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Leaching Behavior of Si–Y–Al–O–N Glasses

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SUMMARY

Oxynitride glasses in the yttrium sialon family were leach tested under static conditions in deionized water at 40, 90 and 200°C for 28 days. Results indicate a lower silicon release in the compositions tested than that of fused silica glass or crystalline quartz when tested under identical conditions.

1. INTRODUCTION

Interest in oxynitride glasses has recently increased to a significant level as attempts are made to identify and develop new glasses and ceramics for potential applications ranging from electrical insulators to structural components in heat engines.[1] Of specific interest has been the effect of nitrogen on glass physical properties such as glass transition temperature, microhardness, fracture toughness, and thermal expansion.[2,3] Additional studies have also examined the electrical properties of selected oxynitride glasses.[4] Little, if any, detailed work has been reported to date on the chemical durability (leachability) of oxynitride glasses. In a paper on the yttrium sialon glass system, Loehman[5] reported that, while no trend in the degree of leaching with nitrogen content was apparent after testing for 350 h in 95°C distilled water, two of the three glass compositions tested showed lower weight losses than literature values for vitreous silica under the same conditions. Other work reported by Loehman[3] indicated that nitrogen increased leach resistance in two additional oxynitride glass systems; the addition of AlN to a sodium–barium–phosphate glass increased its leach resistance by more than a factor of 100, and a high nitrogen content La–Si–O–N glass was reported to be very resistant to alkali attack at elevated temperatures.

In the leach testing reported to date for oxynitride glasses, the main indicator of leachability has been the evaluation of post-test weight loss. Leaching processes are sufficiently complex though, that a simple weight loss determination is insufficient to completely characterize the materials leaching behavior.[6] The experimental work reported here employed static leach test procedures developed to evaluate the chemical durability of proposed nuclear waste materials.[7] As such, emphasis was on the release of specific elements rather than on weight loss alone. The results presented herein compare the behavior of three glass compositions in the Si–Y–Al–O–N system with that of high purity fused silica glass and single crystal quartz, tested under identical conditions of time, temperature, solution, and atmosphere. Also reported is the variation of oxynitride glass leach behavior with temperature and with nitrogen content.

The work reported here is not intended to be a definitive end result, as certainly a more detailed and extensive testing scheme could be developed. But rather, this work presents additional comparative chemical durability data, more detailed than simple weight loss, on a glass system heretofore not extensively tested.

TABLE 1
Chemical Analyses of Oxynitride Glasses (in wt%)

Element	*Glass batch*						
	a		*b*		*h*		
	Nominal	*Analyzed*	*Nominal*	*Analyzed*	*Nominal*	*Analyzed*	
Al[a]	6·0	6·5	12·6	12·7	9·1	9·6	
Si[a]	18·9	18·0	13·2	13·2	14·3	14·3	
Y[b]	39·8	42·6	41·5	43·0	45·1	45·4	
O[c]	32·2	29·3	26·2	24·8	24·4	23·1	
N[d]	3·1	3·3	6·5	6·4	7·1	7·2	
Fe[b]		0·11		0·13		0·09	
B[b]		~0·1		~0·1		~0·1	trace levels

[a] Average of emission spectroscopy and atomic absorption spectroscopy.
[b] Emission spectroscopy.
[c] Vacuum fusion, precision $\pm$ 0·8%.
[d] Kjeldahl distillation, precision $\pm$ 0·2%.

2. MATERIAL PREPARATION AND TESTING

2.1. Glass preparation

Glasses in the system Si–Y–Al–O–N were prepared from oxide and nitride starting materials that were blended, preslugged, and melted between 1650 and 1700°C in boron nitride crucibles in a nitrogen atmosphere. The preparation and properties of the three glasses used in this study (Table 1) have been discussed in detail elsewhere.[8,9]

Parallelepiped leach samples, with a nominal surface area of 150 mm^2, were prepared from bulk glass of each composition by diamond saw sectioning. Cut samples were ultrasonically cleaned twice in acetone and once in methanol, and stored under vacuum until used.

2.2. Leach testing

Leach testing was conducted on the samples described above using a static leach test technique.[7] Samples of compositions ‘b’ and ‘h’ were leach tested in deionized water at 40, 90 and 200°C, while composition ‘a’ was leach tested only at 200°C. The duration of all tests was 28 days with a sample surface area to leach solution volume ratio (SA/V) of 20 m^{-1}. All tests were conducted by placing the glass leach sample and the appropriate volume of solution inside individual 0·38 mm wall thickness, closed-one-end gold capsules. After loading, each capsule was crimped closed, welded shut, marked, and leak checked, prior to placement in either an autoclave system[10] or convection oven. The chamber of the autoclave was partially filled with deionized water to assure pressure equilibration across the capsule wall during testing. The capsules were heated to 200°C from room temperature and allowed to furnace cool at the end of the test, prior to unloading. Average heating and cooling time was about 4 h. Tests at 40°C and 90°C were conducted by placing the sealed capsules in a mechanical convection oven at the appropriate temperature. Leach solution elemental analyses were performed by inductively coupled argon plasma atomic emission spectroscopy (ICP).

3. RESULTS AND DISCUSSION

Table 1 gives the nominal starting and analyzed final compositions of the three glasses investigated. Since all of the oxides in the glass batches were of high purity (99·5% or higher), the iron contamination must have come from the silicon nitride powder used as the nitrogen-containing component.

The low levels of boron indicate that minimal interaction occurred between the glasses and boron nitride crucibles during melting.

For comparison with previously cited work, the results of weight loss measurements on the samples tested are given in Table 2. In agreement with previous weight loss results, all oxynitride glass compositions tested lost less weight than either silica glass or crystalline quartz. From these same data (comparing the different compositions tested at 200°C) it might

TABLE 2
Weight Loss from Leach Testing in Deionized Water at Various Temperatures
(All specimens were tested with $SA/V = 20\,m^{-1}$)

Sample/comp.	*Leach temperature/°C*	*Weight loss/%*
Silica glass	200	0·56
Quartz	200	0·26
a	200	0·02
b	40	0·02
	90	0·05
	200	0·07
h	40	0
	90	0
	200	0·04

also be concluded, as with previous work, that there is no systematic trend in the degree of leaching with nitrogen content. However, as mentioned earlier, weight loss alone is insufficient to completely characterize the total leaching process. Results of silicon, and yttrium and aluminum elemental release are given in Figs 1 and 2, respectively. The release values shown in the figures have been normalized to the mass fraction in the glass, taking into consideration the SA/V ratio, and are reported in units of normalized grams of element released per square meter.[11] Figure 1(A) illustrates that, in terms of silicon release, the oxynitride glasses are at least a factor of two more durable than either silica glass or crystalline quartz. The durability of the oxynitride glasses improves even more as temperature is lowered. (Although they were not tested, the leach resistances of silica glass and crystalline quartz would also be expected to improve as temperature is lowered.) In terms of nitrogen content, Fig. 1(B) indicates that silicon release is essentially constant up to about 13 at% for this glass system and begins to increase significantly at 15 at%. This effect may have resulted from phase separation or other compositional inhomogeneity in the glass at this high nitrogen level. Yttrium release, shown in Fig. 2, is essentially constant with temperature while aluminum release decreases with temperature. The behavior of aluminum in this case is likely due to

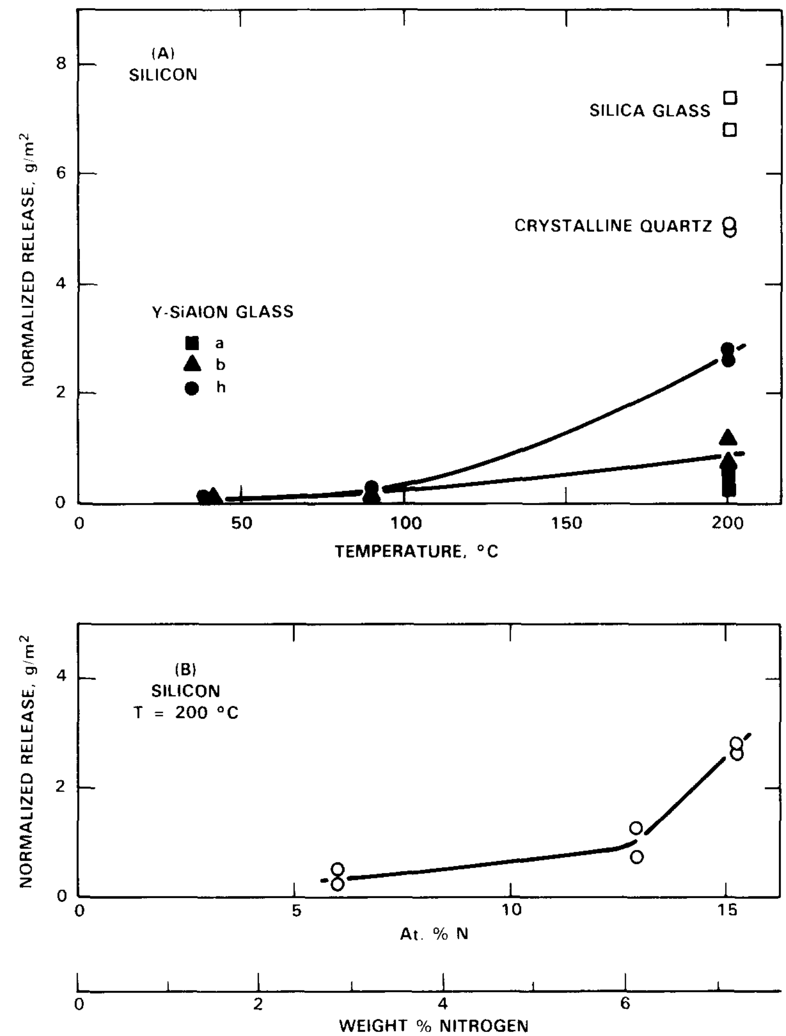

Fig. 1. Silicon release: (A) versus temperature; (B) versus nitrogen level.

the formation of alteration products at the elevated temperature (aluminosilicates), which precipitate from solution onto the sample surface or container walls. At 200°C yttrium release increases up to about 13 at% nitrogen and is essentially constant above this value. Aluminum was below detection limit (< 0·03 ppm) at all nitrogen levels at this temperature.

Although the results suggest a trend toward increased release of both silicon and yttrium with increasing glass nitrogen content, further work would be needed to confirm such behavior. Reasons for this include the scatter in the test results and the fact that previous work on the glasses[8] gave evidence of minor amounts of crystalline phases in high nitrogen

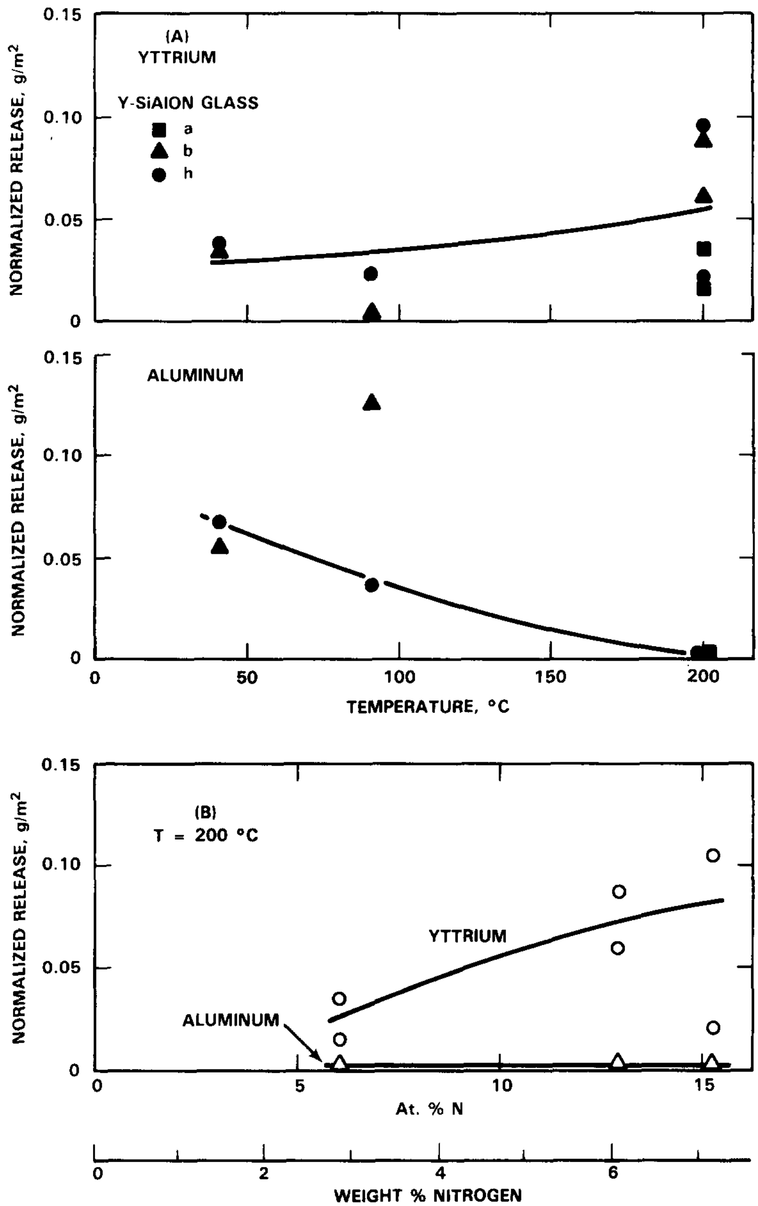

Fig. 2. Yttrium and aluminum release: (A) versus temperature; (B) versus nitrogen level.

(~ 7 wt%) glasses. The presence of such phases could also conceivably increase the leachability of the glass phase.

The leaching process in silicate glasses may be described in terms of solvent attack of Si—O bonds (hydrolysis) to form localized anionic silicate groups which are slowly released to the solution, thereby corroding the surface. In oxynitride glasses it has been reported that nitrogen substitutes for oxygen in the structural framework, allowing for increased crosslinking of the network through Si–N–Si interactions.[12] This increased crosslinking may have improved leach resistance by greatly reducing the hydrolysis reaction. The effect of yttrium and aluminum on leaching in these glasses, however, should also be considered in light of the known positive effects each has on leach resistance. In studies of soda–lime–silica glasses for solar applications, Buckwalter and McVay have reported that very low concentrations of rare earths can greatly inhibit glass/water interactions.[13] Paul and Zaman have shown that incorporation of aluminum oxide in silicate glasses can also increase the chemical durability of glass.[14] Although increased leach resistance is generally associated with rare earth and aluminum incorporation in the glass system, the magnitude of the effect on leaching compared to fused silica glass is not as great as noted in the current tests. This conclusion would lead to the belief that the high leach resistance noted must for the major part be due to the increased structural integrity resulting from nitrogen incorporation in the structural framework.

4. CONCLUSIONS

The data presented support previously published trends that indicate high chemical durability in nitrogen-containing glasses. Although in the present study no attempt was made to adjust cation ratios as nitrogen concentration was increased (test specimens were adapted from other study areas), each glass tested showed lower normalized silicon release than either fused silica glass or crystalline quartz when tested under identical conditions at 200°C. The enhanced durability in nitrogen-containing glasses is believed to be due to increased cross-linking of the silica network through Si–N–Si interactions and the resultant reduction in the hydrolysis reaction at the glass surface. More fundamental investigations would be required and could be conducted to fully address this belief.

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