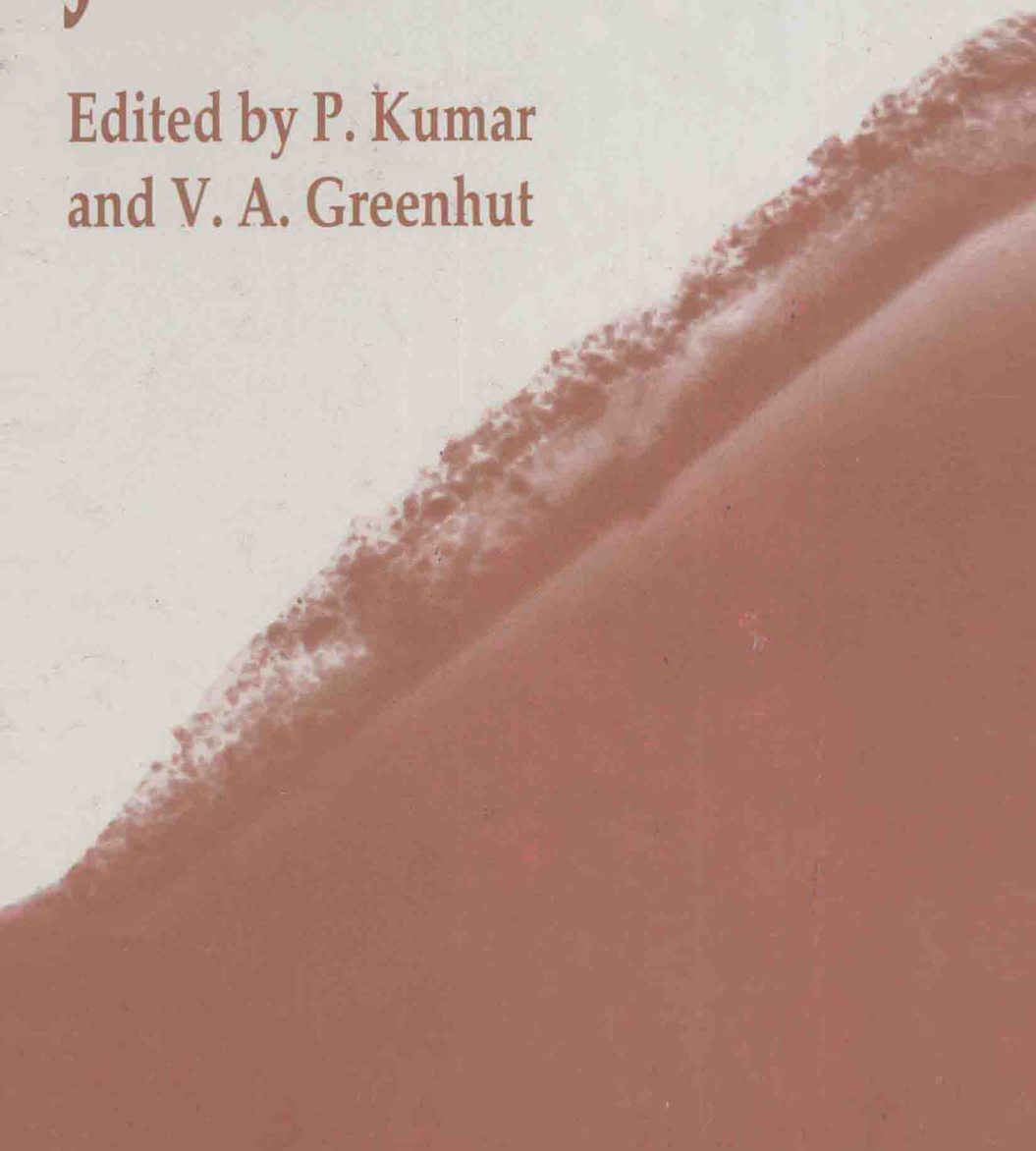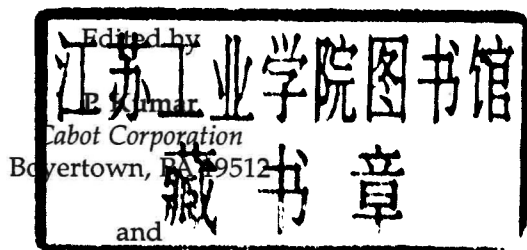# METAL-CERAMIC

JOINING

Edited by P. Kumar
and V. A. Greenhut

METAL-CERAMIC

JOINING

Proceedings of a symposium held on Metal-Ceramic Joining, sponsored by the TMS Refractory Metals Committee, held during the TMS Fall Meeting, Detroit, Michigan, October 8-9, 1990.

Edited by

P. Kumar
Cabot Corporation
Boyertown, PA 19512

and

V. A. Greenhut
Center for Ceramic Research
Rutgers, The State University of New Jersey
Piscataway, NJ 08855-0909

A Publication of

TMS

Minerals • Metals • Materials

Preface

A Symposium on "Metal-Ceramic Joining" was held during the Metals Congress in October 1990. It was sponsored by the Refractory Metals Committee of TMS. Most of the papers which were presented in this symposium are complied in this book. About two-third of the papers are related to the high-temperature applications; the remaining papers pertain to the electronic applications.

Cawley's paper is designed to serve as an introduction to some of the central issues associated with metal-to-ceramic joining. As such it is complementary to the overview of joining techniques, and is intended to serve as an introduction to the broad range of focussed work, reported in this volume.

Kaysser et al. calculated the high, failure-inducing residual stresses between a iron-nickel superalloy and silicon nitride, and compliant interlayers introduced to lower the thermoelastic residual stress. Hot isostatic pressing (HIP) was employed to diffusion bond various materials. Iron alloys with good formability and low thermal expansion were used as intermediate layers. These were combined with vanadium, hafnium and niobium-based layers which had the purpose of promoting bonding. The reactions at layer interfaces were examined by SEM and X-ray fluorescent microanalysis.

Although it has been recognized for a long time that the cool down cycle from the brazing temperature can be very important for the achievement of low residual stresses in metal/ceramic brazes, no methodology until now has permitted simulation of those stresses. The paper by Stephens, et al. examined the incorporation of minimum creep rate correlations for Cu into FEA (Finite Element Analysis) codes, and indicated that quantitative computational treatment of this problem, although in its infancy, shows promise for use as a predictive design tool.

Peteves and Nicholas joined the silicon nitride to sialon ceramics using active metal brazing and active metal diffusion bonding. A variety of materials sources were examined. The active metals, titanium and chromium were included in the alloy and/or vapor deposited upon the ceramic. The wetting response, bond strength and Weibull modulus were determined. The effect of various gas environments during bonding was examined. The structure and composition of the interfaces was examined by optical microscopy, SEM, and X-ray fluorescent microanalysis.

Majumdar and Ahmad also used active-filler metal approach to join cast iron to zirconia. The fracture toughness of the resulting bonds were used to confirm the theoretical model for a mixed-mode fracture in a ceramic-metal joint.

Greenhut gives an overview of the various techniques for joining and metallization of ceramics. He also discusses recent developments in these techniques.

Haber and Greenhut examined the bonding of aluminum to alumina using borosilicate glass in the ceramic composition. They found an optimum level of borosilicate glass addition for maximum strength.

In Levy's paper, the residual stress in brazed ceramic-metal joints was calculated and compared for a closed form model and iterative finite element analysis. The calculated stresses showed agreement with observed failure modes in active metal

V

braze joints between alumina and silicon carbide ceramics with titanium, tungsten, tantalum and titanium aluminide. The microstructure and chemistry of joined interfaces was examined by optical microscopy and SEM/EDS analysis.

Holowczak et al. investigated the effect of sintering aids in alumina on the peel strength of copper-alumina bonds. They conclude that sintering aids significantly affect the peel strength; simultaneous additions of calcia and magnesia improve the bond strength.

Park et al. conducted the active metal brazing of nodular iron and magnesia-stabilized zirconia by predeposition of titanium on the ceramic substrate surface and use of a braze containing titanium active metal. Ultrasonic C-scan tests and direct examination of large scale joints showed voids and poor contact in the case of predeposition. Active filler metal showed superior contact and bonding. Sources for possible titanium oxidation were identified and examined using equilibrium thermodynamic calculations.

In Knapp's paper, alumina ceramics were glass bonded to each other employing a glass with the composition of anorthite. The authors term this technique "silicate brazing" in analogy to metallurgical methods. Bond strength was quite variable as determined by four point bending with an average strength of about 145 MPa. Partial crystallization of the glass bond layer deteriorated strength. Interfaces were characterized for microstructural and elemental distribution by optical microscopy and electron microprobe analysis.

Carpenter of NIST discusses the measurements of a variety of properties of the ceramic-metal bonds in microelectronics and multilayer capacitors. These measurements are required in order to understand local and interfacial properties in a device. In-service failures, design and new applications require such measurements. The increased spatial density of these features requires further development of property measurement techniques. The present state of such techniques as well as possible future developments are discussed as they pertain to: dielectric properties, thermal diffusivity, thermal expansion, stress-strain behavior, adhesion, fracture toughness, residual stress and curing of polymeric materials.

C. H. Li discussed the graded seals for metal-ceramics joints. The thermal coefficient of expansion of these seals varies axially, which minimizes the dynamic mismatch stresses of the joint. These seals are particularly useful for mounting fragile semiconductors and superconductors to metal substrate for improved bond strength, heat dissipation and device performance.

Brow and Loehman investigated the effect of titanium additions to the eutectic braze compositions via the electron microscopy of the interface in metal - AlN system. Titanium reduces the contact angle and improves the wetting. In addition, the formation of TiN at the interface improves the bonding.

Typically, glass technologists and ceramists consider metals to be relatively inert; while metallurgists tend to have the same viewpoint with respect to glasses and ceramics. The fallacy of these viewpoints was exposed in the paper by Knorovsky and Brow looking at a glass ceramic to metal debonding problem between matched coefficient of expansion materials (304L SS and a lithium silicate-based glass ceramic). In this case, an integrated materials system approach was necessary to understand the problem (a phase transformation on the metal side of the interface driven by Cr depletion into the glass-ceramic) and look for solutions.

VI

Chiang et al. investigated bonding of AlN-Cu system using gas-metal eutectic and solder methods. Several important factors were identified to play a major role on the bond-strength. High thermal conductivity of AlN makes it an attractive alternate to alumina in electronic packages.

We would like to thank the authors for sending manuscripts in on time. Catherine Yoder and Olympia McNicols have provided invaluable secretarial assistance.

P. Kumar
V. A. Greenhut

Table of Contents

III. Electronic Applications

High
Temperature
Applications

INTRODUCTION TO CERAMIC-METAL JOINING

James D. Cawley

Department of Materials Science and Engineering
The Ohio State University
2041 College Road
Columbus OH 43210-1178

Abstract

This paper is designed to serve as an introduction to some of the central issues associated with ceramic-to-metal joining. As such it is complementary to the overview of joining techniques, and is intended to serve as an introduction to the broad range of focussed work, reported in this volume.

Joining is a fundamental processing step and consequently has a long history as well as a continually expanding scientific base. Several comprehensive review articles [1-5], a conference proceedings [6] and a text [7] on ceramic joining have all been published in recent years. Rather than attempt a comprehensive overview in this manuscript, a selected set of illustrative examples is employed.

Definitions

Joining may be defined as the controlled formation of a bond between two constituents of a component after a desired geometrical geometrical arrangement has been established. A bond may, in turn, be defined as a low energy state, i.e. an energy penalty is associated with separating two bonded interfaces. It is traditional to discuss bonds of two types: primary (or chemical) and secondary (or physical). Both are usefully exploited in metal-ceramic joining.

The process of joining is simply to bring the adherends (or materials to be joined) into approximate geometry while in a transient high energy state and to allow the system to relax, or dissipate this energy. The driving force for bond formation may include several terms; for example, the reduction of surface energy and the relief of chemical potential gradients through diffusion and/or chemical reaction. The controlled application of heat (either local melting or isothermal annealing) may be used to determine the kinetics of bond formation. In some cases, chemical reactants are brought into contact just prior to bonding and the kinetics of the resultant reaction(s) control bond formation.

Joining may also be defined as a secondary processing step and as such the consequence of the the joining procedure on the microstructure, and any concomitant change in properties, must be considered. In general, joining processes and materials are selected which minimize microstructural changes. This issue is particularly acute when attempting to join materials which are characterized by different classes of interatomic bonding.

As a general rule, interatomic bonding in metals is primarily metallic or mixed metallic/covalent, in ceramics interatomic bonding may be considered either ionic, covalent or mixed ionic/covalent, and organic polymers are characterized by intramolecular covalent bonding and intermolecular hydrogen or van der Waals bonding. One advantage of classifying materials based on interatomic bonding (as opposed to, for example, the end use of the material such as structural materials, electrical materials, optical materials...) is that many of the properties relevant to the design of a joining process are strongly correlated to interatomic bonding, see Table I.

Joining Processes

A wide variety of techniques have been employed in ceramic-to-metal joining. These include: adhesive bonding; metal brazing; silicate brazing; and diffusion bonding. It is possible to identify similarities as well as differences between these processes. The first three all involve the use of a foreign interlayer material between the contacting surfaces of the adherends and therefore (at least) two qualitatively different interfaces and produced during the joining operation. The properties of the interlayers, however, are determined by secondary bonding in the case of adhesive bonds in contrast to chemical bonding in the case of brazing and diffusion bonding.

Table I. Material Properties Associated with Interatomic Bonding

Metallic Bonding
- •Close packed crystal structures
- •Small volume change upon solidification accommodated by dislocation motion
- •High relative thermal expansion
- •May have modest melting temperatures

Ionic Bonding
- •Close packed crystal structures
- •Limited dislocation mobility (localized charges)
- •May have large solidification volume change
- •Intermediate relative thermal expansion
- •High melting temperatures (with multivalent ions)

Covalent Bonding
- •Open crystal structures
- •Limited dislocation mobility (directional bonds)
- •May expand upon solidification
- •Low relative thermal expansion
- •May decompose or sublime

Secondary Bonding
- •Amorphous or partial crystallization
- •Low (several hundred degrees Celsius) melting points

Adhesive joints offer a great deal of flexibility. They may be formed at, or near, room temperature (which presumably will be the use temperature), have near zero residual stress, and distribute stresses during service. However, adhesive joints may be limited in terms of hermeticity, electrical properties, and high temperature service. Metallic brazing, silicate brazing, and diffusion bonding are all exploited in structural and electronic applications; e.g., active metal brazing of silicon nitride turborotors to steel shafts, solder glasses for electronic packaging, and diffusion bonding of pins to ceramic heat sinks for electronic applications.

These three procedures al involve heating dissimilar materials to high temperatures. As a result, the issues of interfacial chemistry and thermal stresses are central to the success of each type of joint.

Interfacial Chemistry

Wetting and spreading are important when a liquid phase is present at the contacting surfaces (i.e. brazing). For nonreactive systems this is typically analyzed using the Young-Dupré equation which relates the equilibrium angle of a sessile drop on a planar surface measured through the liquid, θ, to the surface tensions

associated with the solid/vapor, solid/liquid and liquid/vapor interfaces (γ_{sv}, γ_{sl} and γ_{lv} respectively) and may be written [e.g. 7]

$$\cos\theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}. \qquad\qquad \text{Eqn-1}$$

It is conventional to distinguish three regimes of behavior in terms of θ or $\cos\theta$:

Nonwetting	$\theta > 90°$	$\cos\theta < 0$
Wetting	$\theta < 90°$	$\cos\theta > 0$
Spreading	$\theta = 0°$	$\cos\theta = 1$.

It is evident that spreading is simply a special case of wetting. Since interfacial energy is always positive the sign of the right hand side of Eqn-1 is uniquely determined by the difference $\gamma_{sv} - \gamma_{sl}$. As long as the wetted surface is of lower energy than the exposed surface, wetting will result. The magnitude of the effect is controlled by the value of γ_{lv}. When $\gamma_{lv} >> (\gamma_{sv} - \gamma_{sl})$ then $\cos\theta \to 0$ (or $\theta \to 90°$) regardless of the sign of the numerator. On the other hand, when $\gamma_{lv} << (\gamma_{sv} - \gamma_{sl})$, $\cos\theta \to$ becomes a large positive number and spreading results ($\theta \to 0°$).

In most brazing operations wetting is required, but spreading is undesirable. Spreading may lead to excessive surface flow, deplete the joint region of the filler metal or cause sticking to the support structure or clamps, etc. This problem is schematically illustrated in Fig. 1. A neutral condition, i.e. no spreading or dewetting, is preferred when a foil of the braze metal is preplaced in between the contacting surfaces. Filling a gap through a capillary action does not require spreading either. The expression [8] for the velocity of the fluid front during capillary rise in between two plates, v, is

$$v = d \, \gamma_{lv} \cos\theta / (4 \, \mu \, h)$$

where d is the separation between the plates, h is the rise after a given time and μ is the viscosity of the liquid. The equilibrium rise against gravity, H, (the maximum extent of penetration by the liquid) may be expressed as

$$H = 2 \, \gamma_{lv} \cos\theta / (\rho \, d)$$

where ρ is the density of the liquid. Both quantities are dependent on the product $\gamma_{lv} \cos\theta$ which is equivalent to the difference $\gamma_{sv} - \gamma_{sl}$ and therefore independent of γ_{lv}. The physical significance of this is that capillary penetration does not create liquid surface exposed to the atmosphere. A high value for γ_{lv} may be beneficial, as it results in a large energy penalty for fluid flow out of the joint.
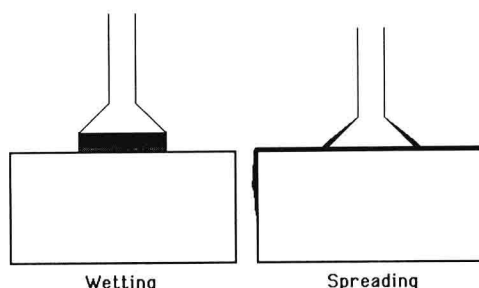
Wetting   Spreading

Fig. 1.The schematic on the left represents the behavior expected when the molten metal wets the contacting surface, but the interfacial tension associated with the liquid vapor interface is high. The figure on the right depicts the deleterious nature of excessive surface flow as a result of spreading, i.e. low liquid surface tension.

The low surface tension of most ceramics has the consequence of making it unlikely for many molten metals to satisfy the wetting condition. As an example, the interfacial energies for aluminum oxide and various nonreactive metals is shown in Table II. In addition, wetting alone is insufficient to assure the formation of a strong bond. Molten silicates may wet a metal surface, but not form chemical bonds at the interface due to the abrupt discontinuity in the type of interatomic bonding.

Material	Interfacial Energy (mJ/m^2)			θ (deg)	T($^\circ$C)
	γ_{sv}	γ_{sl}	γ_{lv}		
Al$_2$O$_3$	905	-	-	-	-
Cu	-	2245	1220	170	1100
Fe	-	2270	1720	128	1550
Fe-3.9C	-	1365	1720	105	1570
Ni	-	2205	1725	138	1475

B. C. Allen and W. D. Kingery, Trans. AIME, 215, p. 30-7 (1959).

All of the above discussion relates to material properties at or very near to the interface and therefore may be easily altered through the use of coatings produced either in a discrete processing step or in situ as the result of a chemical reaction. The goal is often expressed as grading the interatomic bonding near the interface to allow brazing between like-to-like surfaces. Either the surface of the ceramic or the metal may be altered. Metallization of a ceramic (e.g. the moly-mangenese process on debased alumina [8,9] or Cr-metallization of silicon carbide [10]) prior to metal brazing and oxidation of a metal prior to glass-to-metal sealing [8] are examples of the inclusion of a discrete processing step and active metal brazing [4,11] (which

relies on segregation and reaction to form a thin coating on the ceramic) and the use of adherence oxides [3,12] in porcelain enameling are examples of techniques which exploit in situ reactions.

The exploitation of in situ reactions is desirable in that it simplifies the processing sequence, but the often the desired reaction products are metastable and aging of joint at elevated temperatures may lead to degradation of the joint.

The development of a strong bond at elevated temperature, either by brazing or diffusion bonding, does not assure good system performance. Reaction products at the interface may lead to embrittlement and thermal stresses which develop during cooling may be intolerable.

Thermal Stresses

Differential thermal strains during cooling are to be expected in general. To a first approximation, differential thermal strain, $\Delta\varepsilon$, may be evaluated by the mismatch in coefficients of thermal expansion (CTE), $\Delta\alpha$, by

$$\Delta\varepsilon = \Delta\alpha\,\Delta T \qquad\qquad\qquad\qquad \text{Eqn-2}$$

and, depending on the geometry of the specimens as well as the values of the relevant elastic constants and ductilities, the resultant state of stress may be analyzed. As illustrated in Fig. 2, the overlap between metallic systems and ionic ceramics is limited to refractory metals and there is almost no overlap with between metals and covalently bonded ceramics.

Although ceramics are relatively strongly when loaded in compression, it is not sufficient to simply choose a set of materials which should result in compressive stress in the ceramic since, depending on joint geometry, there may be localized regions of high tensile stress, as illustrated in Fig. 3. The formation of direct bonds between a metal and a ceramic therefore requires either an exceptionally good match in CTE or carefully designed joint geometry. The niobium-alumina system is an example of the former and Houskeeper seals [8] (in which feather edged copper is joined to glass of low relative CTE) is an example of the latter.

Even when two materials have similar net thermal strains when cooled from the bonding temperature to room temperature, nonlinear thermal expansion (e.g. glasses heated through the glass transition or as a result of displacive phase transformations) may result in significant transient stresses. This is schematically illustrated for the case of a metal and a silicate glass in Fig. 4. The local stresses may be reduced either through stress relaxation (e.g. viscous flow of a silicate glass or plastic flow of a ductile metal).

Grading of the CTE difference through the use of interlayers is a one standard approach to minimizing the development of residual stress. In one approach a thin slab(s) of a material(s), which remains solid throughout the joining process, having an intermediate CTE is placed between the adherends. The process, therefore, requires the production of two physically distinct joints. In some instances different processes (or braze metals) may be used at the two interfaces. An alternate procedure is to produce a composite interlayer which has an intermediate CTE. Usually this consists of a low expansion phase (e.g. carbon fibers) to be distributed within a high expansion matrix of a brazing alloy (e.g. Ag-Cu alloys). A possible complication associated with such a composite is that the inclusion of a high specific surface area nonoxide phase in a reactive brazing alloy may consume a large fraction of the active element and significantly alter the composition of the alloy.
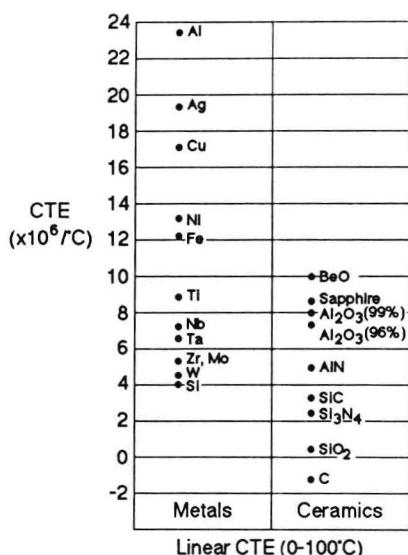
8

Fig. 2. Graphical depiction of the thermal expansion coefficients of selected ceramics and metals at low temperature. Reference to this figures indicates large thermal strains will be associated with brazing alloys based on the silver-copper eutectic and that covalently bonded ceramics are particularly difficult to match. (After T. Tanaka, H. Morimoto and H. Homma, Nippon Steel Tech. Rep. No 37, 1988, p. 35)
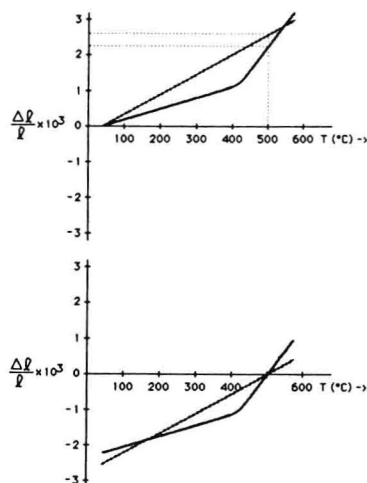

Fig. 3. Schematic illustration of differential thermal strain versus temperature associated with a glass-to-metal seal. The upper graph depicts thermal strains experienced upon heating (with the specimens unbonded and l_o is defined as l at room temperature) and the lower curves refer to shrinkage during cooling from an arbitrary bonding temperature of 500°C (in this case, l_o is defined as l at 500°C). Although the overall thermal strain from 500°C - RT is small and favors compression in the glass differential strain, a large transient tensile stress would be produced during the initial stages of cooling when the contraction rate of the glass is high.

9