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High-temperature glass-ceramics of the $BaO–Al_2O_3–SiO_2–Ta_2O_5$ system and molybdenum metal composites

D. BAHAT
Geology and Mineralogy Department, Ben-Gurion University of the Negev, Beer Sheva, Israel

G. P. K. CHU
G.T.E. Sylvania, Lighting Center, Danvers, MA 01923, USA
Danvers, MA 01923, USA

Glass-ceramics which consist of tantalum pentoxide (Ta_2O_5), hexacelsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$), and aluminium tantalate ($Al_2O_3{\cdot}Ta_2O_5$) are described. These glass-ceramics can form refractory composites up to 1400° C with molybdenum metal. The glass-ceramics and metal have compatible physical and chemical properties which allow close thermal expansion and excellent bonding.

1. Introduction

The investigation presented below concerns an effort to produce a glass-ceramic metal composite stable at high temperatures (up to 1400° C). The present paper is mostly related to the following representative glass composition, $SiO_2 = 24.5$, $Al_2O_3 = 11.5$, $BaO = 14.0$, and $Ta_2O_5 = 50$ nominal weight per cent (which is equivalent to $SiO_2 = 56.2$, $Al_2O_3 = 15.6$, $BaO = 12.6$, and $Ta_2O_5 = 15.6$ mole per cent), and its composite with molybdenum. Glasses and glass-ceramics of the above composition which are notably rich in tantalum oxide were studied in detail since they satisfy the following requirements: (1) Very good heterogeneous nucleation of the glass by the tantalum oxide into crystalline phases of high apparent stablility (not necessarily thermodynamic stability). (2) Both glass and glass-ceramic have close matching of thermal expansion properties with molybdenum. (3) The tantalum components of the glass-ceramic provide excellent bonding with the molybdenum metal. (4) The composite material has exceptional refractory properties (> 1400° C).

The procedure of forming the glass, glass-ceramic, and the composite is given below and the crystallographic, thermal, dilatometric and microstructural properties are characterized.

2. Experimental techniques

2.1. Preparation of glass

The glasses were prepared of Morgan Sand ($SiO_2 = 99.8\%$), T-61 alumina oxide ($Al_2O_3 = 99.7\%$), barium carbonate (reagent), and tantalum oxide (Ta_2O_5, reagent). The batch materials were weighed to an accuracy of 0.1 g and dry mixed. Standard batch mixtures of 1200 g were melted at 1700° C in a gas–oxygen furnace generally for 4 h in platinum crucibles. Quenched patties were made from melts and annealed at 800° C for one hour, also canes were drawn from the melts.

2.2. Glass and molybdenum composites

A molten glass free from seed and cord was directly brought into contact with molybdenum metal which had been degreased and cleaned. Oxides were dissolved from metal by either cathodic treatment in dilute H_2SO_4 or hot $NaNO_2$. For the degassing treatment, the metal was heated in hydrogen and introduced to vacuum.

The sealing between the molybdenum metal and the glass was by one of the following pro-

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cesses: flame working, dipping, pressing, or centrifugal spinning, depending on the size and shape of the metal–glass component. Most of the samples tested in the laboratory were processed by dipping a metal sheet into molten glass or pouring and pressing the molten glass on to the metal component. During the processing, an excessive amount of oxidation was avoided.

After forming the glass–molybdenum composites, they were annealed in vacuum or in an inert atmosphere furnace to relieve the excessive stress which might result from the processing. The extent of stress relieving was examined under a polariscope before and after annealing.

2.3. Glass-ceramics and molybdenum composites

The formed glass and molybdenum composites were treated in either of two ways:

(a) The composites, after hot forming, were immediately transferred into a heat treating furnace at somewhat below the nucleation range of the glass (900° C) and then reheated slowly at the rate of about 300° C per hour to the nucleation range with a designated period of holding (20 to 60 min) depending on the size.

(b) In the other method, the composites were annealed and then examined for defects or failure at room temperature before they were reheated for ceraming according to the above schedule.

2.4. Analytical techniques

Glass-ceramics were routinely examined by X-ray diffraction. Selected specimens were examined by differential thermal analysis (DTA) at 12.5 and $25^\circ \mathrm{C\,min^{-1}}$ heating rates. Alumina was used as the reference. The thermal expansion measurements of the glass and glass-ceramic specimens were obtained on a differential dilatometer with reference to the expansion of alumina. Heating and cooling rates were $400^\circ \mathrm{C\,h^{-1}}$ with readings taken at intervals of 100° C. Interfaces between the molybdenum and glass-ceramics were examined by electron microscope techniques. For the scanning electron microscope investigation, samples were prepared by fracturing a section of the glasses and glass-ceramics, mounting on a specimen holder, and evaporating a conductive film of approximately 400 Å aluminium onto the surface to be examined. Observations were made perpendicular to and at 45° to the samples. For the transmission electron microscope investigation, replicas were prepared from fractured and from fractured-and-etched surfaces.

3. Results and discussion

3.1. Nucleation and crystallization

The first phase that crystallized on heating the glass between 800° C and 1000° C was tantalum pentoxide (Ta_2O_5). By studying glasses of different tantalum oxide concentrations (maintaining the same base glass as far as silica, alumina, and barium oxide were concerned), it was found that tantalum oxide separated readily from the glass on heating only when its concentration in the glass exceeded 20 wt% (equivalent to 4.4 mol%). In glasses with lower concentrations of tantalum oxide, phase separation was poor and consequently heterogeneous nucleation was unsuccessful.

The initial Ta_2O_5 crystals which were formed in the glass after a heat treatment at 1000° C for 2 h were extremely fine (<100 Å) and the X-ray reflections (Table I) were diffuse (Fig. 1). The crystals resembled low tantalum pentoxide reported previously [1] (note also [2]), and did not show similarities to the high tantalum pentoxide [3]. Although these crystals have a high index of refraction (2.20 according to Yound [4]), the glass-ceramic at this stage was transparent.

When the glass was further heated at 1000° C (for 8 h), the X-ray reflections of the tantalum oxide became sharp and, in addition, β-hexacelsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) [5], and aluminium tantalate ($Al_2O_3{\cdot}Ta_2O_5$) precipitated [6]. Doherty *et al.* [7] have described a different kind of large scale phase separation [8]. They showed that in glasses of the $Li_2O–Al_2O_3–SiO_2–TiO_2$ system, early separation of a $Al_2Ti_2O_7$ phase served as hetero-

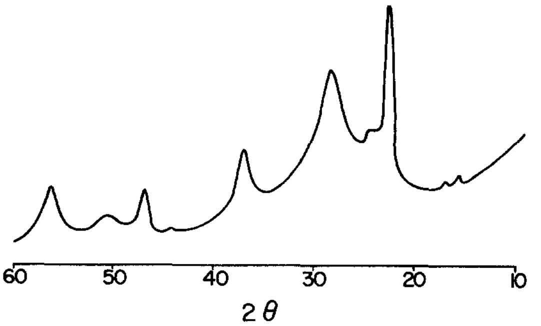

Figure 1 A diffuse X-ray diffraction pattern of Ta_2O_5 fine crystallites in transparent representative glass following a heat treatment of 2 h at 1000° C. A pattern with a rounded trace between $\theta = 22^\circ$ and $\theta = 35^\circ$ representing the bulk glass is shown.

TABLE I X-ray powder data of glass-ceramics

Glass-ceramics*		$AlTaO_4$ [6]		β-$BaAl_2Si_2O_8$ [5]		Ta_2O_5 [2]		Ta_2O_5 (Glass-ceramic†)	
$d_{obs.}$(A)	I/I_1	d (A)	I/I_1	d (A)	I/I_1	d (A)	I/I_1	$d_{obs.}$(Å)	I/I_1
7.76	9			7.79	112				
6.19	10	6.15	10						
5.07	55	5.07	100						
4.46	6					4.295	1		
4.37‡	5								
3.96	80			3.963	47				
3.93	100					3.885	100	3.91	100
3.72	30	3.69	60						
3.59	75	3.58	80						
3.50	40					3.485	1		
3.35	10					3.338	5		
3.23	20	3.22	20						
3.09	55					3.150	100	3.13	65
3.06	100	3.07	80						
2.98	70			2.977	59				
2.92	25	2.89	30						
2.79‡	65								
2.70	50	2.69	60						
2.66	30			2.659	15				
2.61	30			2.602	22				
2.53	20	2.51	30						
2.46	25	2.45	30						
2.41	30					2.447	63	2.45	25
2.37	8	2.36	5						
2.30	20	2.29	30						
2.26	15			2.266	15				
2.24	8	2.23	30						
2.21	10			2.206	11				
2.16	13	2.14	30						
2.10‡	6								
2.04	15	2.04	30						
1.98	20	1.97	20						
1.96	45			1.951	60				
1.91	10					1.945	20	1.95	25
1.88	20	1.89	20						
1.86	20	1.85	20						
1.85	20	1.82	20						
1.84	6					1.800	12	1.80	5
1.78	45	1.77	60						

*Heat treatment at 1250° C for 4 h.
†Heat treatment at 1000° C for 2 h.
‡Unaccounted reflections.

geneous nucleation for volume crystallization of β-quartz solid solution. In the present system a separation of Ta_2O_5 preceeded the separation of $Al_2Ta_2O_8$, and the former served as a nucleating agent for the latter. On heating the glass-ceramic at 1100° C for 4 h, the same phases were maintained (tantalum oxide and β-hexacelsian as major phases, and aluminium tantalate as a minor phase). However, at 1150° C, some changes in the tantalum oxide reflections occurred. The intensity of the reflections generally decreased and there was a slight change in spacing. Corresponding with the above changes, additional reflections at $d = 4.37$, particularly at $d = 2.79$ and at $d = 2.10$ Å appeared, possibly indicating a phase transformation in tantalum oxide.

The X-ray pattern obtained due to a heat treatment at 1150° C remains essentially the same up to 1400° C, except for slight additional changes in spacing of the tantalum oxide reflections. (Note differences of Ta_2O_5 reflections at 1000 and 1250° C, Table I). After a heat treatment at

TABLE II Summary of thermal effects in the representative glass

Temperature (° C)	Thermal effect	Structural change
820	endothermic	annealing of glass
965	exothermic	crystallization of Ta_2O_5
1060	exothermic	crystallization of hexacelsian
1125	exothermic	crystallization of aluminium tantalate
1145	endothermic	resorption of Ta_2O_5
1165	exothermic	precipitation of a tantalum oxide-rich phase
1320	endothermic	slight remelting

1400° C for 3 days, no significant change in X-ray pattern was observed in comparison with the pattern obtained after a heat treatment at 1250° C, except for a small reduction in the intensity of the β-hexacelsian reflections.

3.2. Thermal properties of the representative glass (glass-ceramic)

The characteristic thermal behaviour of the representative glass is summarized in Table II, when the powdered sample (in 100 to 150 mesh size) was subjected to differential thermal analysis (DTA) at a rate of 12.5° C per minute upon heating. The endothermic dip starting at around 820° C indicates the beginning of the annealing. The major exothermic peak at 965° C represents the crystallization of tantalum pentoxide which separates out readily during the heat treatment. Further two small peaks represent minor crystallization around 1060 and 1125° C of hexacelsian and aluminium tantalate, respectively. At about 1145° C, some resorption or partial dissolution of the Ta_2O_5 phase due to a phase transformation occurs, and this is followed at around 1165° C by a further crystalline precipitation. The small dip at 1320° C may involve a small amount of resorption (possibly of hexacelsian) but it does not affect significantly the physical properties of the glass-ceramic.

3.3. Thermal expansion

The thermal expansion of molybdenum is $55 \times 10^{-7}\,{}^\circ C^{-1}$ (between 25 and 1000° C) and the thermal expansion of the tantalum oxide-rich barium aluminosilicate glass is $43.4 \times 10^{-7}\,{}^\circ C^{-1}$ (between 25 and 700° C). One of the advantages offered by the glass-ceramic derived from the glass by a heat treatment was a close expansion to the glass, and somewhat lower than that of the metal ($47.5 \times 10^{-7}\,{}^\circ C^{-1}$ between 25 and 1000° C after a heat treatment at 1100° C for 1 h). As a result of the temperature reduction following the composite processing, the contraction of the metal is higher and the glass-ceramic is brought into compression.

The coefficient of expansion of the glass-ceramic represents a compromise determined by the phases present. The increase of hexacelsian content raises the expansion, and the presence of a higher proportion of crystalline tantalum phases decreases it. Various measurements carried out on the glass-ceramic following variations in heat treatments indicated fairly close rates of expansion and contraction with no hysteresis observed (note Fig. 2). This factor adds to the stability of the composite during the temperature cycling. After a heat treatment for 72 h at 1400° C, the coefficient of expansion of the glass-ceramic remained $46.5 \times 10^{-7}\,{}^\circ C$.

3.4. Microstructure of the glass-ceramic–metal composite

The interface between the molybdenum and the glass-ceramic following a heat treatment of 2 h at 1150° C is shown in Fig. 3. Growth of new crystal-

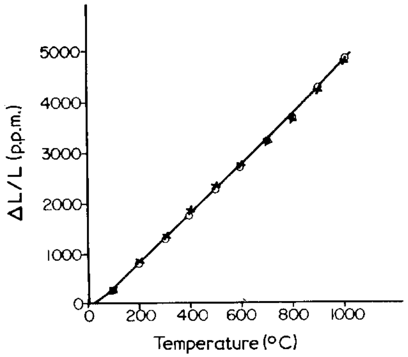

Figure 2 Thermal expansion curves of the representative glass-ceramic following two heat treatments. Heat treatment of 4 h at 1000° C followed by 4 h at 1100° C is marked by circles, and a treatment of 1 h at 800° C followed by 2 h at 1250° C is marked by ×.

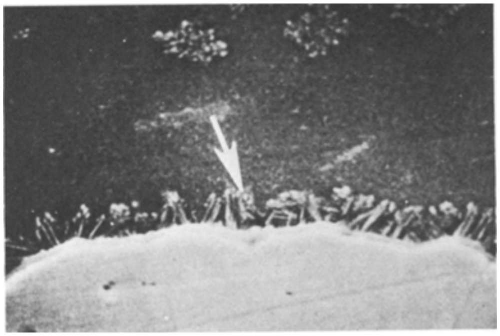

Figure 3 A SEM photograph showing the interface between the glass-ceramic (upper part) and the metal (lower part). The glass-ceramic is mostly fine grained. Larger crystals of about 1 μm, have grown along the interface.

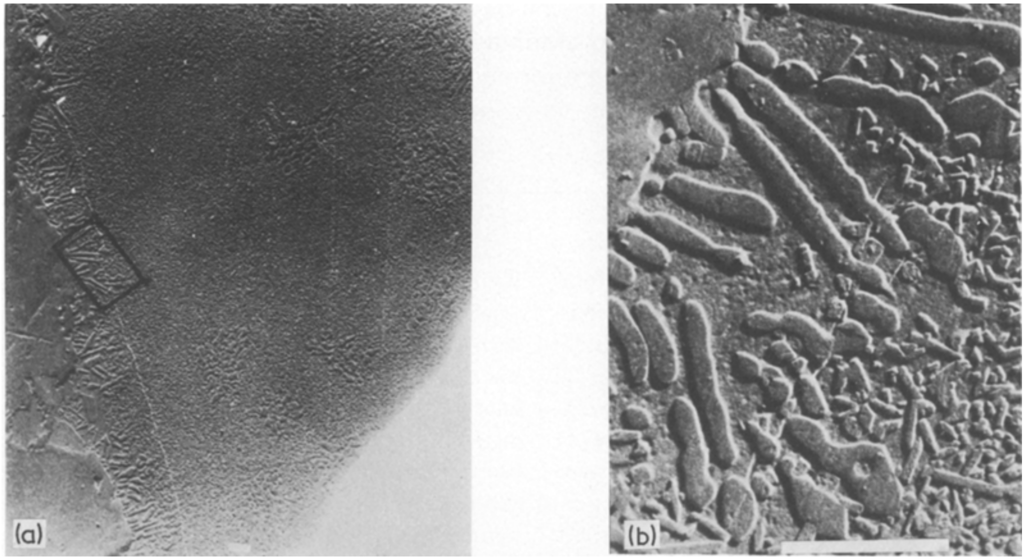

Figure 4 A TEM photograph showing the interface between the glass-ceramic (right side of each photograph) and the metal (left side of each photograph). The photograph in (b) is an enlargement of the rectangle in (a). Crystals in the bulk of glass-ceramic are below 0.5 μm in size. Oriented larger crystals of about 1 to 2 μm are grown along the interface. The white bar on the lower part of the right photograph indicates 1 μm. Note a fracture propagated along the contact between the fine and coarse grain region, rather than along the contact between the glass-ceramic and the metal.

lites at the interface is shown. Fig. 4 shows the intimate contact between the glass-ceramic and metal following a heat treatment of 2 h at 1200° C. When excess stress is applied a transgranular fracture at the glass-ceramic body rather than along the glass-ceramic–metal interface is formed.

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