JOURNAL OF MATERIALS SCIENCE **34** (1999) 5885–5891

Tetragonal to monoclinic transformation in Y-TZP joined with metallic materials

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Joints between Y-TZP (Yttria containing Tetragonal Zirconia Polycrystal) and metallic materials (type SUS304 stainless steel and Mo) were fabricated, using brazing alloy (Ag-Cu-Ti) sheet. Y-TZP disks having different Y_2O_3 contents, grain size were prepared for changing their transformability from tetragonal to monoclinic phase. Y-TZP disks with various thickness were joined with metal disks with constant thickness in order to change the thermal stress states. Transformation in Y-TZP was investigated by changing cooling rates from the joining temperature.
Transformed fraction was larger under presence of tensile thermal stress (σ_{rr}). The transformed fraction decreased when cooled at a faster rate, which was related with time-dependent characteristics of the transformation in Y-TZP. A large fraction of transformation was detected in the coarse grained Y-TZP joined with Mo, although no transformation was detected in the unjoined state when cooled at the same rate. Transformation of Y-TZP joined with metallic materials was discussed, considering the effects of residual stress and the time dependent features of the transformation.

1. Introduction

Y-TZP (Yittria-Tetragonal Zirconia Polycrystal) has higher fracture toughness [1] than the other ceramic materials. Moreover, it has a superior properties against corrosion [2] and abrasion [3]. Various applications have been taken into consideration, such as the insulation of combustion chambers for diesel engines [4], thermal barrier coatings [5] and so on. Their application can be extended by combined use with metallic materials, such as by joining them.

Generally, in the practical fabrication of the joints, thermal stress [6] is generated due to the difference in thermal expansion constants after joining treatments, which are carried out at several hundred degrees centigrade. Many attempts have been made to lower the stress, such as by inserting an intermediate layer [7] and by grading the composition and microstructures in the vicinity of the metal/ceramics interfaces [8]. The analysis of the stress distributions is important for the interfacial designs, and there are many reports concerning the stress analysis [9, 10].

It has been reported that zirconia undergoes the transformation from high temperature tetragonal (t) phase to low temperature monoclinic (m) phase (t-m transformation), accompanying volume expansion of 4% [11]. This transformation has been reported to be induced under the presence of applied stress [12] and therefore, the occurrence of transformation is dependent on the stress states in the joints. On the other hand, the stress distribution in the joints is altered by the transformation. Consequently, they are interrelated with each other. It is of importance to estimate the amount of t-m transformation that takes place during the fabrication process of the joints.

In order to consider the occurrence of the transformation in the joints, the following characteristics of t-m transformation have to be taken into consideration:

1) The transformation is induced under the presence of stress.
2) The transformation occurs readily in the grains with large size [13].
3) The transformation is depressed with an increase of Y_2O_3 content [14].
4) The transformation has a time-dependent characteristic [15, 16].

This study is intended to investigate the transformation of Y-TZP disks joined with metallic materials. Initially, the transformation behavior in the unjoined Y-TZP bars were studied with regard to the above characteristics.

In order to change the conditions for transformation, Y-TZP disks having different thickness, Y_2O_3 contents and grain sizes were prepared. They were joined with stainless steel of type SUS304 and Mo, having constant

thickness. The former has the larger thermal expansion coefficient than Y-TZP and the latter has a smaller value. Variation in Y-TZP thickness and using different metals are intended to change thermal stress distributions in the joints. On the other hand, variation in Y_2O_3 contents and the grain size were intended for controlling their transformabilities. Lastly, the joints were cooled from the joining temperature at different rates in order to control the rate of time-dependent transformation.

Joints with coarse grained Y-TZP do not have the practical significance because of high susceptibility to transformation and having lower strength. In this study, however, they were investigated for obtaining the fundamental knowledge of the effects of various factors on the transformation in Y-TZP joined with metallic materials.

2. Experimental

2.1. Specimen preparation

Y-TZP disks were cut from the sintered compact rods of ZrO_2-Y_2O_3 produced by Tosoh Inc. The compacts having different Y_2O_3 contents (2, 3, 4 mol %: 2Y, 3Y, 4Y) were prepared in order to control their transformability.

Rods of commercial stainless steel (type SUS304) and Mo (99.99_0 purity, Wako Chemical. Inc.) were utilized as the metallic materials. Diameters of the rods were 15 mm, and they were cut into disks. Y-TZP had various thickness between 0.4 and 5 mm, while the thickness of metals were 3 mm and kept constant. The metal surface was wet-polished with alumina fine grains of 0.1 μm. Y-TZP surfaces were polished with diamond paste (finished with Kulzer diamond polishing agent MM140). Y-TZP pieces were annealed in air at 1773 K for 24 h in order to change their grain size. The grain size and microstructures of the Y-TZP specimens were observed by using a transmission electron microscope (TEM).

In order to join these materials, a brazing alloy (Cusil ABA: 63Ag-35Cu-2Ti mass %) sheet was utilized which had thickness of 0.05 mm. The specimen pieces were set in a jig made of stainless steel and they were placed in a silica tube, which was heated externally with an electric resistance furnace. Joining was conducted in Ar (99.995% purity) atmosphere at temperature of 1113 K (20 degree above the melting temperature) for 1.8 ks without applying pressure, and then cooled at different rates.

2.2. Detection of transformation

In this study, transformation in the unjoined Y-TZP compact bars (having scales of typically, $3 \times 3 \times 15$ mm) were detected using a dilatometer. The measurements were conducted between the room temperature and near the joining temperature of 1113 K. In the dilatation measurements, the heating rate was set constant to 0.4 deg/s. The specimens were kept at 1113 K for 1.8 ks then cooled at different rates.

The transformation was also determined by means of X-ray diffraction (XRD). The XRD peak intensities (counts/s) were obtained from the central region on the Y-TZP surface of the joined disks (as shown schematically in Fig. 1) and on the unjoined bars. For estimation of transformed fraction (tf), the following equation was utilized:

$$tf = (I_{\bar{1}\,1\,1\mathrm{m}} + I_{1\,1\,1\mathrm{m}})/(I_{\bar{1}\,1\,1\mathrm{m}} + I_{1\,1\,1\mathrm{m}} + I_{1\,1\,1\mathrm{t}}),$$

where $I_{h\,k\,l}$ stands for the intensity of the ($h\,k\,l$) diffraction peak, and m, t stand for monoclinic and tetragonal phase of zirconia, respectively.

TABLE I Values of material properties input for FEM analysis

	α ($\times 10^{-6}$ K^{-1})	E (GPa)	ν
Y-TZP	9.0	200	0.3
SUS304 steel	18.7	195	0.3
Mo	5.7	320	0.38

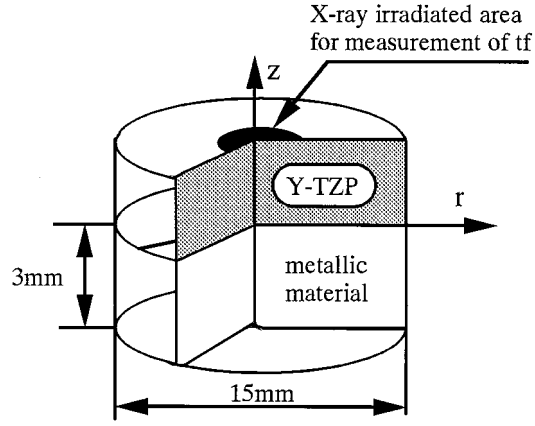

Figure 1 Schematic illustration of joints and r, z coordinates.

2.3. Calculation of thermal stress distribution

In order to estimate the residual stress generated due to the difference in thermal expansion coefficients between Y-TZP and metallic materials, axisymmetric thermoelastic finite element analysis (FEM) was conducted. The FEM program used was listed in the text [17]. The r, z coordinates taken for the analysis are shown in the schematic illustration of a joint (Fig. 1). Material properties listed in Table I were inputs for the FEM calculations. The FEM analysis conducted in this study was elastic, therefore the effects of yielding of the metals were neglected, which might significantly affect the actual stress values.

3. Results

3.1. Transformation behavior of the unjoined Y-TZP

Microstructures of the as-received and the annealed 2Y-TZP (ZrO_2-2mol %Y_2O_3) specimens were observed by means of TEM, and examples are shown in Fig. 2. The average grain size of Y-TZP was about 0.4 μm and 1.4 μm, respectively. In the latter case, the most of the grains were transformed and plenty of twins

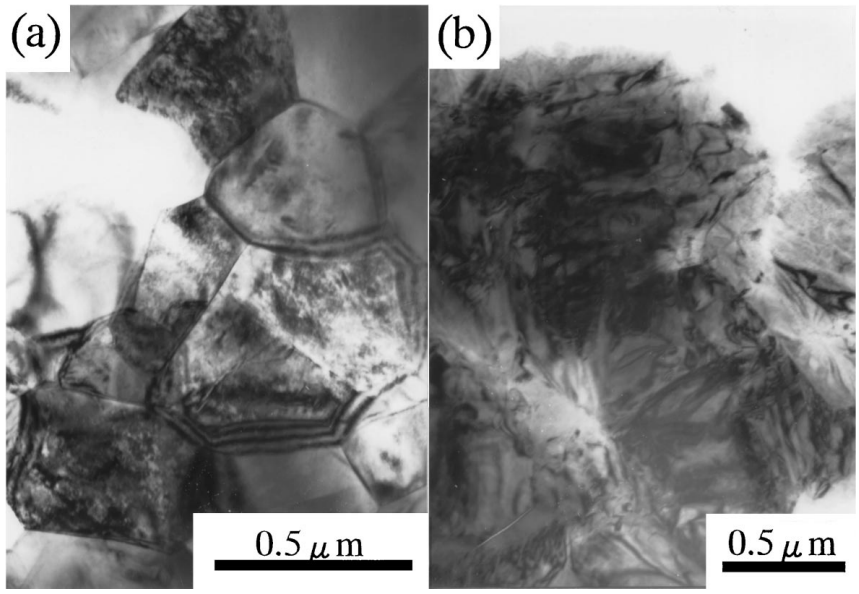

Figure 2 TEM photographs of specimens. (a) As-received and (b) annealed at 1773 K for 84.6 ks.

TABLE II Transformed fraction (tf) of unjoined Y-TZP

mol % Y_2O_3	Conditions	tf (%)
2	Fine grain	
	As-ground	4.5
	Heated to 1113 K,	
	Cooled at 0.03 deg/s	33.5
	Coarse grain	
	Heated to 1113 K,	
	Cooled at 0.03 deg/s	60
	Cooled at 0.1 deg/s	<5
3	Fine grain	
	As-cut	2.5–5
	As-ground	2.9
	Heated to 1113 K,	
	Cooled at 0.03 deg/s	2.5
4	Fine grain	
	As-cut	~0
	As-ground	~0
	Heated to 1113 K,	
	Cooled at 0.03 deg/s	~0

in monoclinic phase were observed. They were transformed in the preparation process of TEM specimens. The amount of twin was much less in the case of TZP with larger Y_2O_3 contents. According to the author's previous study [18], the increased transformability by annealing at 1773 K was due to the enlarged grain size rather than a lowered Y_2O_3 contents caused by phase separation.

The tf values in various Y-TZP specimens were measured by means of X-ray diffraction. They are listed in Table II. The tf value was larger in the annealed (coarse grained) specimens than in the as-sintered (fine grained) specimens. However, it was noticeable that a considerable transformed fraction (tf: 33.5%) was obtained in the fine grained 2Y specimens when they had undergone the same heat treatment as that of the joining process (cooled at 0.03 deg/s). The dynamic transformation behavior of 2Y specimens was detected by means of thermal dilatometery. The displacements of the specimen length with variation of temperature are

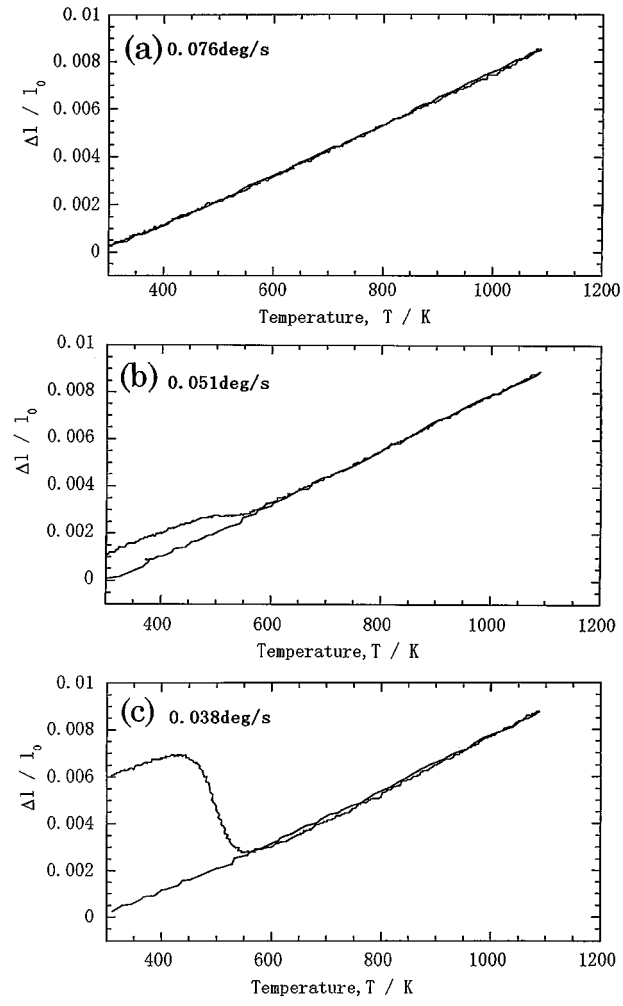

Figure 3 Dilatation curves of unjoined coarse grained 2Y-TZP, obtained at various cooling rates.

shown in Fig. 3. They were heated to 1113 K (joining temperature), then cooled at different rates.

No transformation was detected in the fine-grained 2Y-TZP, regardless of the cooling rates. Therefore, the tf value of 33.5% in fine-grained 2Y-TZP (listed in

Table II) is considered to have occurred on the specimen surface, and not in the bulk.

In the dilatometry curves, abrupt increase in the specimen length occurred at about 570 K due to the onset of t-m transformation, when cooled at a slower rate than 0.051 deg/s. The amount of dilatation increased as the cooling rate decreased. Variation of tf value with cooling rate was considered to be related with the time-dependent characteristics of the transformation in Y-TZP. It was noticeable that the transformation start temperature (M_s point) remained almost unchanged. If the dilatation is caused only by micro-crack formation, phenomena of constant onset temperature cannot be explained. The dilatation can be accompanied by cracks, however, they were comparatively small in population, as shown in the previous study [18].

3.2. Transformation behavior of Y-TZP joined with metallic materials

The tf value on the Y-TZP surface joined with metallic materials was measured with the variation of several experimental parameters. Different residual stress states in the joints were obtained by changing the thickness and by selection of metallic materials. Distributions of residual stress generated by the temperature difference (ΔT) between the joining temperature (1113 K) and transformation start temperature (570 K) were calculated by FEM. In the central part on the Y-TZP disk surface, it turned out that radial and tangential stress components ($\sigma_{rr}(=\sigma_{\theta\theta})$) were significant and the other components were almost zero [19]. The distribution of σ_{rr} in the Y-TZP/SUS304 steel joint having thickness of both 3 mm is shown in Fig. 4. In this case, σ_{rr} was negative (compressive) in the interfacial area and changed to be positive (tensile) in the surface area. The calculated σ_{rr} at the center of Y-TZP disk-surface is plotted in Fig. 5. σ_{rr} values in two types of the joints had opposite dependence on the thickness of Y-TZP. As illustrated in Fig. 4, the sense of stress component on the TZP surface changed as Y-TZP thickness increased from compression to tension in the case of joints with SUS304 steel and vice versa in the case of joints with Mo.

a. Dependence on Y_2O_3 contents

Y-TZP disks having different thickness and Y_2O_3 were joined with SUS304 steel. The relationships between the Y-TZP thickness and the tf values are plotted in Fig. 6. It was observed that the tf value decreased with increasing Y_2O_3 content, and no monoclinic phase was detected in 4Y-TZP. In this study, 2Y-TZP was investigated intensively, because the tf value was larger and detection of transformation was easier. The monoclinic phase content on 2Y-TZP was about 30% in the case of a joint having Y-TZP thickness of 2 mm in Y-TZP

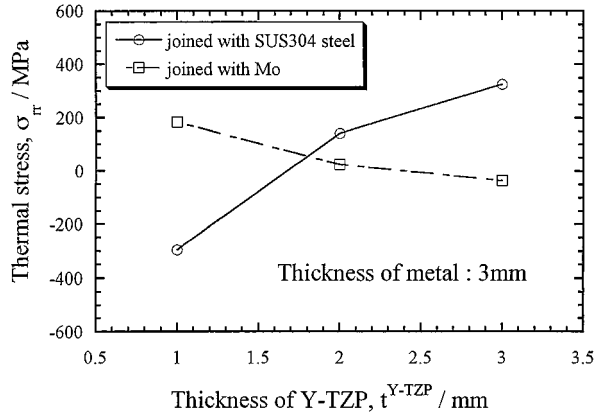

Figure 5 Calculated σ_{rr} at the central part on the surface of Y-TZP disk with different thickness, joined with SUS304 steel and Mo.

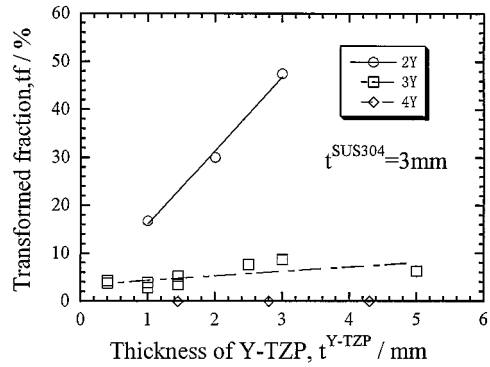

Figure 6 Relationship between Y-TZP thickness and transformed fraction (tf) in Y-TZP having different Y_2O_3 content.

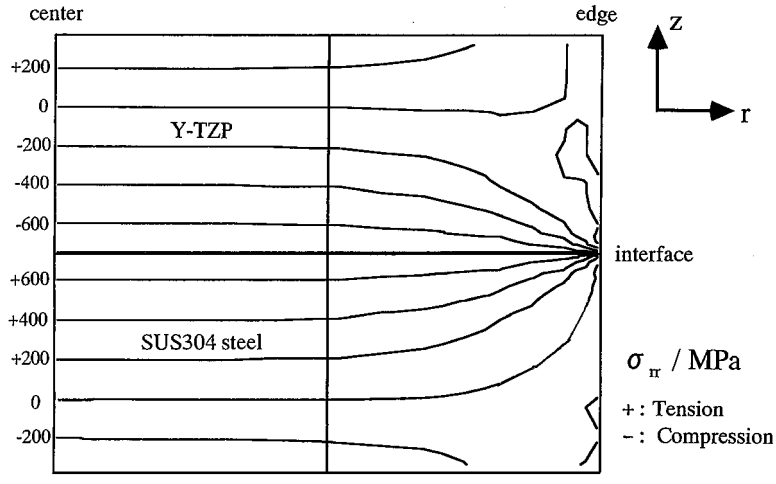

Figure 4 Thermal stress distribution in the Y-TZP/SUS304 steel joints, calculated by means of FEM.

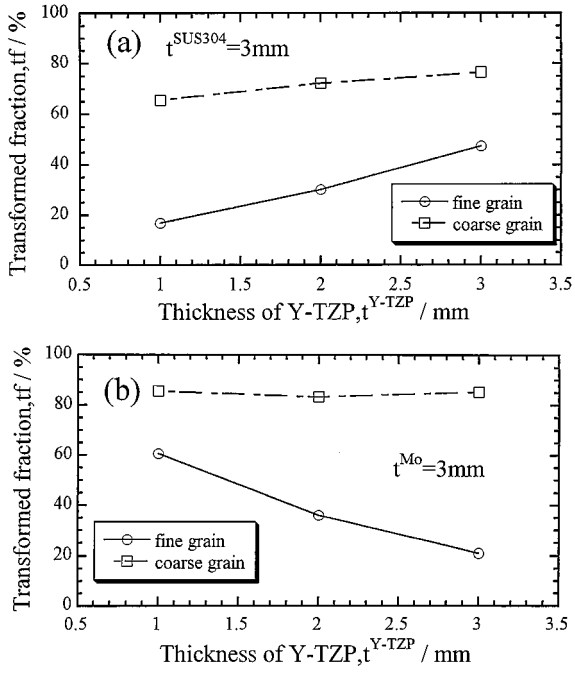

Figure 7 Transformed fraction (tf) on the surface of Y-TZP having various thickness in the joint pairs of (a) Y-TZP/SUS304 steel, and (b) Y-TZP/Mo.

and SUS304 steel of 3 mm, where σ_{rr} on Y-TZP was estimated to be smaller than the case of other thickness ratios. It is noteworthy that this fraction was closer to the values (tf: 33.5%) obtained in the unjoined Y-TZP after heat treatment (Table II), and that the tf value was larger under presence of a positive (tensile) σ_{rr} and smaller in the negative (compressive) case.

b. Dependence of the transformed fraction on the thickness ratio of the joints

Y-TZP (2Y) disks having different thickness and grain size were joined with SUS304 steel and Mo. The tf value on Y-TZP surface of the joins were measured for the both material pairs. They are plotted in Fig. 7a,b. In the case of fine grained Y-TZP, dependence of the tf value on the Y-TZP thickness was opposite between the two joint pairs. As Y-TZP thickness increased, tf increased in the former pair and decreased in the latter pair.

The calculated σ_{rr} on Y-TZP surface changed from compressive to tensile in Y-TZP/SUS304 steel joints and vice versa in Y-TZP/Mo joints. The tf value on the Y-TZP is considered to be related with the residual stress state in the joints, namely, the tf value was larger when σ_{rr} was positive (tensile) and smaller when σ_{rr} was negative (compressive).

The tf values on the coarse grained Y-TZP are also included in Fig. 7a,b. They were much larger than the fine grained Y-TZP case, and the thickness dependence was less obvious. Especially, in the Y-TZP/Mo joints, the dependence was weaker. In this material pair, thermal stress σ_{rr} in the interfacial area of Y-TZP is expected to be always tensile. Transformation is considered to have occurred in the interface area readily, because of the large grain size of Y-TZP and large tensile stress. Al-

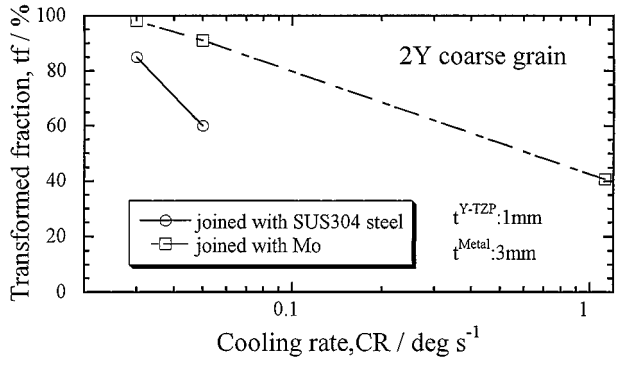

Figure 8 Relationship between cooling rate and transformed fraction (tf) in the coarse grained Y-TZP joined with metallic materials.

though the transformation stresses were not measured, the volume expansion caused by the transformation in the interface area raised the tensile stress to larger and induced the successive transformation in the surface region. Consequently, the tf value was large in the Y-TZP having thickness of 3 mm even under presence of compressive thermal stress states.

As a whole, transformation occurred in spite of the presence of compressive stress. The enhanced transformability due to either larger grain size or lower cooling rate overcame the effect of the compressive stress state.

c. Dependence on the cooling rate from the joining temperature

In the case of the unjoined coarse grained Y-TZP, the larger tf value was obtained when cooled at the lower rate (Fig. 3). It is of interest to study the relationship between the cooling rate and the tf value in the Y-TZP joined with metals. Coarse-grained Y-TZP were joined with metallic materials and they were cooled from the joining temperature at different rates. The relationship between the cooling rate and the tf value is plotted in Fig. 8.

It should be mentioned, however, that the successful joining was possible when cooled at relatively higher rate, because otherwise the large fraction of transformation occurred, causing the large volume increase. Cooling rate of 1.33 deg/s was attained in Y-TZP/Mo joints by pulling out the silica tube containing the specimen into air. The tf decreased by increasing the cooling rate. This tendency is consistent with the results of the dilatometry of the unjoined Y-TZP.

4. Discussion

Transformed fraction was larger in 2Y-TZP than the other cases, therefore, discussions were made, based on the experimental data using 2Y-specimens.

4.1. The effect of thermal stress on t-m transformation

The tf value on the surface of fine-grained 2Y-TZP disks was dependent on the Y-TZP thickness and on the selection of metallic materials, as shown in Fig. 7a,b.

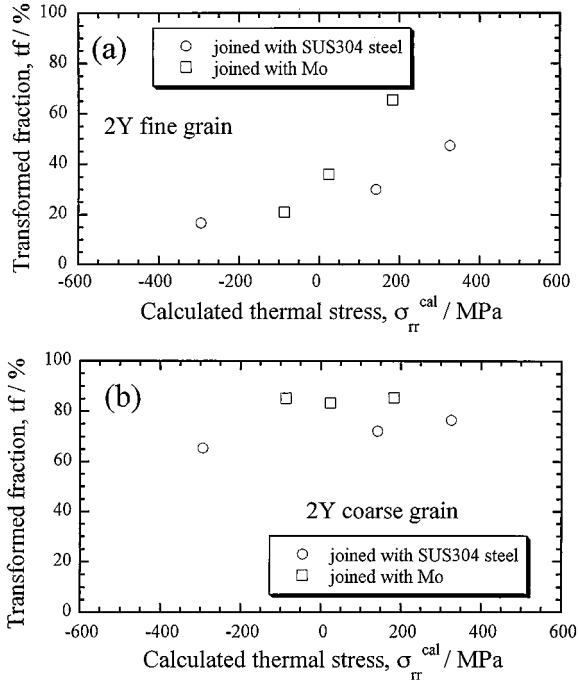

Figure 9 The relationship between the calculated thermal stress and the transformed fraction (tf). (a) In fine grained Y-TZP joints and (b) in the coarse grained Y-TZP joints.

This dependence was pointed out to be related with the residual stress. Values of residual stress related with enhancing or depressing the transformation was estimated by FEM for the temperature difference between the joining temperature (1113 K) and the transformation start temperature (570 K: M_s). The actual temperature difference might have been smaller, if the deformation of brazing sheet was taken into consideration.

In calculation, it was assumed that M_s was not altered by an applied stress. This assumption is plausible as observed before (Fig. 3). The elastic constants were reported [20] to vary with temperature. Nevertheless, the calculated residual stress was not influenced very much within the range of their variation. Therefore, it was also assumed that the elastic properties were constant through the experimental temperature and they do not change by annealing.

The relationships between the calculated residual stress and the measured tf value on the fine grained Y-TZP (Fig. 9a) and on the coarse grained Y-TZP (Fig. 9b) in the both joint pairs are plotted. In the former case, tf value increased as the residual stress on Y-TZP changed from compression to tension. The effect of σ_{rr} on the transformed fraction was evident. On the other hand, the correlation was not clear in the latter case. The difference in transformability and occurrence of subsidiary transformation are considered to be the cause for the difference.

4.2. The effect of cooling rate on the transformation fraction

In the case of unjoined Y-TZP, the tf value increased as the cooling rate decreased. The effect of time-dependent transformation was considered to be the cause of this effect. The unjoined coarse grained Y-TZP had critical cooling rate of about 0.05 deg/s, above which transformation did not occur. However, transformation occurred in Y-TZP disks joined with Mo when cooled at large rate of 1.13 deg/s as shown in Fig. 8. In these cases, detection of transformation was conducted by X-ray diffraction, however, considerable fraction of transformation was considered to have occurred in the bulk area of the Y-TZP disk.

It is of interest that the tf value in the joined Y-TZP also increased as the cooling rate decreased. These phenomena support the assumption that Y-TZP has characteristics of time dependent transformation under the presence of applied stress. The nature of the stress effect on the time-dependent transformation is not evident in the present stage, however, the following interpretation might be possible:

The incubation time before the onset of t-m transformation decreased and the rate of the transformation was accelerated by the presence of applied tensile stress. This caused the increase in the tf value at lower cooling rate. This phenomena has been analyzed, quantitatively [21] by means of the shift of TTT-diagram of the iso-thermal (pearlite formation) transformation, in the case of steels. More precise and quantitative analysis are needed in order to predict the transformation behavior in the Y-TZP joints.

5. Conclusion

Y-TZP disks were joined with that of SUS304 steel and Mo. In fabrication of the joints, transformability of Y-TZP, stress distribution in the joints and cooling rate from the joining temperature were changed. Transformed fraction in Y-TZP disks was measured and their relation with various parameters were investigated.

It turned out that correlation existed between the thermal stress (σ_{rr}) and the transformed fraction, such that tensile radial stress enhanced the transformation. The transformed fraction in the joined Y-TZP was larger when cooled at lower rate.

Considering the time dependent characteristics of t-m transformation, possibility was suggested that the increase of tf value at lower cooling rate was caused by acceleration of the transformation rate by the applied tensile stress.

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Received 2 April 1997
and accepted 2 June 1999