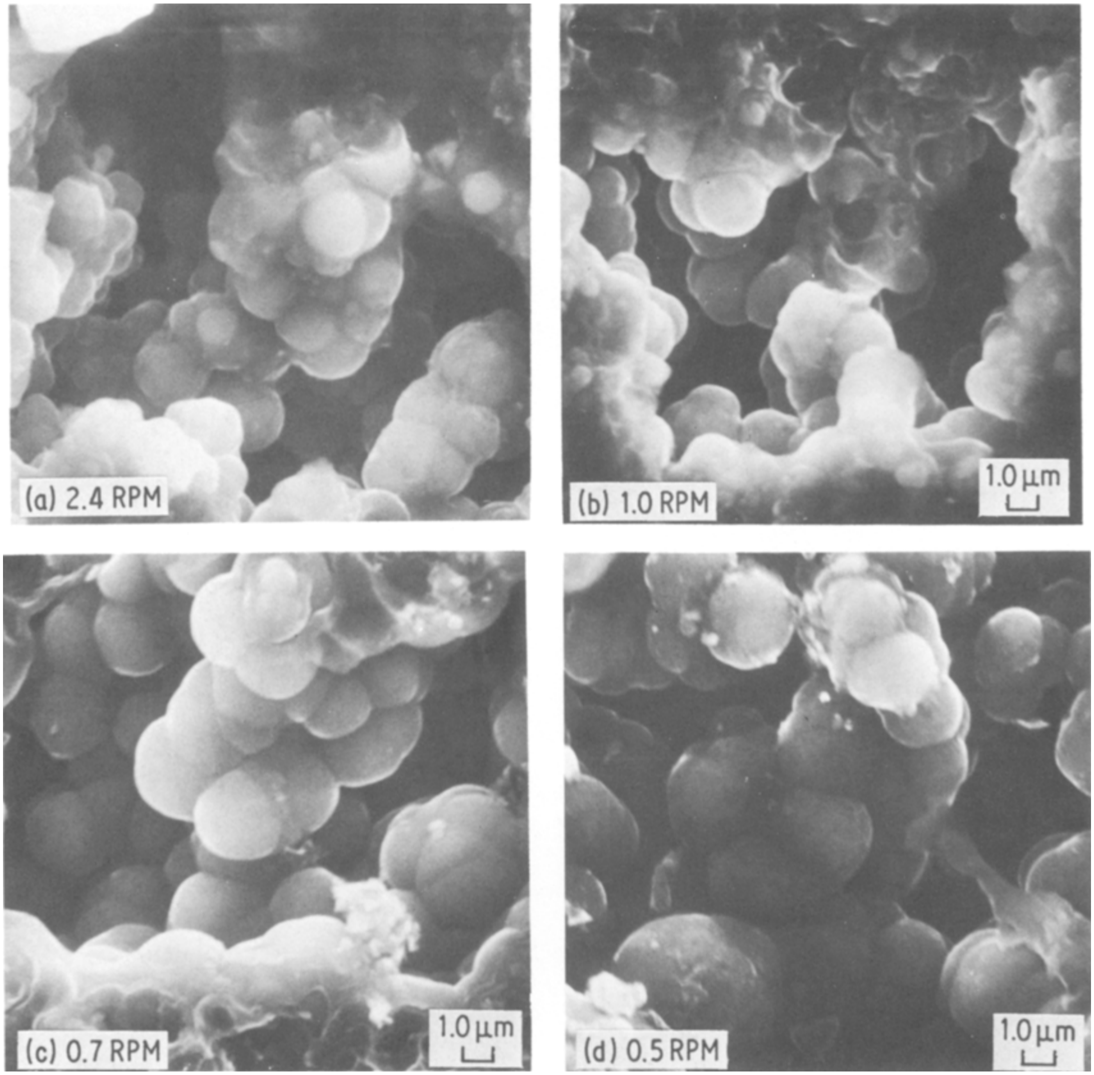

Figure 3 Scanning electron micrographs containing a closed macropore among the pyrolytic carbons deposited at a propane concentration of 23%, no bed particle, a total flow rate of $1.4\,\mathrm{l\,min^{-1}}$, and a deposition temperature of 1200° C.

particular, plume or filamentous carbon nucleates and grows very quickly, consuming a large amount of carbon source form the bed. Owing to the lack of carbon source, surface carbon growth does not effectively occur on the gas-borne droplet deposited on the substrate, forming the very porous deposit as shown in Fig. 2f. However, as it is possible that the carbon source diffuses through the open pore within the deposit, surface growth can occur on the droplets existing within the deposit, increasing the size of the particles. Because a pronounced amount of hydrogen can occur on the surface of the droplet within the deposit, a weakening of the bonding between the particles occurs.

TABLE I Variation of particle size of isotropic carbon with rpm in a tumbling bed

rpm	Particle size (μm)
2.4	0.5 to ~ 0.7
1.0	0.6 to ~ 0.8
0.7	0.8 to ~ 1.0
0.5	1.0 to ~ 1.2
0.3	1.0 to ~ 1.2

The macropores in the pyrolytic carbons deposited at low rpm (below 2.4) are the closed pores of 10 to 20 μm diameter, shown in Fig. 3. Je [13] showed that the thickness of pyrolytic carbon deposited by two tumblings of the disc substrate was about 1 μm. Then the substrate tumbles 20 to 40 times. Thus carbon is supplied mainly on them,

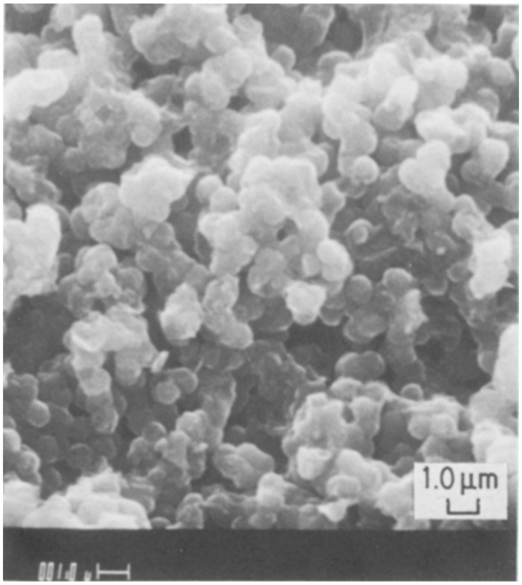

Figure 4 Scanning electron micrographs of the deposit on the right-hand side of a vertical graphite substrate of 22 mm × 22 mm × 7 mm at 0 rpm, a propane concentration of 23%, a total flow rate of 1.4 l min^{-1}, and a deposition temperature of 1200° C.

increasing the size of the particles. The increase in size of these microstructures on the inner surface of the macropore with decreasing rpm, is also due to the increased period of static state of the substrate, with decreasing rpm. The reason why the pore is so big, is believed to be that it is hard to close once formed. That is, if a void is created for a certain reason during deposition, it is too large to be filled during one period of static state of the substrate. Thus, successive tumbling of the substrate deposits new gas-borne droplets with the void unfilled and it remains open to the gas atmosphere. If a bottleneck [1] is then formed, the void is closed and the growth of the particles on its inner surface stops. The particles do not grow to a large size, despite the fact that the deposit may contain an open pore such as that in Fig. 2e, because of the lack of source carbon caused by formation of plume or filamentous carbon.

It is believed the microstructure of the deposit in Fig. 4 is no porous because of insufficient surface growth of the droplets after they are deposited onto the substate. In the fluidized bed or tumbling bed, the sufficient surface carbon growth can usually occur on the droplets after they are deposited on to the substrate. However, for the deposition conditions of Fig. 4, the gas-borne droplets are continuously deposited on the rear surface of the vertical substrate by drag force, with insufficient time for the surface carbon growth to occur. The other factor causing insufficient surface carbon growth, is the lack of source carbon around the rear surface of the substrate, because the gas-recirculation activates homogeneous nucleation and growth, consuming the source carbon around the rear surface of the substrate. This is supported by the fact that the deposition rate of isotropic carbon is very high, 2000 µm h^{-1} under these deposition condition [13]. The deposition time of the isotropic carbon is that during which the gas-borne droplets are deposited onto the substrate, plus the time during which the surface carbon growth occurs on them after they are deposited onto the substrate. The amount of deposit is, of course, much more on deposition of the gas-borne droplets than on the surface carbon growth. Therefore, the fact that the deposition rate is very high under this deposition condition means that surface carbon growth on the substrate does not occur.

As shown in Figs. 2 and 6, the size of the microstructures of the isotropic carbons deposited from propane and methane in a low rpm tumbling bed is larger than that deposited in a fluidized bed, from

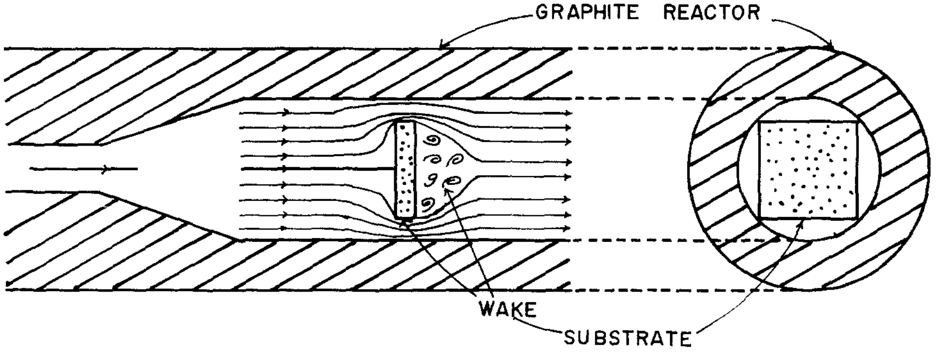

Figure 5 Cross-sectional view of a flow pattern around a vertical substrate.

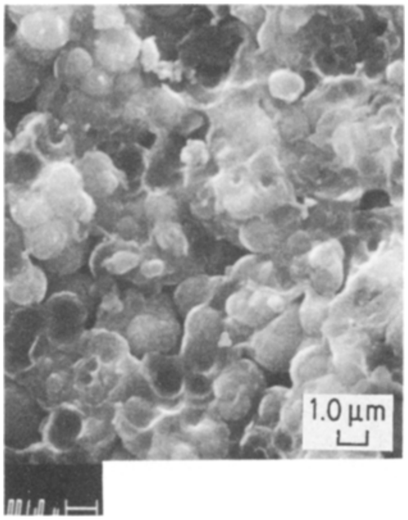

Figure 6 Scanning electron micrograph of the fracture surface of the cross-section of pyrolytic carbon deposited at 1.0 rpm, a methane concentration of 100%, a total flow rate of $1.4\,\mathrm{l\,min^{-1}}$, no bed particle, and a deposition temperature of 1200°C.

propane a particle size of 0.5 µm [9, 10], is obtained, while from methane it is 1.0 µm [16]. This is because the static state period of the substrate is lengthened in the low rpm tumbling bed and the surface carbon growth can occur sufficiently on the droplets after they are deposited on the substrate. However, at 2.4 rpm, the size of the particles is small, about 0.5 to 0.7 µm, which means that the static state period of the substrate is shortened with increasing rpm, resembling that in a fluidized bed. The size of the particles in Fig. 4 is also large, about 0.8 µm, but it is believed that the reason for this is that the surface carbon growth occurred abundantly on the droplets in the gas phase by gas-recirculation before they were deposited onto the rear surface of the substrate.

5. Conclusions

The factors influencing the growth of particles of isotropic carbon are the same as those causing a surface carbon growth. The surface growth on the droplets can occur in two ways: (1) by surface growth due to a decrease in the tumbling factor (e.g. decreasing rpm) after they are deposited on the substrate; (2) surface growth in the gas phase by strong gas-recirculation which exists in a dynamic bed before deposition on the substrate.

Gas-recirculation plays two roles during deposition: (1) for the gas-borne droplets to collide with the substrate thus depositing the isotropic carbon; (2) to activate the surface growth on the droplets before they are deposition onto the substrate.

The size of particles of isotropic carbon deposited in a low rpm tumbling bed is bigger than those deposited in a fluidized bed because of the increased static state period of the substrate in a tumbling bed.

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