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Microstructural development of the isothermal phase transformation during ageing at 250°C in 2Y-TZP ceramics

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The behaviour of isothermal phase transformation, during ageing at 250 °C, in 2Y-TZP and related microstructural development, were investigated. The mode of microstructural development due to isothermal phase transformation was greatly dependent on grain size and the density of the sintered body. Isothermal phase transformation and related microstructural changes began at the specimen surface, near the pores, where the change of strain free energy for a t–m transformation was small and water vapour was easily contacted. The transformed region showed porous microstructures, which appeared due to the formation of cracks upon isothermal transformation.

1. Introduction
Ceramics have been restricted in use as engineering materials because of their low reliability due to brittle fracture. As a material solution to this problem, yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics received much attention owing to their superior mechanical properties (i.e. high strength and fracture toughness, good wear resistance, etc.) [1, 2]. However, their applications were almost completely limited to below 150 °C, because thermal instability appeared in the 150–300 °C temperature range [3, 4]. This thermal behaviour of Y-TZP is known to occur by isothermal phase transformation which degrades its mechanical properties [5]. Other observations [4–7], indicated that the degradation of mechanical properties during ageing was caused by the transformation from tetragonal to monoclinic which proceeded from the surface to the interior of the specimen, creating many cracks on the transformed surface owing to volume expansion upon transformation. In addition, water vapour was reported to be the catalyst which accelerated phase transformation. Several mechanisms of isothermal phase transformation in Y-TZP have been proposed [5–7]; however, this phenomenon is still not clearly explained.

In this study, the grain size and the density of the sintered body in 2Y-TZP, which are associated with the change of surface free energy and strain free energy in isothermal phase transformation, were varied. The behaviour of the isothermal phase transformation during ageing at 250 °C in these specimens and its related microstructural development were also examined.

2. Experimental procedure
The 2Y-TZP powder used as a starting powder in this study was TZ-2Y powder, prepared using a spray drying method at Tosoh Co. This powder retained the metastable tetragonal phase and spherical shape, as shown in Fig. 1. The powder also contained 2 mol % Y_2O_3, had an average grain size of about 25 nm, and a granule size of about 50–70 μm. A cylindrical compact disc was prepared by cold isostatic pressing at a pressure of 200 MPa and was sintered at 1450 °C in air for soaking times of 0.5, 2, 5, 10 and 20 h, respectively. The density of the sintered body was measured using the Archimedes method and grain size was measured using the intercept line method from scanning electron micrographs of the polished surface. Ageing of the polished specimens was performed at 250 °C in a humid atmosphere. The amount of transformed monoclinic phase accompanying ageing was analysed by X-ray diffraction on the surface and the ratio of tetragonal to monoclinic was determined using the Garvie– Nicholson formula [8]. Microstructural development of aged specimens was observed on the transformed surface using SEM.

3. Results and discussion
3.1. Grain size and apparent density of the sintered body
As a result of X-ray diffraction (XRD) analysis, zirconia particles were stabilized to the tetragonal phase at room temperature in sintered specimens, except in the specimen sintered for 20 h. On the polished surface of the specimen sintered for 20 h, the monoclinic phase

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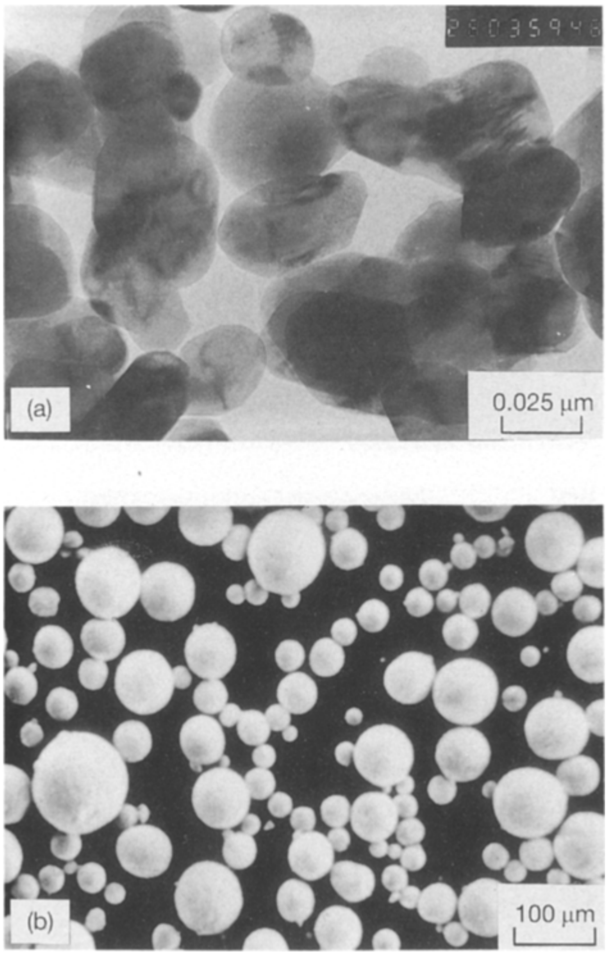

Figure 1 Starting powders prepared by Tosoh Co.: (a) crystallites; (b) granules.

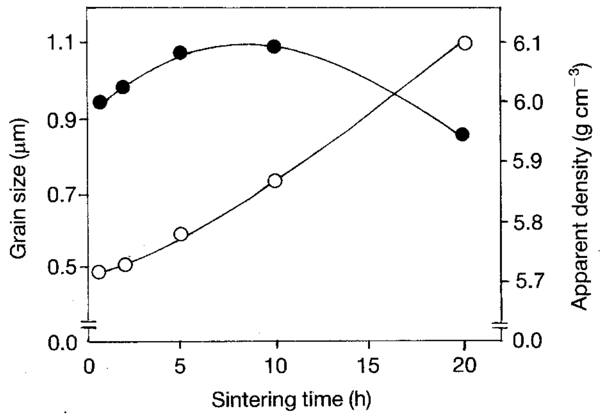

Figure 2 Variation of (○) grain size and (●) apparent density with sintering time in 2Y-TZP specimens sintered at 1450 °C.

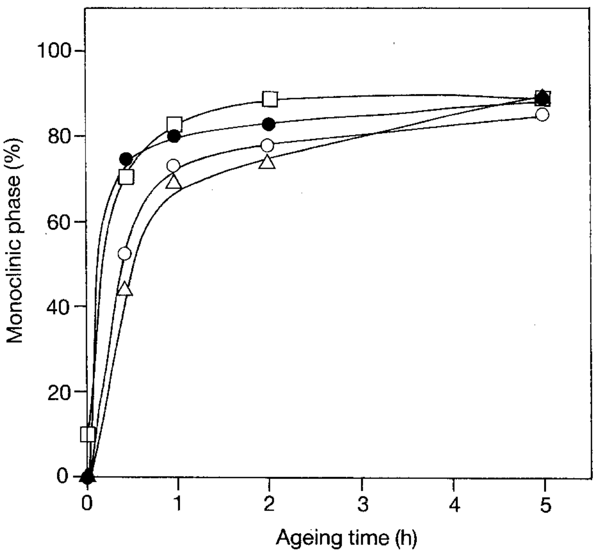

Figure 3 The amount of transformed monoclinic phase with ageing time in sintered 2Y-TZP ceramics when aged at 250 °C in water vapour. Specimens were sintered at 1450 °C for (●) 0.5 h, (○) 2 h, (△) 5 h and (□) 20 h.

existed on about 40% of the surface. However, on the specimen surface where polishing was performed sufficiently, only about 10% monoclinic phase existed. Variations of the grain size and apparent density with sintering time is shown in Fig. 2. Less than 97% theoretical density was achieved in most of specimens; maximum density was obtained in the specimen sintered for 10 h. From SEM observation, lenticular pores and microcracks were found to exist on the specimen surface sintered for less than 2 h and for 20 h respectively. The lenticular pores assumed to form by preferred intragranular sintering within granules [9]. Alternatively, the microcracks were considered to be created by transformation of tetragonal to monoclinic phase upon cooling. The grain size measured from scanning electron micrographs of the polished surface gradually increased in size from 0.45 μm to 1.10 μm with sintering time, as shown in Fig. 2.

3.2. Isothermal phase transformation during ageing at 250 °C

The amount of the transformed monoclinic phase with ageing time is shown in Fig. 3. Isothermal phase transformation in 2Y-TZP proceeded rapidly when treated at 250 °C. Almost 80% of the tetragonal phase on the surface was transformed to monoclinic when aged for 5 h, in most sintered specimens. Specifically, the amount of the transformed monoclinic phase was inversely proportional to the apparent density, but independent of the grain size of the sintered body. These results suggest that the isothermal phase transformation in 2Y-TZP was related more to the change of strain free energy than that of surface free energy. This will be discussed later.

Generally, in martensitic transition, the rate of transformation is dependent on the grain size, solute content, and the amount of constrained force from adjacent grains, which relate to the change of surface free energy, chemical free energy, and strain free energy [10–12]. In constrained matrix systems, the change of free energy (ΔG_{t-m}) for a transformation from tetragonal to monoclinic is given as follows [10, 11]

$$\Delta G_{t-m} = \Delta G^{c}_{t-m} + \Delta G^{se}_{t-m} + \Delta G^{s}_{t-m} \qquad (1)$$

where ΔG^{c}_{t-m}, ΔG^{se}_{t-m} and ΔG^{s}_{t-m} are the change of the chemical free energy, the change of the strain free energy, and the change of the surface free energy for a t–m transformation, respectively. In systems with constant ΔG^{c}_{t-m} owing to the fixed amount of solute, as in this experiment, ΔG_{t-m} is dependent on ΔG^{se}_{t-m} and ΔG^{s}_{t-m}. However, in this system, we consider the contribution of ΔG^{s}_{t-m} for a t–m transformation as relatively small in comparison with that of ΔG^{se}_{t-m} and ΔG^{c}_{t-m} because of a small amount of solute (i.e. 2 mol% Y_2O_3) as well as large constrained forces created by adjacent grains in sintered specimens. Contrary to the 2Y-TZP case, the rate of isothermal phase transformation in 3Y-TZP was very slow and proportional to grain size, which possesses small driving forces of transformation due to an increase of solute [13].

3.3. Microstructural development by ageing at 250 °C

The microstructural changes which appeared during isothermal phase transformation due to ageing at 250 °C were investigated by SEM on the specimen surface and within the interior. Tetragonal to monoclinic transformation during ageing proceeded from the surface to the interior in most specimens. After ageing, many micro-cracks or macro-cracks developed in the transformed region. The mode of crack formation was dependent on the grain size and the density of the sintered body.

Fig. 4 shows the aged surface of the specimen sintered for 0.5 h. The density was relatively low, as shown in Fig. 2, and lenticular open pores existed on the surface. In this specimen, tetragonal to monoclinic transformation proceeded towards the interior with the centre of open pores at the surface, as shown in Fig. 4a and b. This was due to the small change in strain free energy for the t–m transformation near the pores, and the water vapour which accelerated the transformation could easily diffuse to the interior through the open pores. Therefore, the tetragonal phase near the pores was easily transformed to monoclinic, and the craters and cracks appeared as results of volume expansion caused by the t–m transformation, as shown in Fig. 4c.

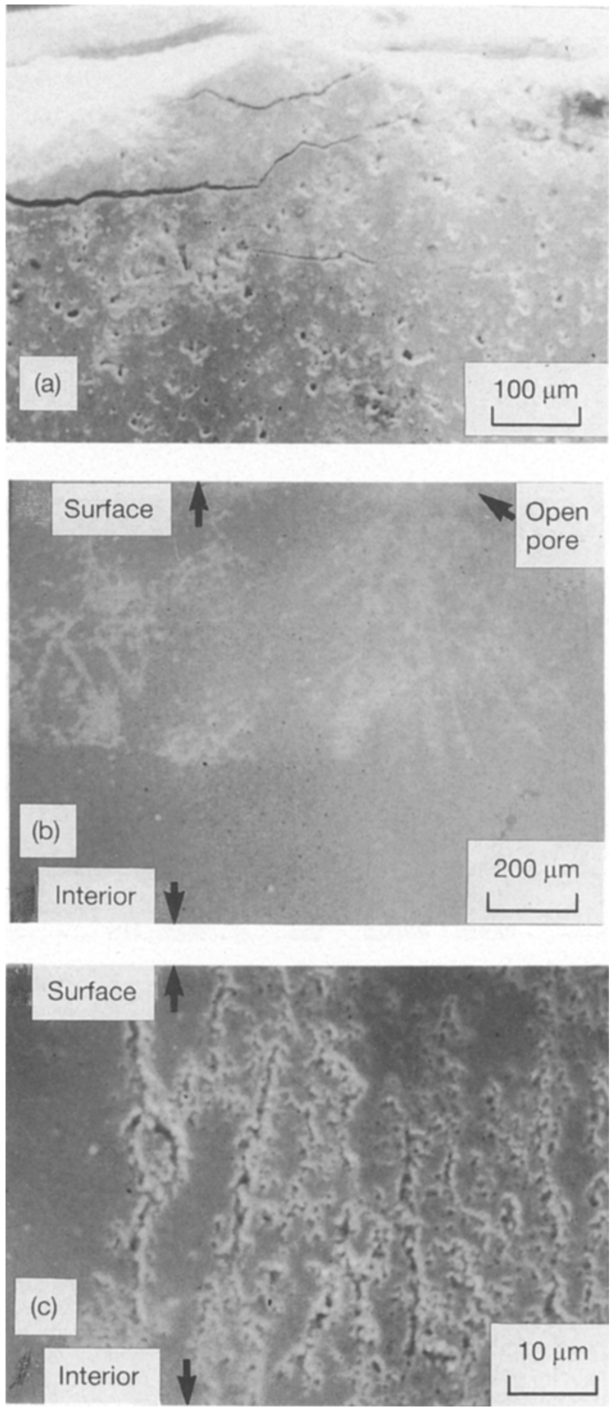

Figure 4 Microstructural development in an aged specimen sintered for 0.5 h; (a) specimen surface aged at 250 °C for 5 h; (b, c) perpendicular face aged at 250 °C for 5 h.

Fig. 5 shows the surface upheaval phenomenon and the linear transformed boundary from the surface with ageing in specimens sintered for 5 h which retained the relative high density. Upon transformation, surface upheaval occurred by volume expansion in the direction of the free surface where the change of strain free energy for the transformation was less than that on the inside [14]. The spherical shape of the surface upheaval was attributed to the influence of the granular powder used as a starting material, as shown in Fig. 1b. The diameter of the spherical surface upheaval, as measured by SEM, was about 30–50 μm, which suggests the size of the densified granule during sintering. We believe the cause of this phenomenon is a result of the difference in bonding strength between the inter-granular and intra-granular particles.

Generally, in compacts obtained from granular powder, preferred intragranular sintering among the primary particles occurs at the beginning of sintering. Because of this, in the final sintered specimen, bond strength between the primary particles within granules is higher than that between the granules [9]. On transforming the martensite of the sintered body, the nucleation and growth of the new phase started at a high potential grain. If one of the grains was once transformed to tetragonal, the other grains adjacent to the transformed grain would be easily transformed to monoclinic by induction of stress fields or strain energy due to the volume expansion of the previous transformation. This effect is called the "autocatalytic effect" [14, 15, 16]. This phenomenon appeared mainly in martensitic transformation, whose mechanism was a nucleation-controlled reaction, and whose growth of martensite was very rapid. Therefore, the transformation of grains within granules continuously proceeded very rapidly in the shape of a sphere by the

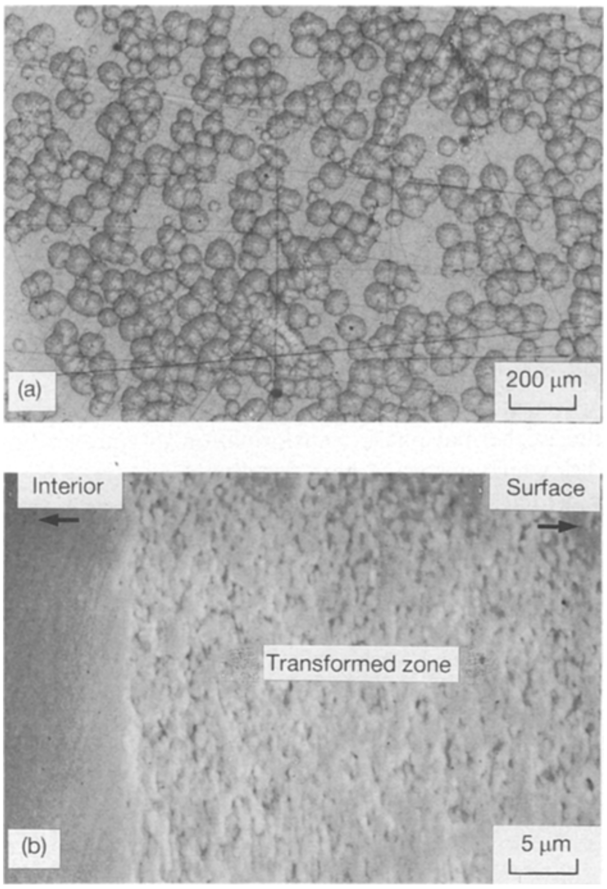

Figure 5 Microstructural development in an aged specimen sintered for 5 h: (a) surface upheaval phenomenon on the specimen surface aged at 250 °C for 5 h; (b) linear transformed boundaries at the perpendicular face of a specimen aged at 250 °C for 5 h.

autocatalytic effect and stopped at the intergranular boundary which could absorb the stress field and strain energy.

Fig. 5b shows the transformed boundary layer upon ageing, which proceeded to the interior homogeneously in all directions compared with the specimens sintered for 0.5 h. The trend of transformation in this specimen can be explained as follows: owing to the possession of compacted surface structures in this specimen, the transformation of tetragonal to monoclinic began first on the surface, where the change of strain free energy was small during transformation. If a tetragonal grain initiated to transform the monoclinic grain on the surface, the adjacent tetragonal grains of transformed monoclinic phase contained the free surface which formed by generation of cracks on transformation. Because of the small constrained force and direct contact with water vapour on the free surface, the tetragonal grains retaining the new free surface were under the same conditions as were the initial tetragonal grains on the surface before. So they were easily transformed to monoclinic by ageing. Through successive processing, as mentioned above, transformation gradually proceeded into the interior from the surface, and the porous structures developed in the transformed area, as shown in Fig. 5.

The specimen sintered for 10 h showed catastropic failure after ageing for almost 2 h as in Fig. 6. We consider this failure to have occurred by autocatalytic

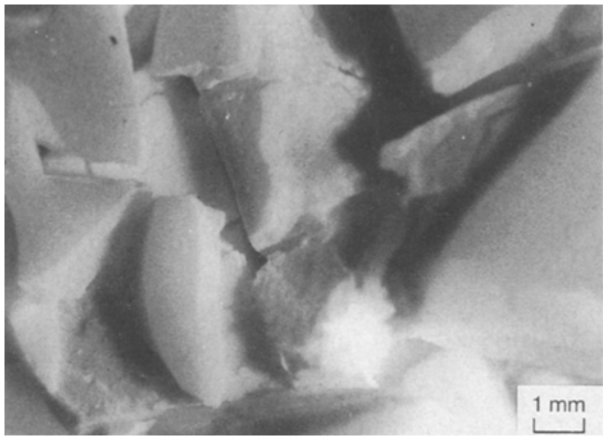

Figure 6 Catastropic failure formed by ageing at 250 °C for 2 h in a specimen sintered for 10 h.

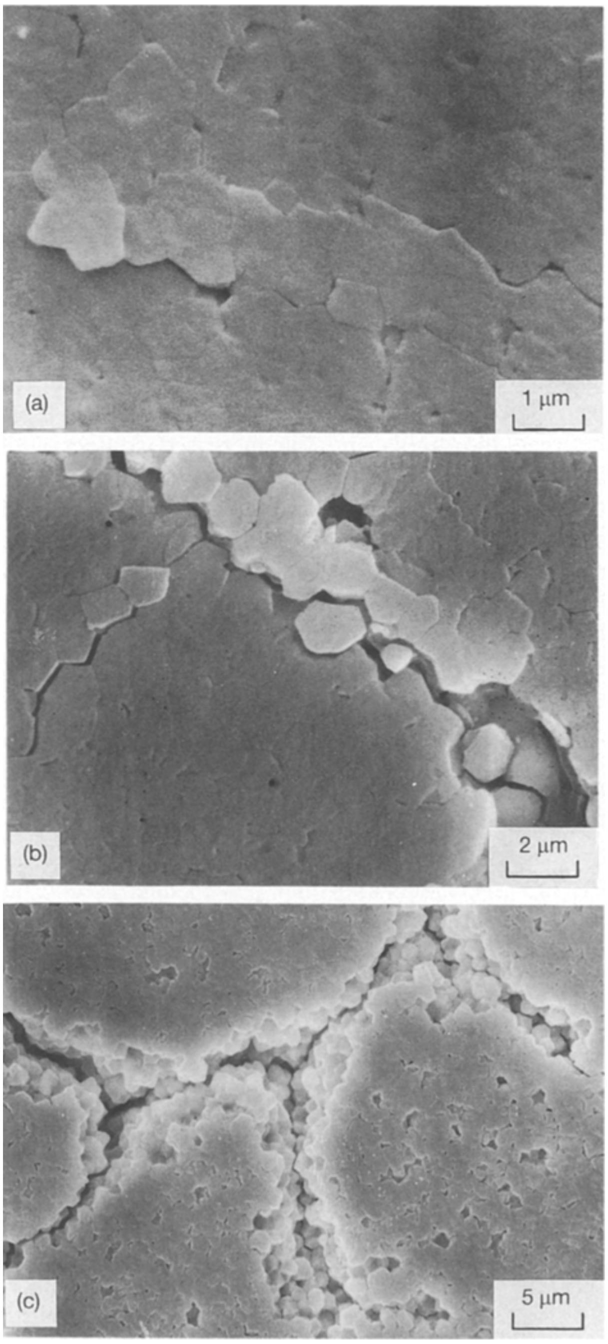

Figure 7 Scanning electron micrographs showing cracks formed on the specimen surface in a 2Y-TZP specimen sintered for 20 h and aged at 250 °C for (a, b) 5 h, and (c) 20 h.

effects which acted abruptly for short periods of time on the surface of this specimen, which had very dense structures and large driving forces during transformation due to a small solution of Y_2O_3 [14, 15]. In order to propagate cracks by the autocatalytic effect in the whole specimen, the magnitude of the stress field created by transformation on surface should be large enough to pass the grain boundaries and induce successive nucleation of adjacent grains. In addition, the sintered specimen must possess sufficiently highly dense structures not to absorb the stress or strain in the inner part. The smashed pieces of the specimen were in the monoclinic phase on the surface and the broken side, but in the tetragonal phase in the inner parts.

Fig. 7 shows the nucleation of a microcrack and growth into a macrocrack on the surface in the specimen sintered for 20 h. Surface upheaval due to the isothermal phase transformation appeared at grain level, as shown in Fig. 7a. These were the results of the influence of microstructures within the sintered body (i.e. microstructure which was almost homogeneous with large grain size due to the long sintering time, and microcracks created by monoclinic phase formation upon cooling). Fig. 7b shows the evolution of macrocracks from a microcrack, as shown in Fig. 7a. If microcracks were created, due to transformation, along the grain boundaries, the adjacent tetragonal grains could easily be transformed to monoclinic grains by reduction of the strain energy, which appeared because of the decrease of the constrained force between the grains and the increased contact with water vapour [14]. Therefore, the transformation due to ageing occurred preferentially near cracks, and cracks gradually propagated into the interior from the surface with increasing magnitude. Fig. 7c shows a large-scale macrocrack formed by ageing for a long time. Note that many grains near the crack are separated from the body as a result of the weakening bond strength between grain boundaries.

4. Conclusions

By investigating the behaviour of isothermal phase transformation occurring during ageing at 250 °C in 2Y-TZP specimens and their related microstructural development, the following conclusions are drawn.

1. The rate of isothermal phase transformations in 2Y-TZP was mainly dependent on the density but not the grain size of the sintered body.
2. The propagated mode of transformation from the surface to the interior showed different aspects with variation of microstructure in the sintered body (i.e. density, grain size, and the existence of open pores).
3. Isothermal phase transformation during ageing began at the specimen surface near the pores, where the change of strain free energy during transformation was small and water vapour was easily contacted.
4. Autocatalytic effects were more accelerated in the isothermal phase transformation in sintered bodies which possessed high density.
5. The transformed region showed porous microstructures, which appeared by the formation of cracks during isothermal transformation.

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