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Effects of grain-boundary GeO_2 particles on intergranular fracture of Cu-GeO_2 polycrystals

H. SATO, T. FUJII, S. ONAKA*, M. KATO
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8502, Japan
E-mail: onaka@iem.titech.ac.jp

The Cu-GeO_2 alloy polycrystals containing plastically hard GeO_2 particles are tensile tested to study intergranular fracture behavior of the alloys at intermediate temperatures. The effects of large GeO_2 grain-boundary particles on the intergranular fracture are discussed using the specimens containing the particles of the fixed size (3 μm in diameter) and different area-fractions. The ductility of the Cu-GeO_2 alloy polycrystals is larger than that of Cu polycrystals. The grain-boundary GeO_2 particles improve the ductility by suppressing grain-boundary sliding. The grain-boundary voids to cause the intergranular fracture preferentially nucleate between the grain-boundary GeO_2 particles. The ductility of the Cu-GeO_2 alloys increases with increasing the area fraction of the grain-boundary GeO_2 particles. The area-fraction dependence of the ductility is explained by considering the amount of GBS as a criterion of the intergranular fracture.

1. Introduction

Dispersion of second-phase particles in materials changes significantly their mechanical properties. In previous studies [1–11], effects of the second-phase particles on deformation and fracture behavior of materials have been investigated using Cu alloys containing GeO_2, SiO_2 and B_2O_3 particles. These oxide particles are incoherent with Cu and spherical in the Cu matrix [12, 13]. The Cu alloys containing such oxide particles have been considered as simplified model materials of the alloys containing second-phase particles.

When the Cu polycrystals with and without the oxide particles are deformed at intermediate and high temperatures under low strain rates, intergranular fracture often occurs [5, 14–18]. One of the reasons of the intergranular fracture is active occurrence of grain-boundary sliding (GBS) under the deformation conditions [5, 14–17]. Plastically hard particles on grain boundaries suppress GBS [5, 6, 11, 15, 17]. The distribution, i.e., the size and area fraction of grain-boundary particles may affect the suppression of GBS. Hence, it is necessary to understand the effects of the distribution of grain-boundary particles on the fracture behavior for development of high-strength structural materials.

Miura *et al.* [7, 8] have investigated fracture behavior of the Cu-SiO_2 alloys at intermediate and high temperatures and discussed the effects of area fraction of the grain-boundary SiO_2 particles on the fracture behavior. However, the grain-boundary SiO_2 particles in their specimens are small, less than 1 μm in diameter, where the suppression of GBS by the grain-boundary particles is partly or fully relaxed by the operation of diffusion around the particles at intermediate temperatures [6–8]. Fracture behavior of the alloys containing second-phase particles at intermediate temperatures has not been discussed in previous studies when grain-boundary particles are large enough to suppress GBS firmly.

In the present study, the results of tensile tests at intermediate temperatures are reported for Cu-GeO_2 alloys containing various amounts of large GeO_2 grain-boundary particles (about 3 μm in diameter). Pure Cu polycrystals are also used to obtain results for specimens without grain-boundary particles. Discussing the results of the tensile tests and microstructural observation, we will examine the effects of area fraction of the grain-boundary particles on the intergranular fracture when grain-boundary particles suppress GBS firmly.

2. Experimental

The as-rolled sheets of Cu-Ge alloys with five different Ge contents from 0.3 to 2.0 mass% were annealed at 1123 K for 24 h in vaccum (about 1 Pa) to obtain polycrystals with equiaxed grains. After the anneal, the Cu-Ge alloys were chemically polished using dilute nitric acid. Internal oxidation of the Cu-Ge alloys was made by the powder pack method [5, 9] at 1123 K for 24 h using the powder mixture of $Cu:Cu_2O:Al_2O_3 = 1:1:2$ (mass ratio). By the internal oxidation, GeO_2 particles were obtained in grains and on grain boundaries of Cu. Tensile specimens with gage length of 10 mm were

*Author to whom all correspondence should be addressed.

spark-cut from the Cu-GeO_2 alloys and annealed at 1123 K for 24 h in vacuum (about 1 Pa) to remove oxygen solved in the Cu matrix during the internal oxidation. From the 99.99 mass%Cu polycrystal cold-rolled and annealed at 1123 K for 24 h in vacuum (about 1 Pa), tensile specimens without particles were also prepared. The Cu specimens also had equiaxed grains and gage length of 10 mm. For the Cu-GeO_2 and Cu specimens, the sizes of grains and oxide particles on grain boundaries were measured with scanning electron microscopy (SEM) and optical microscopy (OM).

The tensile tests until fracture were made in an argon-gas atmosphere at 800 K with an Instron-type testing machine under the initial nominal strain rate of 10^{-4} s^{-1}.

The testing temperature of 800 K was selected since it has been reported that the intermediate temperature embrittlement of Cu and Cu alloys occurs at this temperature [5, 7, 8, 18]. After the tensile tests, the fracture surfaces of the specimens were observed with SEM and OM. Deformation of some specimens was interrupted at certain strains and the microstructural observation of the specimens before fracture was made.

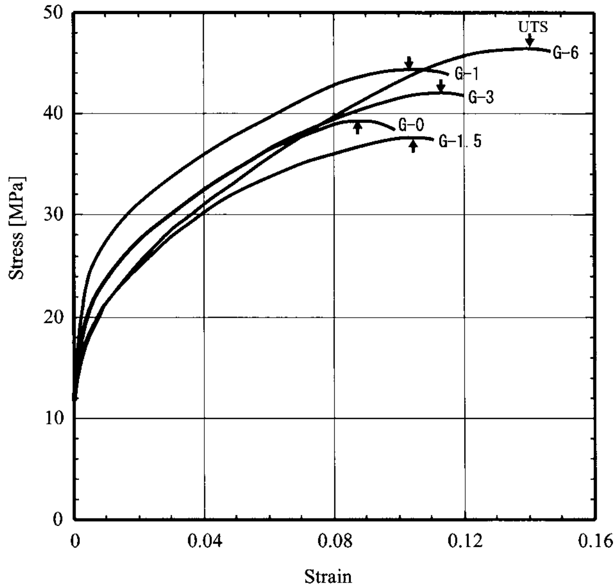

Figure 1 Stress-strain curves of the specimens G-0 to G-6 deformed at 800 K under 10^{-4} s^{-1}. The arrows show the points on the stress-strain curves corresponding to the ultimate tensile strength (UTS).

3. Results

3.1. Distribution of GeO_2 particles on grain boundaries

Table I shows the details of specimens used in the present study. The specimens are designated, for example G-1, as shown in Table I. The numbers included in the specimen result from the values of area fraction (%) of the GeO_2 particles on grain boundaries.

The diameters of the GeO_2 particles on grain boundaries were about 3 μm for all specimens. GBS in Cu occurs under the conditions of the present tensile tests [5, 7, 8]. When plastically non-deformable GeO_2 particles exist on grain boundaries, these particles suppress GBS in the Cu-GeO_2 alloys. GBS in the Cu-GeO_2 alloys can continue only until the applied stress acting on the boundary balances with the internal stress (the back stress) developed by the suppression effect [6]. If certain relaxation processes such as the interfacial diffusion along Cu/GeO_2 interfaces operate actively, the suppression of GBS is relaxed and GBS across the grain-boundary particles can proceed. However, the rates of the diffusional relaxation decrease with increasing the particles size [6]. Previous theoretical results on the kinetics [6] have shown that the effects of the diffusional relaxation at 800 K are negligibly small for the grain-boundary GeO_2 particles with diameters of about 3 μm. The grain-boundary GeO_2 particles contained in the present specimens can be considered to be fairly strong obstacles to GBS.

The grain sizes of the specimens G-0 and G-1 are smaller than those of the other specimens. However, it is the common feature of all the specimens that the grain sizes are much larger than the diameters and inter-particle spacings of the GeO_2 particles on grain boundaries. Under such circumstances, the sliding behavior of grain boundaries containing particles is insensitive to the difference of grain sizes [6].

3.2. Stress-strain curves

Brittle intergranular fracture occurred in all the specimens. Fig. 1 shows the nominal stress-nominal strain curves of the specimens G-0 (Cu) and G-1 to G-6 (Cu-GeO_2 alloys) tested in the present study until the plastic strain slightly larger than the ultimate tensile strength (UTS). The arrows in Fig. 1 indicate the points on the stress-strain curves corresponding to UTS of the specimens. As will be shown in the next section, the small voids to cause the intergranular fracture were first observed on surfaces of the specimens when the specimens were deformed until the plastic strains at UTS, ε_{UTS}. Hence, ε_{UTS} is adopted in the present study as a measure of the ductility of specimens.

Fig. 2 shows the variation of ε_{UTS} as a function of the area fraction A_f of the GeO_2 particles on grain boundaries for the specimens tested in the present study. As

TABLE I Details of the specimens used in the present study

Specimens	Alloys	Area fraction of particles on G.B. (A_f) (area%)	Surface-surface particle spacing on G.B. (λ) (μm)	Particle diameter on G.B. (d) (μm)	Grain diameter of matrix Cu (L) (μm)
G-0	Pure Cu	–	–	–	300
G-1	Cu-0.3 mass%Ge	1.0	23	2.8	300
G-1.5	Cu-0.5 mass%Ge	1.5	20	3.0	1300
G-3	Cu-1.0 mass%Ge	3.2	13	3.2	1300
G-6	Cu-2.0 mass%Ge	6.4	9	3.8	1300

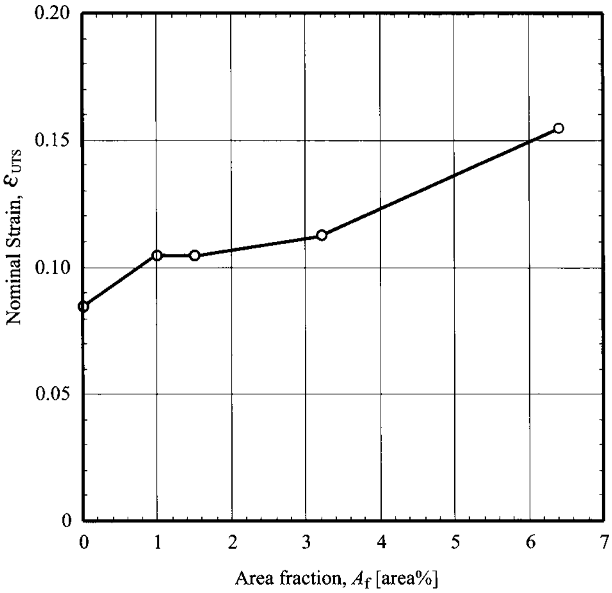

Figure 2 The relationship between the area fraction A_f of the grain-boundary GeO_2 particles and the plastic strain ε_{UTS} at UTS.

shown in Fig. 2, ε_{UTS} of the specimen G-0 (Cu) is the smallest and ε_{UTS} increases with increasing A_f. The ductility of the Cu-GeO_2 alloys is larger than that of Cu and the occurrence of the intergranular fracture is retarded as the area fraction A_f increases.

3.3. Microstructural observation

Fig. 3 is an example of an optical micrograph showing a void on a grain boundary, which was observed on a surface of the specimen G-1 deformed until the plastic strain slightly larger than ε_{UTS}. As shown in Fig. 3, the grain-boundary void is nucleated between the grain-boundary GeO_2 particles. As described in the preceding section, such voids were first observed when the specimens were deformed until ε_{UTS}. Recrystallization during deformation that has been reported for some dispersion-hardened materials [5, 7, 8, 15, 17] was not observed in the present specimens.

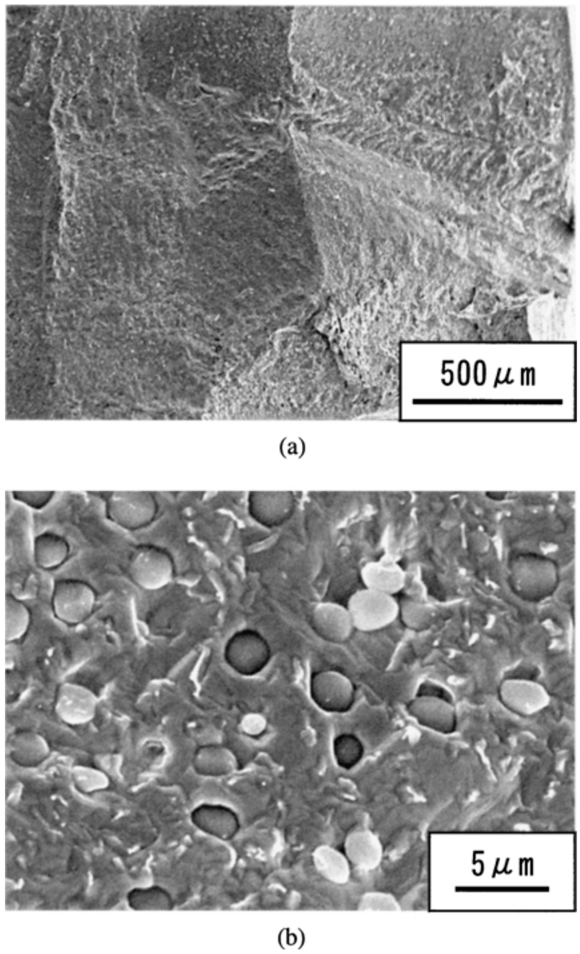

Figure 4 Scanning electron micrographs showing (a) macroscopic and (b) microscopic features of the fracture surface of the specimen G-3.

Fig. 4 are scanning electron micrographs of a fracture surface of the specimen G-3 showing typical features

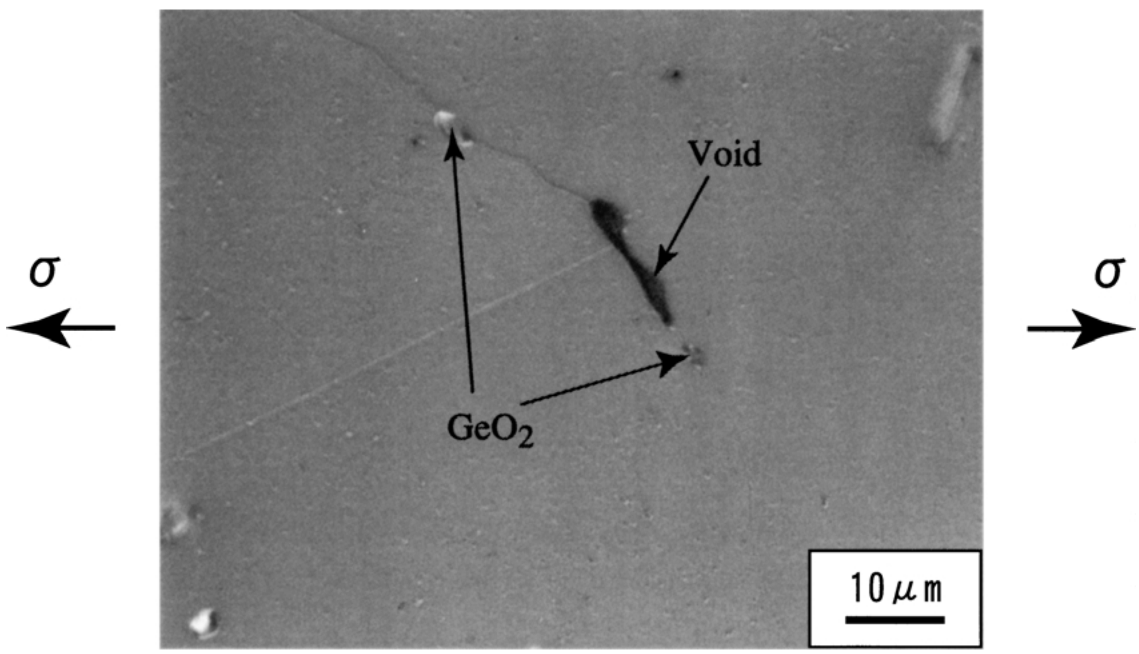

Figure 3 An optical micrograph showing a grain-boundary void between the GeO_2 particles observed in the specimen G-1.

of the brittle intergranular fracture of the present specimens. Fig. 4a shows the microscopic features of the fracture surface made of grain-boundary facets. Fig. 4b shows the microscopic features of the fracture surface showing GeO_2 particles on a flat grain-boundary facet without dimples.

4. Discussion

4.1. Intergranular fracture of the Cu-GeO_2 alloys

Onaka *et al.* [14] have investigated intergranular fracture of bi- and tri-crystals of a Cu-Al solid-solution alloy at intermediate temperatures. They have shown that voids to cause the intergranular fracture of the bi- and tri-crystals generate at locations where the amounts of GBS become maximum [14]. Triple junctions of the tricrystal specimens where GBS is suppressed are not preferential sites of the void nucleation at intermediate temperatures [14]. Although magnitude of stresses acting on grain-boundaries may be different between single-phase and dispersion-hardened alloys, the properties of grain boundaries in the Cu-Al alloy and the present Cu-GeO_2 alloys are essentially the same. We can consider that grain-boundary voids which cause the intergranular fracture in the Cu-GeO_2 alloys also generate where the amounts of GBS become maximum. This is supported by the void observed between the grain-boundary GeO_2 particles shown in Fig. 3.

Let us now consider the fracture process of the Cu-GeO_2 alloys at intermediate temperatures. The discussion in the preceding section shows that the grain boundaries between the particles are preferential sites for the void nucleation. If voids preferentially nucleate and grow at peripheries of the grain-boundary GeO_2 particles, dimples containing the particles may be observed. However, such dimples were not observed on the fracture surfaces of the Cu-GeO_2 alloys as shown in Fig. 4b. Considering the above, the fracture process of the present Cu-GeO_2 alloys is represented schematically as shown in Fig. 5. Fig. 5a shows the occurrence of GBS between the grain-boundary particles and the nucleation of a void at the location of the maximum amount of GBS. The intergranular fracture is caused by the growth and coalescence of these voids as shown in Fig. 5b. The fracture surfaces of the Cu-GeO_2 alloys without dimples shown in Fig. 4b can be understood by this fracture process.

4.2. Effects of the area fraction of grain-boundary GeO_2 particles on ductility

Mori *et al.* [6] have evaluated the amount of GBS of dispersion-hardened polycrystalline materials. When the grain-size of the polycrystal is much larger than the diameter and spacing of the grain-boundary particles, the maximum amount U of GBS at mid points between grain-boundary particles is evaluated as [6]

$$U \propto \frac{\sigma}{\mu}\frac{d}{A_f}, \tag{1}$$

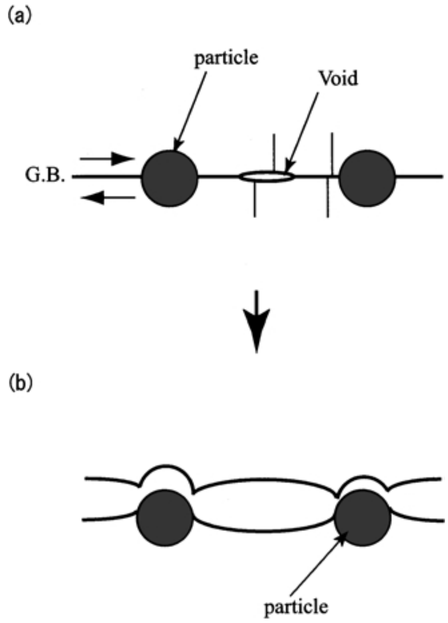

Figure 5 Schematic illustration showing the fracture process of the present Cu-GeO_2 alloys: (a) The nucleation of a void between the grain-boundary particles and (b) the occurrence of the intergranular fracture caused by the growth and coalescence of the grain-boundary voids.

where μ is the shear modulus, σ the shear stress acting on the grain boundary, A_f the area fraction of grain-boundary particles and d the grain-boundary particle diameter.

As shown by (1), the maximum amount U of GBS between the grain-boundary particles decreases with increasing A_f when d is kept constant. This means that the suppression of GBS becomes more effective as A_f increases. Fig. 2 shows that the ductility of the Cu-GeO_2 alloys increases with increasing A_f when d values of the alloys are almost the same. As shown in Fig. 2, ε_{UTS} of the specimen G-0 (Cu) is the smallest. GBS in the specimen G-0 without grain-boundary particles naturally occurs more easily compared with GBS in the Cu-GeO_2 alloys. Considering the maximum amount of GBS as a criterion of the intergranular fracture, the A_f dependence of the ductility shown in Fig. 2 is also understood.

4.3. Comparison with previous studies

Miura *et al.* [7, 8] have studied intergranular fracture of the Cu-SiO_2 alloys by tensile tests and discussed the effects of the area fraction of grain-boundary SiO_2 particles on the intergranular fracture. Both the SiO_2 and GeO_2 are amorphous oxides that behave as plastically hard particles on grain boundaries of Cu. However, the diameters of the grain-boundary SiO_2 particles in the Cu-SiO_2 alloys used by Miura *et al.* [7, 8] are less than 1 μm and smaller than those of the GeO_2 particles in the present Cu-GeO_2 alloys.

The results of tensile tests by Miura *et al.* [7, 8] show that the ductility of the Cu-SiO_2 alloys at intermediate temperatures increases with increasing A_f. This A_f dependence of the ductility in their study is the same as that in the present study. However, Miura *et al.* [7, 8] have observed fracture surfaces with dimples

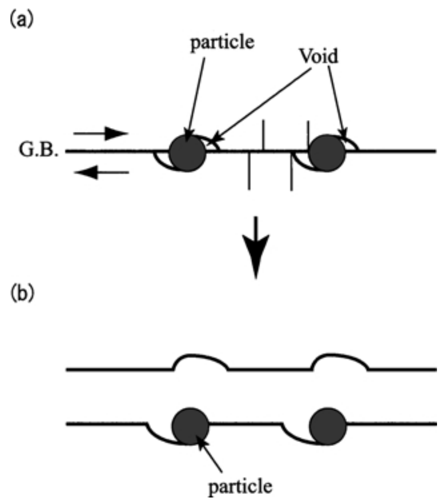

Figure 6 Schematic illustration showing the fracture process of the Cu-SiO_2 alloys proposed by Miura *et al.* [7, 8]: (a) The nucleation of a void at peripheries of grain-boundary particles and (b) the occurrence of the intergranular fracture caused by the growth and coalescence of the grain-boundary voids.

containing SiO_2 particles in the Cu-SiO_2 alloys deformed at around 800 K and proposed the fracture process different from that in the present study [7, 8]. Fig. 6 show the fracture process proposed by Miura *et al.* as a result of the microstructural observation. Fig. 6a shows that voids preferentially nucleate at peripheries of the grain-boundary particles. Fig. 6b shows the occurrence of the intergranular fracture caused by the growth and coalescence of these voids.

The differences of the fracture processes of the alloys shown in Figs 5 and 6 can be attributed to the difference of the operation of the diffusional relaxation around the grain-boundary particles due to their sizes. During the tensile tests of the Cu-SiO_2 alloys containing smaller grain-boundary particles, diffusion around the SiO_2 particles, which enables GBS across the grain-boundary particles, occurs actively at intermediate temperatures [6–8]. The active diffusion increases the concentration of vacancies around the smaller grain-boundary particles and may cause the nucleation of voids at the peripheries of the particles. On the other hand, during the tensile tests of the Cu-GeO_2 alloys containing larger grain-boundary particles, diffusion distance around the larger GeO_2 particles is long enough and the GBS across the grain-boundary particles hardly occurs at intermediate temperatures [6]. The suppression of GBS around the smaller grain-boundary particles is insufficient in comparison with the larger grain-boundary particles.

Comparing the stress-strain curves at around 800 K of the Cu-SiO_2 and Cu-GeO_2 alloys containing smaller SiO_2 and larger GeO_2 grain-boundary particles with almost the same area-fraction, we find that the Cu-GeO_2 alloys containing larger GeO_2 grain-boundary particles are more ductile [8]. Insufficient suppressing of GBS due to the smaller grain-boundary particles is less-effective to increase the ductility. As a result of the above analysis, we can say that the denser and larger grain-boundary particles are more effective in increasing the ductility of the alloy containing the second-phase particles.

5. Summary and conclusions

The Cu-GeO_2 alloy polycrystals containing plastically hard GeO_2 particles have been tensile tested to study intergranular fracture behavior of the alloys at intermediate temperatures. The effects of the large grain-boundary GeO_2 particles on the intergranular fracture are discussed using the specimens containing the grain-boundary GeO_2 particles of the same size (3 μm in diameter) and different area-fractions. The conclusions obtained are summarized as follows.

1. The GeO_2 particles on grain-boundaries improve the ductility of Cu by the suppression of GBS.
2. The grain-boundary voids preferentially nucleate between the grain-boundary GeO_2 particles. The intergranular fracture is caused by the growth and coalescence of these grain-boundary voids.
3. The ductility of the Cu-GeO_2 alloys increases with increasing the area fraction of the grain-boundary GeO_2 particles. The area-fraction dependence of the ductility is explained by considering the amount of GBS as a criterion of the intergranular fracture.

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