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Deformation behavior and joining of a MgF_2 optical ceramic

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Abstract

Compressive deformation behavior of a polycrystalline magnesium fluoride (MgF_2) ceramic was investigated at temperatures ranging from 760 to 830 °C in an argon atmosphere at strain rates between 2×10^{-6} and 4×10^{-5} s^{-1}. Steady-state flow stresses increased with increasing strain rates and ranged between 2 and 38 MPa. Stress exponents of $\approx 1.4 \pm 0.2$ were determined at temperatures >760 °C, indicative of a viscous diffusion-controlled deformation mechanism. Activation energy, determined from flow stress as a function of temperature, at a constant strain rate, was $\approx 476 \pm 60$ kJ/mol. Self-joining by plastic deformation of MgF_2 was demonstrated at 830 °C at a strain rate of 5×10^{-6} s^{-1}. The joined samples were characterized by optical transmission measurements and their transmittivity was ≈80% of the unjoined sample in the 2.5–8 μm wavelength range.

Keywords: Magnesium fluoride; Optical properties; Creep

1. Introduction

Polycrystalline magnesium fluoride (MgF_2) is almost transparent in the infrared (IR) wavelength regime (2–8 μm).[1,2] Due to this unique property, MgF_2 has applications for IR windows and coatings in optical instruments, space vehicles, and frontal domes in heat-seeking missiles.[1–3] Magnesium fluoride is an excellent candidate for thermal lensing because it has one of lowest temperature dependent refractive index distortions.[3] As compared to IR transparent single crystals, polycrystalline MgF_2 is relatively simple and inexpensive to fabricate. However, fabrication of complex shaped engineering components using polycrystalline MgF_2 still remains a major challenge.

Polycrystalline MgF_2 is fabricated using typical ceramic processing routes by hot-pressing magnesium fluoride powder in a die in a controlled environment.[1] This process allows fabrication of simple shapes. One approach that is being considered is to join multiple simple-shaped parts to produce a complex part. In this regard, development of a joining process for optical materials such as MgF_2, without degradation of optical characteristics, becomes important.

In the literature, self-joining of MgF_2 has been demonstrated by a diffusion bonding process without an interlayer[4] or using a lithium fluoride (LiF) interlayer.[5] Diffusion bonding entailed applying a thin film of LiF on the mating surfaces of the pieces being joined and maintaining a constant compressive stress for >3 h at 550–575 °C. Without any interlayer, diffusion bonding was accomplished by applying constant pressure at 800–830 °C for about 6 h[4]. Limitations of this process are two-fold: (a) long hold times at elevated temperatures which can result in grain growth and (b) use of an extraneous interface material. Both factors can cause degradation of the optical and mechanical properties of the joined component. Thus, plastic deformation, as discussed in this paper, presents an approach to self-joining MgF_2 that precludes the limitations imposed by the diffusion bonding process.

High-temperature plastic deformation process has been demonstrated for joining various structural ceramics and composites.[6–9] The joining process requires heating the components to elevated temperatures and deforming them at a constant displacement rate such that total strains are typically <10%. The mechanism by which pore-free joints are obtained is due to the interpenetration of grains at the interface as the result of grain boundary sliding (GBS).[6–9] There are several attributes that make the plastic joining process attractive: (a) it requires no surface preparation or interlayer material, (b) permanent deformation is minimal, and (c) the process occurs at lower temperatures and for shorter times relative to the conventional diffusional bonding.[10] The interface formed by plastic deformation is indistinguishable from the bulk material.[9] This attribute

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is particularly significant when optical properties are of concern as in the case of joining of polycrystalline MgF_2.

High-temperature deformation behavior of polycrystalline MgF_2 has not been reported. Because of the importance of deformation in processing and fabrication of components, a study of high-temperature deformation behavior of a polycrystalline MgF_2 ceramic was undertaken. In addition, self-joining of MgF_2 using plastic deformation was explored, so that complex shaped parts could be fabricated by joining simple geometries. Finally, the quality of joined MgF_2 components was established by microstructural and optical characterizations.

2. Experimental details

2.1. Polycrystalline magnesium fluoride

Polycrystalline magnesium fluoride samples were procured from a commercial source (Superconix Inc., Lake Elmo, MN). Samples were fabricated by hot-pressing MgF_2 powders. As-received samples were 10 mm × 10 mm × 40 mm. The density of as-received samples was determined by the Archimedes method. The microstructure of the sample was examined on the fracture surface using a Hitachi Model S-4700-II (Tokyo, Japan) field emission scanning electron microscope (FE-SEM). Grain size was measured by the standard linear intercept method.[11] Phase analysis was conducted by room-temperature X-ray diffraction (XRD) measurements using a Phillips X-ray diffractometer (Model X'PERT, Almelo, The Netherlands) with a Cu $K\alpha_1$ radiation. Data acquisition was conducted using a step-scan program run at 100 s/° with a step size of 0.01° over a 2θ range of 20–75°. In addition, stability of the MgF_2 phase was characterized by conducting XRD analysis on samples that were deformed and compared with the as-received samples.

2.2. Deformation study and joining

For deformation and joining experiments, right parallelepiped specimens (≈3 mm × 3 mm × 5 mm) were cut from as-received MgF_2 samples using a low speed diamond saw. Surfaces were as-cut. Specimens were subjected to uniaxial compression, at a constant cross-head displacement rate on an Instron machine (Model 1125, Canton, MA) equipped with an atmosphere-controlled high-temperature furnace.[9] All deformation and joining tests were conducted in an argon atmosphere. The furnace chamber was flushed with argon atmosphere prior to joining or deformation. Deformation tests were conducted in the temperature range from 760 to 830 °C at strain rates varying from 2×10^{-6} to 4×10^{-5} s^{-1}. For joining tests, two samples of MgF_2 were mated and compressed. To ensure plastic deformation of MgF_2 during joining, strain rate and joining temperature were selected on the basis of results from the deformation study of MgF_2. The joining temperature selected was 830 °C at a strain rate of 5×10^{-6} s^{-1}. All joinings were completed within 0.5 h. The total permanent strains introduced during the plastic joining process ranged from ≈0.05 to 0.08.

Microstructure of the as-received and deformed samples was examined by transmission electron microscopy (TEM). TEM foils were prepared by first sectioning thin slices using a diamond blade and then further thinning by mechanical polishing. Thereafter, samples were ion milled using a Gatan (Pleasanton, CA) Model 691 precision ion polishing system. TEM was conducted using a Phillips CM-200 electron microscope operating at 200 kV.

After joining, samples were sectioned, polished, and the joint interface was examined using an SEM (Hitachi S-4700, Tokyo, Japan). In addition, efficacy of the joint was established by conducting optical transmission measurements on samples before and after joining. Optical transmission measurements were conducted using a Brucker (Billerica, MA) Vertex 70 Fourier Transform Infrared (FTIR) spectrometer running OPUS software. This spectrometer has a resolution of 0.5 cm^{-1}. Prior to evaluating the optical transmission, sample surfaces were polished to a mirror finish and cleaned in acetone.

3. Results

The density of the as-received MgF_2 measured by the Archimedes method was 3.1 g/cm^3, which was approximately 98% of the theoretical density of MgF_2 taken as 3.17 g/cm^3.

Fig. 1 is a photomicrograph of a fractured surface of as-received MgF_2. The microstructure was uniform with an average grain size of 0.1–0.2 μm. In addition, the fracture morphology was intergranular. Fig. 2 shows the XRD pattern of an as-received MgF_2 sample for which the major peaks correspond to magnesium fluoride.

Fig. 3 shows the typical stress-strain behavior obtained during compressive deformation of polycrystalline MgF_2 at different strain rates. Initially, the stress increases linearly (elastic regime) with applied strain followed by deviation from linearity, indicative of plastic deformation. With further increase in strain, a steady-state stress was reached which is referred to as the flow stress. However, at the highest strain rates such as 1×10^{-5} s^{-1} at 828 °C (Fig. 3), there was evidence of work hardening. In such situations, it was difficult to determine the appropriate steady-state flow stress. In addition, there was an increase in the flow stress at a given strain rate after some strain had accumulated

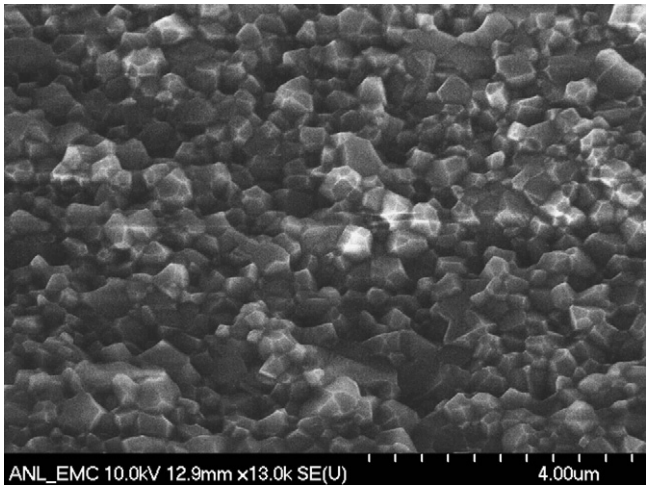

Fig. 1. Fracture surface of the as-received polycrystalline MgF_2.

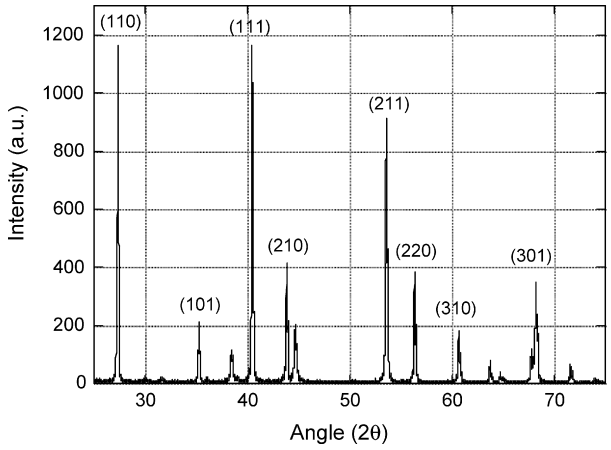

Fig. 2. X-ray diffraction pattern of as-received polycrystalline MgF_2.

(see tests conducted at $5 \times 10^{-6}\ s^{-1}$ in Fig. 3). This may be due to experimental uncertainties because of the low stresses. It is clear from Fig. 3 that the flow stresses increase with increasing applied strain rates at a constant test temperature. Similar stress-strain responses were obtained at other test temperatures.

Fig. 4 represents the strain-rate dependence of the flow stress on a log–log basis for the four temperatures investigated. If no microstructural changes occur during testing, a steady-state phenomenological creep equation can be used to define the dependence of strain rate on the flow stress[12]:

$$\dot{\varepsilon} = A\sigma^n \exp(-Q/RT) \tag{1}$$

where $\dot{\varepsilon}$ is the strain rate, σ the flow stress, n is the stress exponent, A is a constant, Q the activation energy, R the gas constant, and T is the absolute test temperature. A stress exponent of $n = 1$ indicates that deformation process is diffusion-controlled.[13] Average value of n, estimated from best fits of the experimental data at the three test temperatures to Eq. (2), was 1.4 ± 0.2. For comparison, the bold line on Fig. 4 corresponds to $n = 1$.

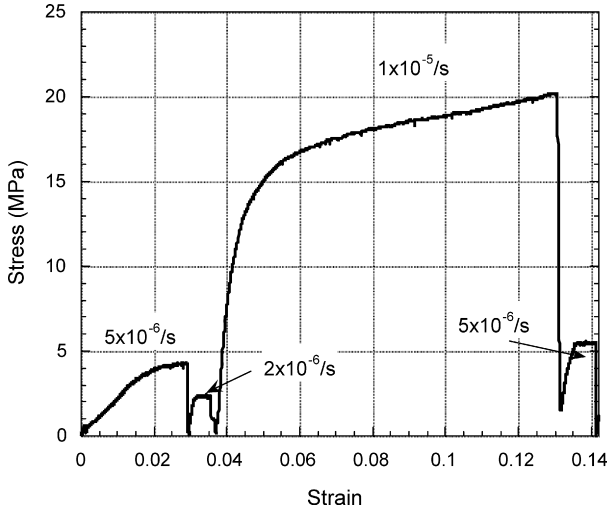

Fig. 3. Typical stress vs. strain behavior obtained during compressive deformation test performed at 828 °C on MgF_2 at various strain rates.

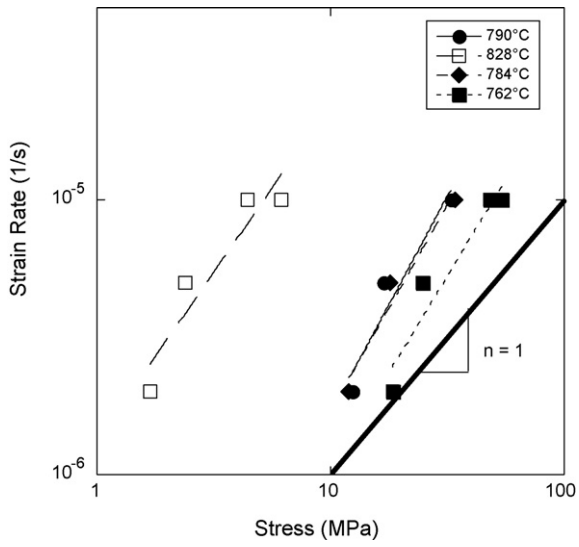

Fig. 4. Strain rate vs. steady-state stress behavior of polycrystalline MgF_2 during compressive deformation at various temperatures.

At a constant strain rate, activation energy, Q, for the deformation process can be represented as

$$Q = nR\frac{\partial \ln \sigma}{\partial (1/T)_{\dot{\varepsilon}}} \tag{2}$$

Fig. 5 shows the Arrhenius plot of flow stress as a function of reciprocal absolute temperature at the three different strain rates tested. Activation energy determined, from the slopes of the various lines, was 476 ± 60 kJ/mol. It is assumed that the stress exponent, n, was constant over the temperature range and a value of $n = 1.4$ was used for the calculation.

Fig. 6(a) and (b) are TEM micrographs of as-fabricated and 790 °C deformed (total deformation ≈0.2) MgF_2 samples, respectively. There was no cavitation observed at the grain boundaries. No discernible changes in the grain shape were

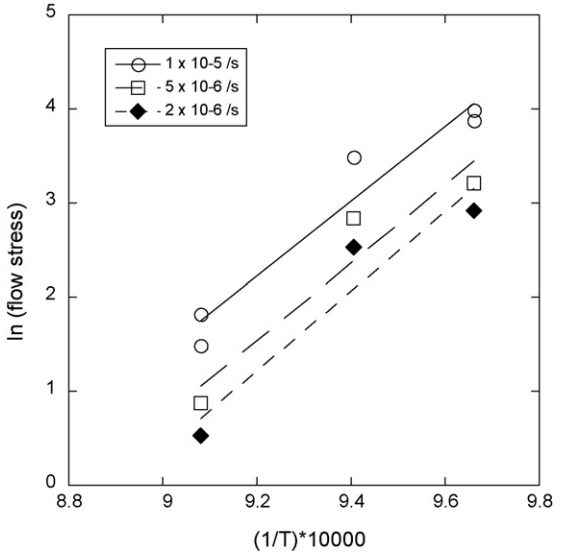

Fig. 5. Variation of flow stresses as a function of temperature for the strain rates tested in polycrystalline MgF_2.

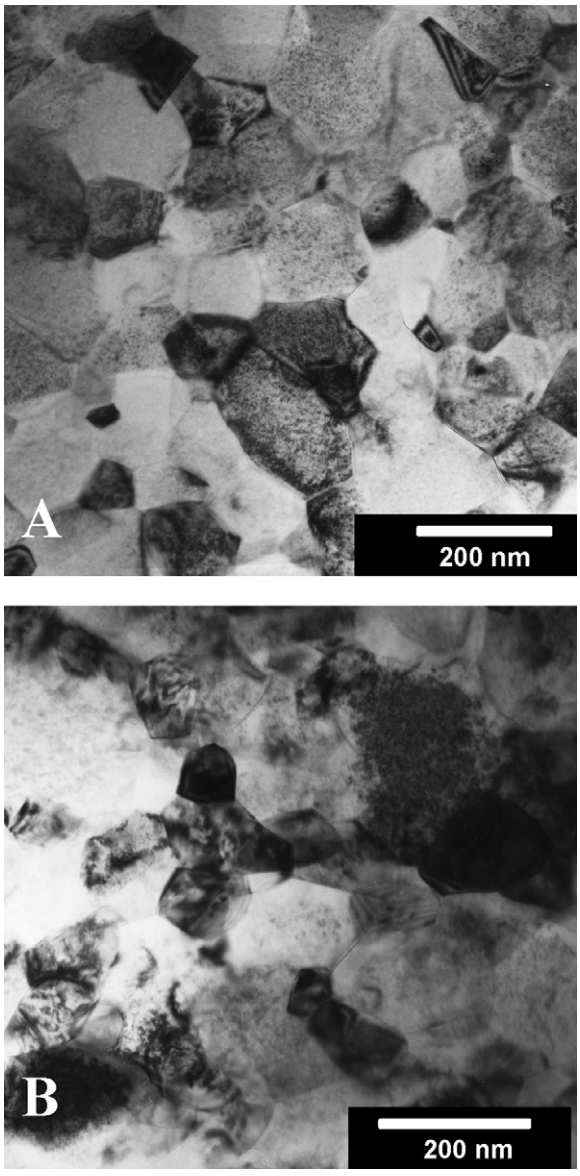

Fig. 6. TEM micrographs of polycrystalline MgF_2: (A) as-received and (B) post-deformation (790 °C, exposure time = 4.5 h, total $\varepsilon \approx 20\%$).

observed. In addition, no dislocation networks were seen in the deformed sample.

Fig. 7 is a typical stress-strain plot obtained during joining of two pieces of MgF_2 at 830 °C and a strain rate of 5×10^{-5} s^{-1}. The stress increased monotonically up to ≈2 MPa; thereafter, it deviated from linearity, indicating plastic flow of the material. Typically, the cumulative deformation was ≈0.07 before samples were unloaded.

Fig. 8 shows an SEM image of the area in the vicinity of the joint. Location of the interface is shown by the arrows but is indistinguishable from the bulk MgF_2. Sample was not etched to reveal the grain structure.

Fig. 9 compares the optical transmission between the joined polycrystalline MgF_2 and the unjoined sample. Optical transmissions were compared over the wavelengths ranging from 2.5 to 8 μm. At wavelengths >5 μm, joined samples have a transmittance behavior similar (within 95%) to the as-received sample.

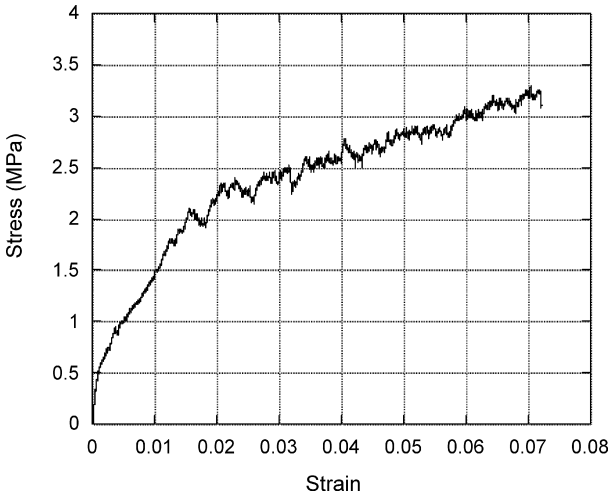

Fig. 7. Typical stress–strain profile obtained during joining of polycrystalline MgF_2 by plastic deformation.

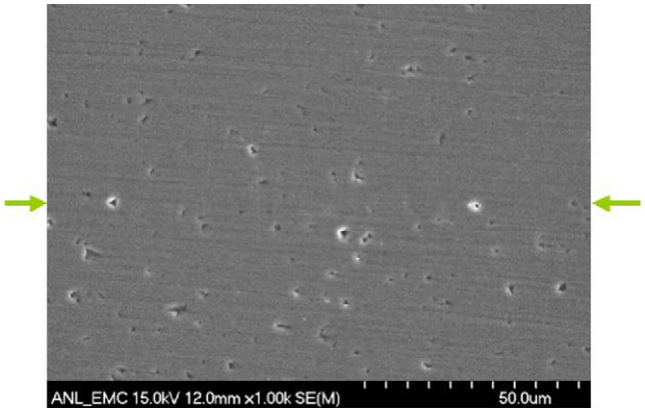

Fig. 8. Scanning electron micrographs of MgF_2 sample joined at 830 °C at 5×10^{-5} s^{-1} strain rate; arrows indicate the joint interface.

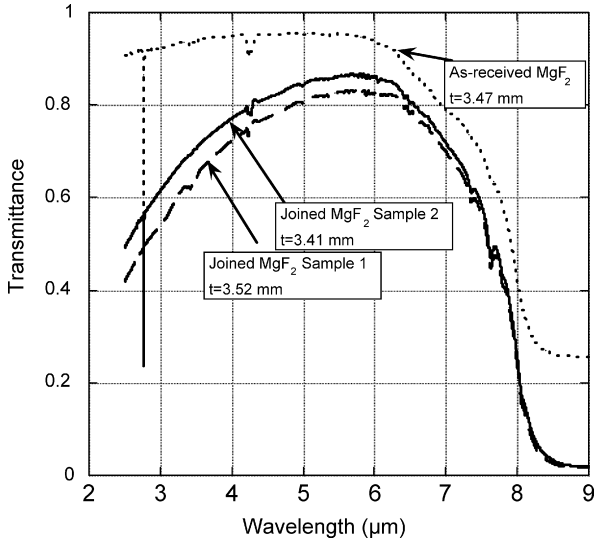

Fig. 9. Optical transmission of the joined polycrystalline MgF_2 compared with the as-received monolithic MgF_2.

However, at wavelengths <5 μm, the discrepancy in the optical transmission of the joined and unjoined samples was larger. Relative areas under the transmission curves, over the entire wavelength range, provide a quantitative comparison of the optical transmission. It was determined that the samples joined by plastic deformation were approximately 80% as efficient as the monolithic sample. It should be noted that there are minor differences in the sample thicknesses, as listed in Fig. 9, along the optical path that were ignored.

4. Discussion

Fine-grained polycrystalline ceramics[14,15] such as Al_2O_3 and 3Y-TZP are known to plastically deform at elevated temperatures by grain boundary sliding (GBS). Grain boundary sliding is accommodated by a diffusion process.[14,16] Fine-grain structure assists in accommodating the local strains that are generated during GBS. Without this strain accommodation, the material will cavitate.[13] Evidence of grains rotation during GBS has been recently documented[17] in fine-grained $SrTiO_3$. It is believed that polycrystalline ceramics that exhibit GBS during deformation and concurrent grain rotation are excellent candidate materials for joining via the plastic deformation process.[17]

Based on the deformation behavior of polycrystalline MgF_2 obtained in this study, it appears that the deformation behavior was a diffusion-assisted GBS mechanism. Deformation tests conducted at temperatures >760 °C and strain rates between 2×10^{-6} and $1 \times 10^{-5}\ s^{-1}$, yielded a stress exponent value of 1.4; indicative of a diffusion-controlled deformation process.[13] Furthermore, as shown in TEM images of a deformed sample (Fig. 6), there was no evidence of cavitation and any deformation-induced dislocation structures. Also, no discernible changes in the grain shape and size were observed between the deformed and undeformed polycrystalline MgF_2 (Fig. 6). These observations are consistent with the GBS as the deformation mechanism.

Activation energy of the diffusion-assisted deformation process can identify the slowest moving specie or the rate controlling process. The activation energy for deformation of MgF_2 ceramic was 476 ± 60 kJ/mol determined from the Arrhenius plot of Fig. 5. Per the authors' knowledge there are no known values of deformation or self-diffusion activation energies for poly or single-crystalline MgF_2 reported in the literature. MgF_2 and TiO_2 both have a tetragonal (rutile) structure with coordination number of 6 for cation and 3 for the anion.[18] Additionally, the ratio of cation to anion radii is about the same in MgF_2 and TiO_2. Deformation and diffusion data exist for the TiO_2 in the literature. It should be stated that comparing an oxide with the fluoride neglects any chemical effects that could be important. Polycrystalline rutile has been crept in four-point bending from 1100 to 1200 °C by Philpot, et al.[19] They found that the strain rate was linearly proportional to the stress with a threshold stress. The creep rate also depended on the grain size and the oxygen partial pressure. They measured both undoped and 1% Ta doped TiO_2 and reported activation energies of 264 kJ/mol for the undoped and 510 kJ/mol for the doped rutile. Activation energies of MgF_2 and doped TiO_2 are quite similar on a normalized (Q/RT_m) basis, where, T_m is the absolute melting point. This implies that doping affects the activation energy in TiO_2 and possibly in MgF_2.

This study demonstrated that polycrystalline MgF_2 ceramics can be successfully self-joined using plastic deformation. Microstructurally there was no discernible difference between regions along the interface and regions away from the interface. As indicated by the arrows in Fig. 8, no additional surface residual interfacial porosity was observed.

Optical transmission measurements further attest to the efficacy of the joint produced by plastic deformation. As shown in Fig. 9, the transmission spectrum as a function of wavelength was typical[2] of a polycrystalline MgF_2. The sharp external absorption peak at 2.75 μm corresponds to that of water.[2] Joining by plastic deformation was approximately 80% as efficient (determined from area under the curve) as the transmittance of the as-received samples over the IR wavelength range from 2.5 to 8 μm. This is in agreement with the 85% optical transmittance reported by Yen et al.[4] for a pure diffusional joint without an LiF interlayer. Clearly, at longer wavelengths (>5 μm), the transmission behavior of the joined samples is much closer to the as-received sample. However, the discrepancy is quite large at wavelengths <5 μm. At shorter wavelengths, transmission losses are attributed to scattering of incident radiation from subsurface micropores.[2] The presence of some residual porosity is expected at the joint interface that contributed to the observed experimental discrepancy. It should be noted that limited joinings were made in this study and there was no process optimization. It is believed that by further process control, the discrepancy between the optical transmission behavior of joined and as-fabricated samples can be further reduced.

Change in grain size can significantly affect the optical transmittance in polycrystalline MgF_2. Lin et al.[20] found that there is an inverse relationship between grain size and optical transmission. Moreover, the effect is more profound at shorter wavelengths 0.7–3 μm as opposed to longer wavelengths (>5.5 μm). At a wavelength of 2.5 μm, transmittance decreased by approximately 12% as the grain size increases from 0.5 to 1.0 μm. Although, the TEM micrograph (Fig. 6) of post-deformed MgF_2 sample does not show any grain size increase, this effect cannot be entirely discounted. A systematic study on the changes of grain in MgF_2 during plastic deformation joining and its correlation to the optical transmittance needs to be conducted.

Finally, elevated temperature structural stability is an issue for halides, especially decomposition of fluorides. In this regard, X-ray diffraction was conducted on joined MgF_2 samples and compared to the diffraction pattern of the as-received sample (Fig. 2). No difference was observed, indicating that the material was stable, within the resolution of the XRD, during the entire joining process (temperature and time).

5. Conclusions

A compressive deformation study was conducted on a polycrystalline MgF_2 optical ceramic in the temperature range from 760 to 830 °C using strain rates of 2×10^{-6} to $4 \times 10^{-5}\ s^{-1}$.

Steady-state plastic flow behavior was observed in this material and was attributed to a viscous diffusion-controlled mechanism. Activation energy of the deformation process was ≈476 kJ/mol and was comparable, on a normalized basis, to that observed for creep in doped TiO_2. Microstructural evidence indicated that the probable deformation mechanism was diffusion-assisted grain boundary sliding. Self-joining of MgF_2 was demonstrated by plastic deformation at 830 °C at a strain rate of $5 \times 10^{-6}\ s^{-1}$. The resulting joined samples were characterized for transmittance by FT-IR measurements and were found to be ≈80% as efficient as the unjoined MgF_2 in the IR wavelength range.

Acknowledgments

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