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Mechanical spectroscopy connected to creep and stress relaxation in a high resistant silicon nitride

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Abstract

Silicon nitride processed by gas pressure sintering contains a very small amount of glassy phase and consequently exhibits a strong resistance to deformation until 1450 °C. Above this temperature, both relaxation kinetics and creep rate rapidly increase. To explain such a behaviour, the formation of a liquid phase by dissolution of YSiAlON phases was proposed. The present paper shows that mechanical spectroscopy argues for the existence of such a liquid phase at high temperature. The mechanical loss is very low in the as-sintered material. Nevertheless, the internal friction peak generally observed in silicon nitride, and attributed to the glass transition in the glassy pockets, is also observed in the gas pressure sintered silicon nitride. Moreover, the peak is much higher in annealed and "quenched" specimens and it increases with annealing time. These results show that the annealed and "quenched" material contains much more glassy phase and so argues for the dissolution of crystalline phases at high temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Creep; Grain boundaries; Mechanical spectroscopy; Si_3N_4; Sintering

1. Introduction

Technical ceramics such as alumina, zirconia or silicon nitride are processed from powder mixtures sintered at elevated temperature. Because of the covalent bonds of Si_3N_4, the densification of silicon nitride ceramics needs sintering aids like Al_2O_3, AlN, MgO, or Y_2O_3 powders.[1] After a liquid phase sintering, the silicon nitrides generally contain a residual amorphous phase localised between neighbouring grains (glassy films) and at multiple grain junctions (glassy pockets).[2] The characteristics of this secondary phase (quantity, composition, viscosity, glass transition temperature) deteriorate the intrinsic resistance of Si_3N_4.[3,4] Accordingly, to improve high temperature properties, the amount of residual glassy phase has to be reduced for instance by improving the sintering process. The gas pressure sintered silicon nitride studied here contains a very small amount of residual glassy phase and so presents a high creep resistance up to 1450 °C.[5] This paper presents mechanical spectroscopy experiments performed on this advanced silicon nitride. The results are analysed in comparison with creep and relaxation tests already done.[6]

2. Advanced silicon nitride

2.1. Processing and microstructure

The technical ceramic studied here is a fully dense silicon nitride developed by Norton-Desmarquest.[7] Two commercial α-Si_3N_4 (SN-E-10, UBE) and α-YSiAlON (SY5, UBE, $Y_{0.5}Si_{9.75}Al_{2.25}O_{0.75}N_{15.25}$) powders were mixed and then sintered at 1800 °C by a gas pressure sintering technique using a nitrogen pressure of 5 MPa. After a slow cooling, the microstructure is made of randomly oriented β-SiAlON elongated grains (7–30 μm) and of smaller α-YSiAlON grains (Fig. 1).[6] The gas pressure sintered silicon nitride equally contains many crystallised YSiAlON pockets whose composition is not

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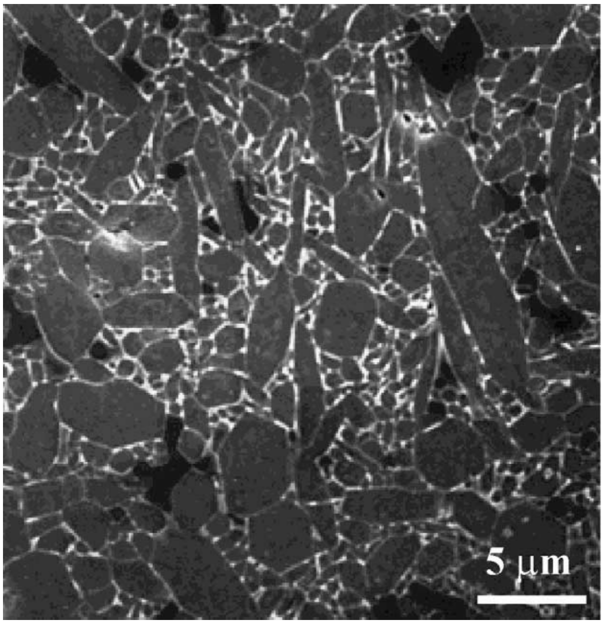

Fig. 1. Microstructure of the gas pressure sintered silicon nitride observed by scanning electron microscopy after polishing and then SF6 plasma etching.

constant.[7] According to transmission electron microscopy,[5,7] no intergranular glassy film and only few small glassy pockets were observed in the as-sintered material. Such microstructure explains the high creep resistance observed up to 1450 °C for stresses in the order of 100 MPa.[8]

For comparison materials called NSC9[9] and SN-G[10] have also been studied. The silicon nitride NSC9 was processed from Si_3N_4 powder mixed with 10% in weight of sintering additives (Al_2O_3, AlN and Y_2O_3), by slip casting and then pressureless sintering at 1750 °C under nitrogen atmosphere. The silicon nitride SN-G was obtained by sintering at 1800 °C a α-Si_3N_4 powder with 6% in weight of Y_2O_3 and 5% in weight of 6AlN-SiO_2 additives. It must be noticed that these two silicon nitrides are sintered with a significant amount of oxide phases. Accordingly, the microstructure of these two classical silicon nitrides is composed of silicon nitride grains embedded in a non-negligible amount of amorphous phase.

2.2. Creep and stress relaxation behaviour

Compressive stress relaxation and creep tests were performed between 1400 and 1650 °C on the gas pressure sintered silicon nitride.[6]

The stress relaxation kinetic $\sigma(t)$, normalised by the initial stress σ_o, was analysed by the Kolhraush–Williams–Watt equation: $\sigma/\sigma_o = \exp[-(t/\tau)^b]$ where τ is an apparent relaxation time and b a parameter between 0 and 1 associated to the relaxation time distribution spectrum.[11] As shown in Fig. 2, the relaxation time rapidly decreases and the parameter b increases when the temperature increases. For example, the relaxation time equal to 5600 hours ($b = 0.2$) at 1400 °C reaches a value of 0.6 h ($b = 0.7$) at 1650 °C.[12] In relaxation models,[13] the parameter b is a correlation factor related to the mobility of the structural unit at the atomic or molecular scale: b is null when the correlation is high (elastic solids) and b tends to unity when the correlation is low ($b = 1$ in liquids). So, the evolution of the structural parameter b measured in the gas pressure sintered silicon nitride reflects a smooth transition between a quite rigid state towards a more fluid state. According to the evolution of the relaxation time, this transition occurs around 1450 °C. The same behaviour transition was equally observed during creep. The rapid increase in the creep strain rate above 1450 °C yields a high value of activation energy in good agreement with microstructural changes in the material.[8] Besides, the variation of the stress exponent from a value of $n = 1$ in the 1280–1400 °C range[7] to a higher value of $n = 1.8$ at 1550 °C[8] would account for a transition from a creep regime controlled by volume diffusion to creep controlled by dissolution–diffusion–precipitation at the grain boundaries, respectively.

To explain the mechanical behaviour transition revealed by both creep and stress relaxation measurements, the formation of a liquid phase by dissolution of YSiAlON crystalline phases was proposed.[6,8] In that way, the transition temperature of 1450 °C corresponds to the beginning of the dissolution of such phases. Besides, many large glassy pockets were observed by transmission electron microscopy in samples tested at high temperature (Fig. 3).

3. Mechanical spectroscopy

For temperature lower than 1350 °C, the mechanical loss spectra of silicon nitrides are composed of a peak and an exponential background.[8,14–16] The internal friction peak emerges around 1000 °C for a 1 Hz frequency and has been attributed to the main relaxation (often called the α-relaxation[13]), which is associated with the glass transition in the amorphous pockets.[17–19] As a matter of fact it was observed that the peak disappears with the crystallisation of the glassy phase forming these pockets[9] and that this peak has exactly the same characteristics (relaxation time, activation enthalpy) as the α-relaxation peak measured in a YSiAlON glass.[17] Peak temperature and height as measured in classical silicon nitrides are given in Table 1.

The exponential background corresponds to the rapid increase of the mechanical loss at higher temperature than the peak and has been interpreted as due to the extensive grain boundary sliding, which is responsible for the high temperature plastic deformation of these ceramics.[9] The exponential background could also be

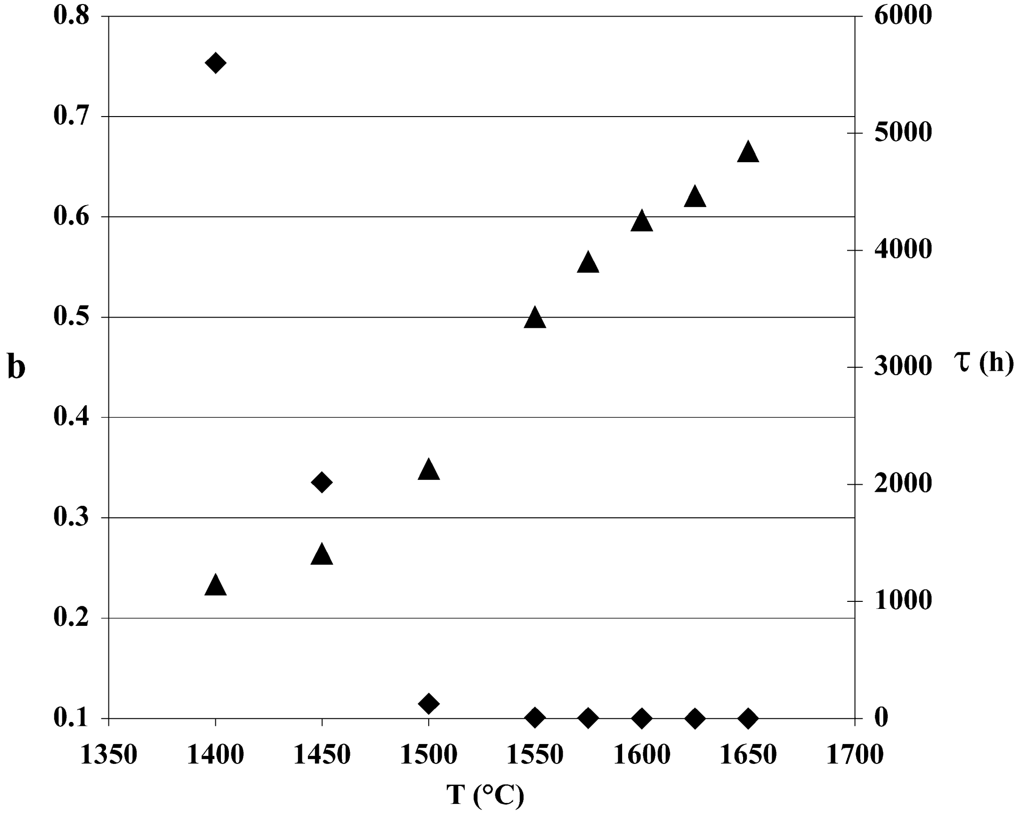

Fig. 2. Evolution of the relaxation time τ(→) and of the correlation parameter b(s) measured between 1400 and 1650 °C in the gas pressure sintered silicon nitride.[12]

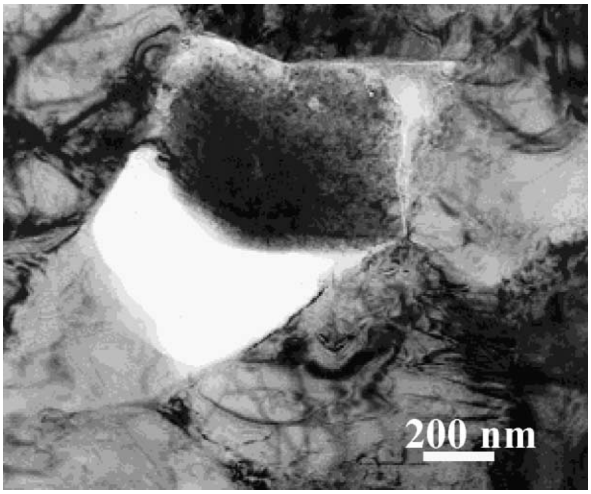

Fig. 3. Glassy pocket observed near a cavity by transmission electron microscopy in a gas pressure sintered silicon nitride sample deformed at 1600 °C.

Table 1
Characteristics of internal friction peaks measured at 1 °C/min and 1 Hz in various silicon nitrides

Material	Position (°C)	Intensity (10^{-3})
As-sintered	930	0.76
2h-Annealed	976	6.02
4h-Annealed	983	22.1
NSC9[8]	997	33.0
SN-G[9]	950	12.0

the low temperature part of a relaxation peak located at higher temperature. As a matter of fact, Pezzotti et al.[19] observed a relaxation peak at about 1600 °C in high-purity silicon nitride. They interpreted this peak as due to grain-boundary sliding. However, in chlorine-doped silicon nitride the same authors observed the peak at about 1225 °C.[20] This shift in temperature of the peak was attributed to the change in grain-boundary chemistry, which lowers the viscosity of the grain-boundary film.[20] As the peak is superimposed on an exponential increase in damping at still higher temperature (higher than 1800 °C), these authors[20] interpreted peak and background as follow: the peak as due to anelastic slip along the grain boundaries, the background resulting from an irreversible diffusional-creep mechanism. For summarizing, the mechanical loss spectrum of silicon nitride ceramics is mainly composed of one or two relaxation peaks and an exponential background. When the ceramic contains a great amount of glassy phase, a peak is observed at relatively low temperature (about 1000 °C). This peak disappears with the crystallization of the glassy phase and re-appears with the re-amorphization of crystalline phases.[9] When the ceramic is very pure, another peak is observed at much higher temperature,[19] which would be due to localized grain-boundary sliding. With respect to the relaxation peaks, the exponential background accounts for non-limited motion of the relaxing species and here it can be interpreted as due the irreversible or extensive grain-boundary sliding: onset of creep.

New and original results obtained by mechanical spectroscopy in advanced materials like the gas pressure sintered silicon nitride are described hereafter.

3.1. Experimental techniques

The mechanical spectroscopy measurements were performed in a forced torsion pendulum described elsewhere.[21] In this inverted pendulum, the sample of size $(50\times2.5\times1.5)$ mm^3 is submitted to a mechanical torsion stress by the magnetic coupling between a permanent magnet and Helmholtz coils. The current applied at the Helmholtz coils is a measure of stress. Strain is measured by an optical system made of a laser beam, mirror and photocells. The mechanical loss or internal friction "IF" is obtained through the phase lag between stress and strain. The results presented in the following were obtained at a frequency of 1 Hz. During the measurements, the heating and cooling rate were 1 °C/min, and the vacuum level 10^{-3} Pa, respectively.

The experiments were performed on different samples: as-sintered material (gas pressure sintered silicon nitride) and annealed-materials. The annealed-materials were obtained by annealing the gas pressure sintered silicon nitride under nitrogen at a temperature of 1600 °C reached with a heating rate of 10 °C/min. Two different annealing times have been tested at this temperature: 2 h (2h-annealed material) and 4 h (4h-annealed material). The purpose of these thermal treatments was to fix the microstructure of the material in its state at high temperature. So, at the end of the annealing, the furnace was switched off to rapidly decrease temperature. With respect to specimens annealed and slowly cooled down, the specimens treated as mentioned above can be considered as annealed and "quenched" specimens.

3.2. Description and analysis of internal friction results

3.2.1. As-sintered material

The results of mechanical spectroscopy obtained with the as-sintered material are presented in Fig. 4. At low temperature ($T<800$ °C), the mechanical loss is low and almost constant. Then, an internal friction peak is observed at 930 °C. In the high temperature range ($T>1100$ °C), the mechanical loss increases exponentially with temperature. So the internal friction curve of the as-sintered material presents the same general shape as the internal friction spectra observed in classical silicon nitrides.[15–18] Nevertheless, the data reported in Table 1, and the curves reported in Fig. 5, show that the mechanical loss measured in the gas pressure sintered silicon nitride is much smaller than in silicon nitrides NSC9 and SN-G. This comparison accounts well for the very small amount of glassy phase observed by transmission electron microscopy in the gas pressure sintered material.[5,7]

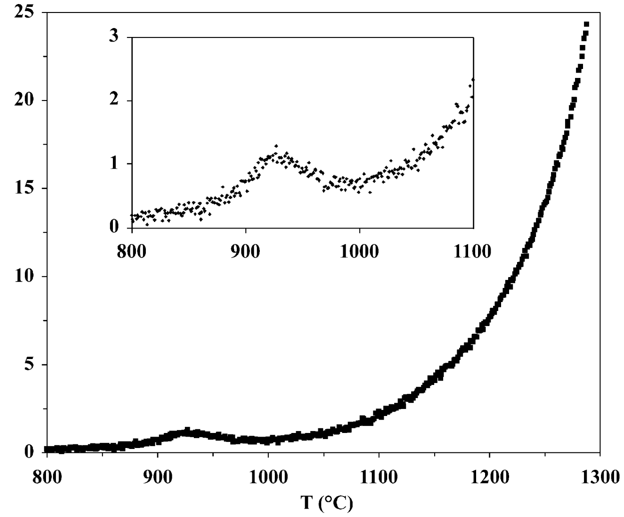

Fig. 4. Internal friction spectrum of a gas pressure sintered silicon nitride, as measured during heating at 1 °C/min and frequency of 1 Hz.

In Table 1, one can see that the position of the peak depends on processing and so on the properties of the intergranular glassy phase. For a frequency of 1 Hz, the peak is located at 930 °C in the gas pressure sintered silicon nitride, whereas Lakki et al.[9] have reported a temperature of 997 °C in NSC9, and Roebben et al.[10] a

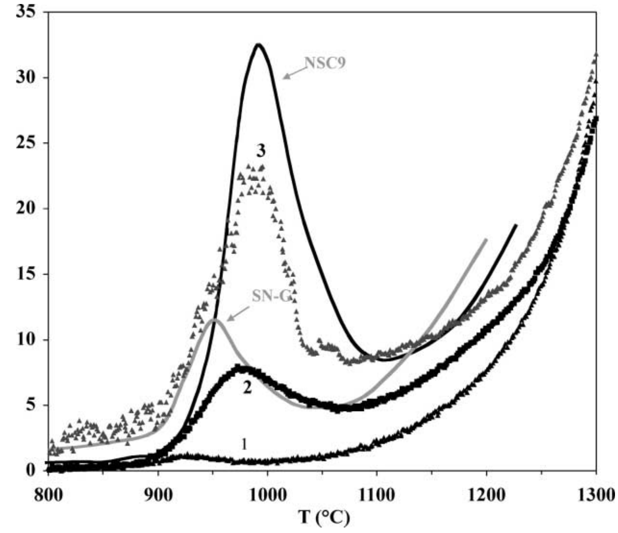

Fig. 5. Internal friction spectra of gas pressure sintered silicon nitride measured at a frequency of 1 Hz during heating at 1 °C/min: as-sintered (1), 2h-annealed and "quenched" (2) and 4h-annealed and "quenched" (3) materials. The curves measured in silicon nitrides NSC9[9] and SN-G[10] have also been reported for comparison.

temperature of 950 °C in SN-G (Table 1). These differences are due to the origin of the internal friction peak, i.e. to the glass transition phenomena. It can be argued that the glass transition temperature, T_g measured in glasses depends on their composition. For example, there is a difference of 90 °C between a MgYSiAlON glass (T_g=825 °C)[22] and a YSiAlON glass (T_g=916 °C).[23] Moreover, the glass transition temperature of YSiAlON glasses can differ from several ten degrees just by changing the ratio of each element.[23]

3.2.2. Annealed material

As shown in Fig. 5, the mechanical loss is much higher after annealing at 1600 °C followed by rapid cooling (in annealed and "quenched" specimens). In the 2h-annealed material, the intensity of the peak is equal to 6×10^{-3}, whereas a value less than 10^{-3} is measured in the as-sintered material. Besides, the increase of the annealing time involves an increase of the mechanical loss and the peak intensity reaches 22×10^{-3} in the 4h-annealed material. The results obtained in annealed materials are close to the ones obtained in classical silicon nitrides (Table 1). As a useful method to investigate the amount of glassy phase in various silicon nitrides, mechanical spectroscopy shows that the annealed materials contain much more glassy phase than the as-sintered one. This may indicate that a liquid phase was created during the annealing at 1600 °C. The liquid phase was then transformed into a glassy phase during rapid cooling.

Values reported in Table 1 equally indicate that the annealing at 1600 °C shifts the position of the peak from 930 °C (as-sintered material) towards temperatures near 980 °C (annealed materials). This difference can be explained by the modification of the composition of the secondary phase occurring during the formation of the liquid phase by dissolution of the YSiAlON phases.[6]

During mechanical spectroscopy measurements performed as a function of increasing temperature, the crystallisation of the glassy phase occurs and is promoted by the very slow heating rate (1 °C/min).[9] The crystallisation effect on the internal friction is shown in Fig. 6. During heating, the 2h-annealed material presents a well-defined peak. Then, after heating until 1330 °C, the material is measured during cooling in the same conditions: 1 Hz and 1 °C/min. The peak is not observed during cooling because crystallisation of the YSiAlON glasses occurred during the slow cooling. Moreover the high temperature exponential background has been strongly decreased by the thermal cycling. This may account for an increase in the friction forces, which act on grain-boundary sliding, due to crystallization of the intergranular phases. The trend of re-crystallisation was observed by TEM in silicon nitride samples deformed at high temperature.[6] Many crystalline phases exist in the YSiAlON system,[24] but Dinger et al.[25] reported that crystallisation could begin from 1027 °C. This corresponds to the temperature range swept during the here described mechanical spectroscopy measurements.

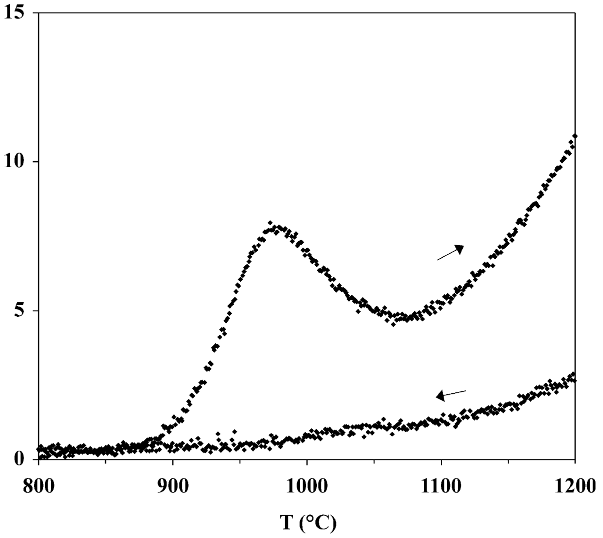

Fig. 6. Crystallisation effect observed by mechanical spectroscopy at 1 Hz in the 2h-1600 °C annealed material: heating at 1 °C/min after annealing and "quenching"; subsequent cooling at 1 °C/min from 1330 °C. Upon cooling, the peak has disappeared and the exponential background is much lower.

4. Conclusions and prospects

Like in classical silicon nitrides, the gas pressure sintered silicon nitride presents an internal friction peak and a high temperature exponential background. Nevertheless, according to the small amount of glassy phase contained in the as-sintered material, the intensity of the peak is very small. On the other hand, the peak grows after annealing at 1600 °C followed by a rapid cooling ("quenching") and its intensity reaches values near to intensities measured in silicon nitrides sintered with additives and so containing an important amount of glassy phase after sintering. This study shows that, at 1600 °C, the material may contain a liquid phase, which would be then fixed into an amorphous state during rapid cooling.

These results can be connected to creep and stress relaxation results[12] (Figs. 2 and 3). Both TEM observations[6] and mechanical spectroscopy measurements indicate that the dissolution of YSiALON crystalline phases occurs at high temperature. Considering that the internal friction peak height increases with the annealing time, the dissolution is a gradual process. The liquid phase formation explains the behaviour transition observed in the both creep and stress relaxation curves and so explains the sudden lost of creep resistance at around 1450 °C, which was reported in Testu et al.[12]

The difference in the glass transition temperature measured between as-sintered and annealed materials suggests a modification of the glassy phase composition. More investigations must be done to fully understand the mechanisms of dissolution, but the non-constant composition of the YSiAlON crystallised phases in the as-sintered material may complicate the analysis. Nevertheless, three probably conjugated mechanisms would occur: the melting of the small glassy pockets, the dissolution of YSiAlON crystallised pockets and the formation of a transitory liquid phase during the "α to β phase transformation" of the Si_3N_4 grains. To interpret the mechanisms of deformation at high temperature, the gas pressure sintered silicon nitride has to be considered like a material containing a liquid phase whose characteristics (quantity, composition, viscosity, size of the pockets, formation of films...) change during testing.

Acknowledgements

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