Degradation and destruction of historical blue-green glass beads: a study using microspectroscopy of light transmission

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Received 16 January 2014, revised 10 March 2014
Accepted for publication 14 March 2014
Published 23 April 2014

Abstract

Blue-green historical beads are sometimes described as unstable because of their degradability. At present, it is not known what causes the deterioration of these beads. We explore the internal microstructure of degrading blue-green historical beads and its evolution in the process of bead deterioration. Investigating the transmittance and scattering spectra of visible and near infrared light we observe the formation of microscopic internal inhomogeneities of sizes less than 150 nm in the glass bulk, and growth of their density with an increase in the degree of bead degradation. By means of laser scanning microscopy we also observe numerous microinclusions and microcracks on the cleavage surface of a partially degraded bead. We discuss possible physical factors resulting in the destruction of the blue-green beads.

Keywords: microspectroscopy, light transmission, light scattering, glass bead destruction

PACS numbers: 78.40.Pg, 81.05.Kf

(Some figures may appear in colour only in the online journal)

1. Introduction: background and problem statement

In many museums throughout the world, historical art articles featuring beads, made using different techniques and in different epochs, are kept. In the years since their manufacture, the surfaces of some beads have corroded, cracks have appeared in them, the colours of some kinds of beads have changed, and some beads have broken up into parts, i.e., beads degrade and crumble [1–3]. It is known from the practice of museum keeping of articles made of beads that blue-green beads are more subject to strong deterioration than ones of other colours [2, 3]. At the same time, both undamaged beads of this colour and beads at various phases of deterioration can be present simultaneously, e.g. in articles made from the early to mid 19th century embroidered with beads (figure 1; the main stages of deterioration of the blue-green beads of the first half of the 19th century are illustrated by figure 2). Moreover, deteriorated museum blue-green beads of the first half of the 19th century superficially resemble ones of the same colour found during the archaeological dig of a mound near Kholmy village in Russia [10] (the mound is dated as 17th to 18th century [11]) which are dramatically damaged.

We have found recently that the aging of beads goes through a number of phases common to all the studied samples [3]. They are as follows (figure 2): first cracks appear in
the blue beads; then bead cracking increases and the bead colour starts to change into the greenish tone; after that the bead colour goes on changing, cracks change their colour to the greatest degree and they become brown-green; then discolouration of the beads begins and the surface corrosion develops; at the last stage, the beads become completely faded and finally they fragment.

However, causes of the degradation of blue-green beads have not been clarified thus far, and this prevents the development of restoration techniques and conservation conditions of articles made of such beads. Ascertaining these causes is believed to be of special importance.

Unfortunately, degrading blue-green beads are usually explored by means of integral analytical techniques and their
microstructure is investigated very rarely [9]. It is commonly assumed that the reasons for bead deterioration are purely chemical, i.e. only chemical reactions taking place on a bead surface are responsible for its degradation: a high concentration of potassium oxide \((>20\text{ wt.\%})\) gives rise to the formation of a considerable amount of potassium silicate and a high rate of hydrolysis of potassium silicate on the surface results in the corrosion and destruction of this kind of beads [2]. Archaeological beads found at Kholmy village [10] contain much smaller quantities of potassium oxide \((<7\text{ wt.\%})\); however, they have strongly degraded in spite of the much lower K content.

Additionally, adjacent beads in a historical beaded article are often seen to be at radically different phases of corrosion — heavily degraded beads often adjoin intact ones (figure 1) — while they are obviously very similar and seem to have close chemical composition including potassium content. These facts make us assume that some other processes may be responsible for the blue-green bead destruction and leads us to try to find out what the cause of this ‘selective’ corrosion of similar beads could be.

In this article, we explore an internal microstructure of the degrading blue-green historical beads and its evolution in the process of bead deterioration. Investigating transmittance and scattering spectra of visible and near infrared light we observe the formation of microscopic internal inhomogeneities in the glass bulk, and growth of their density with an increasing degree of bead degradation. We also discuss possible physical factors resulting in the destruction of the blue-green beads.

2. Experimental details

2.1. Samples

Photographs of the samples investigated by light transmission spectroscopy are shown in figure 3. We have chosen a representative set of samples corresponding to major phases of the blue-green beads’ destruction. Sample 1 is an example of the intact blue bead; it is a lustrous opaque blue with no visible traces of cracking. Sample 2 represents a bead at the very initial phase of destruction; it is seen to be cracked but still opaque blue without any greenish tinge, the cracks and regions around them have not changed their colour either. Sample 3 is a seriously degraded bead with blue and brown-green segments; the blue domains have a greenish tint; the brown-green segments are seen to drastically change their colour and be heavily cracked. Samples 4a and 4b are parts of a destroyed bead; they are composed of differently coloured grains, often also cracked, separated by sharp boundaries.

2.2. Equipment and techniques

For the experiments on the spectroscopy of light transmitted by beads, a home-made microspectrometer was assembled from the Avantes AvaSpec-2048 fiber optic spectrometer attached to the LOMO Biolam 70-P13 transmitted light stereo microscope. A tungsten lamp with a frosted glass bulb was used for sample illumination. The light transmission spectra were obtained at a magnification of 600× in the range from violet to near-infrared light. The procedure of obtaining characteristic spectra was as follows: several transmittance...
spectra, \( Tr(\lambda) \), were measured at similar points of each sample (or at similar points of each specific domain of a sample) with the required integration time and averaging over an appropriate number of scans, then after comparison the obtained spectra were averaged over every set of analogous points for further analysis of features typical for different stages of the bead degradation.

Additionally, a Carl Zeiss LSM-710 laser scanning microscope (LSM) was applied to obtain detailed images of cleavage surfaces of the destroyed beads. An Eleran Renom FV x-ray fluorescence (XRF) spectrometer was used for the elemental analysis of beads.

3. Results and discussion

3.1. XRF spectral analysis

To characterize glasses of which the studied beads are made chemical analysis of some blue-green beads was accomplished by means of XRF spectroscopy. Typical results of such analysis obtained from a blue bead and from a bead with blue and brown-green segments are given in Table 1. The table presents values for the XRF line intensity \( I_{\text{rel}} \) and a relative concentration \( C_{\text{rel}} \) for revealed chemical elements; it also gives weight fractions of corresponding oxides \( F_{\text{ox}} \) in the glass which are usually utilized in glass manufacturing. \( C_{\text{rel}} \) are normalized in such a way as to give a sum total of 100 wt. %. The values of \( F_{\text{ox}} \) are calculated from \( C_{\text{rel}} \) and also normalized to give a sum total of 100 wt. %.

The beads are seen to be made of lead-potassium glass with a rather high content of copper; appreciable quantities of calcium, arsenic, antimony and iron have also been detected in the glass. CuO dyes the glass into blue or a slightly greenish colour. We suppose that Sb is present in glass in the form of \( \text{SbO}_3 \), as an opacifier (both antimony and arsenic was used for opacifying beads in the early 19th century [12]) or as an oxidant to ensure the prevailing of the iron impurity in the \( \text{Fe}^{3+} \) state (\( \text{Fe}_2\text{O}_3 \)) rather than \( \text{Fe}^{2+} \)\( \text{(FeO)} \) since the latter in the mixture with ferric oxide colours the glass green.

We should also mention that the intact blue bead contains several times less antimony than the degraded one while the fractions of potassium oxide in the samples differ only by about 1.4 times.

3.2. Light transmittance

The resultant transmittance spectra of the examined beads obtained following the procedure described above (section 2.2) are presented in Figure 4. The spectra of the samples 1 and 2 (curves 1 and 2) are very close in the whole spectral range. This means that arising cracks make no contribution to the absorption or scattering of light.

The spectra of the blue region of sample 3 (curve 3) also nearly coincide with those of the intact sample throughout the studied spectral range except for the interval from green to blue light (\( \lambda < 550 \text{ nm} \)) where \( Tr(\lambda) \) of the sample 3 first slightly and then (\( \lambda < 500 \text{ nm} \)) significantly decreases in comparison with \( Tr(\lambda) \) of the sample 1. This behavior of \( Tr(\lambda) \) reflects the greenish colour of these domains; it may be caused by the growth of either absorption or scattering, or by the simultaneous increase in both absorption and scattering.

A dramatic reduction of transmittance is observed in the spectra obtained from the brown-green segments of sample 3 (curve 4) and in the spectra of sample 4 (curve 5). This effect may also result from significantly increasing absorption and/ or scattering of light in these samples.

3.3. Rayleigh scattering of light

We can easily discriminate between the reduction of \( Tr \) caused by growing absorption and that caused by increasing scattering of light, if one of these factors prevails, by subtracting \( T_{\lambda_i} \), from \( Tr_{\lambda_i}(\Delta Tr(\lambda) = T_{\lambda_{i+1}} - T_{\lambda_i}(\lambda)) \), where \( i \) is the number of the sample, and plotting the result.
\[ \Delta Tr \text{ as a function of } 1/\lambda^4. \text{ If the differential spectra obey the Rayleigh law, i.e. if } \Delta Tr \propto \lambda^{-4}, \text{ the light scattering dominates; otherwise the impact of light absorption is significant.} \]

Figure 5 demonstrates the \( \Delta Tr (\lambda^{-4}) \) spectra for samples 3 and 4 and linear fits of their fragments in the range of the visible light. All the presented spectra, even the spectrum obtained in the blue-green segments of the sample 3, are seen to strictly obey the Rayleigh law, so we can conclude that the observed changes in \( Tr(\lambda) \) result from increasing light scattering in the bulk of the degrading beads.

3.4. Microinclusions, microcracks and internal stress

From the \( \Delta Tr (\lambda^{-4}) \) spectra given in figure 5, we can estimate the characteristic dimensions of the scatterers as \( a \ll \lambda_{\text{inel}}/\pi \sim 150 \text{ nm}. \) Hence, we can make an assumption about the possible nature of the inhomogeneities scattering light. They are likely to be some microscopic inclusions in the glass of the beads, or tiny cracks. Their density is obviously much higher in the vicinity of the observed large cracks of sample 3, than in the relatively undamaged blue-green domains of sample 3.

Numerous microinclusions and microcracks of various sizes, from tens of nanometers to several micrometers, are observed on the cleavage surface of a segmented bead shown in figure 6. In addition, a rather large aggregation of some clusters is also seen in the same images. We believe that these inhomogeneities are the most likely candidates to be the sought-for scatterers of light.

Let us dwell on possible reasons for bead cracking. To explain this phenomenon one should look for a source of internal stress resulting in local inelastic deformation and rupture of the glass. We suppose that some precipitates that are large enough, likely crystalline, might be such sources. They seem to be available in the bead glass since LSM images of some inclusions in figure 6 resemble typical images of faceted crystallites. They may arise as a result of decomposition, diffusion and crystallisation of some chemical components of glass, such as pigments, opacifiers, fluxes or stabilizers, during glass bead manufacturing. Emerging, they give rise to a strain field resulting in both the glass cracking and the gettering of additional impurities and chemical components dissolved in the glass, which in turn form a new generation of micro-precipitates and impurity atmospheres around the cracks and promote further internal corrosion of the bead.

From our viewpoint, this is a probable model describing the process of destruction of the blue glass beads. For example, the diffusion of copper could increase its concentration in the form of \( \text{CuO (Cu}^{2+}) \) around cracks to values far exceeding 2\% and colour these regions green. At the same time, antimony and its chemical compounds which were often utilized as opacifiers until the mid 19th century [12] could form crystallites resembling those seen in figures 6(a), (b) (or, e.g. rhombohedral modification of \( \text{Pb}_2\text{Sb}_2\text{O}_7 \) observed in opaque yellow Roman glasses [13]; such precipitates might be sources of local strain required for cracking. In addition, antimony oxide dyes glass yellow so that might also explain the observed changes of the beads’ colour to green. Moreover, the formation of \( \text{Sb}_{2}\text{O}_3 \) precipitates and/or the migration of \( \text{Sb} \) to strained domains reduces its concentration in the form of \( \text{Sb}_{2}\text{O}_3 \) dissolved in glass as a consequence of increasing the fraction of ferrous oxide (\( \text{Fe}^{2+} \)) and dyeing glass green.
However, presently this model is only a hypothesis which, to be confirmed or refuted, requires further explorations. Moreover, the proposed physical mechanism of bead degradation does not exclude the possibility of chemical corrosion, both on the surface and in the bulk of the beads. The processes of chemical surface corrosion mentioned in section 1 may accompany the proposed physical processes of the bulk corrosion. Additionally, fracturing of beads resulting in the formation of a developed volumetric network of cracks reaching the glass surface may stimulate penetration of chemical agents, say water and/or dissolved ions, into the bead bulk. In this case chemical corrosion may start in the glass bulk which facilitates the crumbling of beads.

4. Conclusion

Summarizing the above we would like to emphasise the main statements of the paper.

We have analysed the chemical composition of the blue-green beads by means of XRF spectroscopy and found that they had been made of lead-potassium glass with rather a high content of copper; appreciable quantities of calcium, arsenic, antimony and iron are also present in the glass.

We have studied a microstructure of the blue-green beads and explored its evolution in the process of bead deterioration. Investigating transmittance and scattering spectra in visible and near infrared ranges we have detected emergence of microscopic inhomogeneities of sizes much smaller than 150 nm inside the beads and significant growth of their density during the bead degradation. By means of laser scanning microscopy we have also observed numerous microscopic foreign inclusions and fine rifts on the cleavage surface of a fragmented bead.

We have come to the conclusion that the most probable physical driving force of destruction of the blue-green beads is the strain induced by the crystalline microinclusions precipitated during and/or after the beads’ manufacture, and by their agglomerates, which give rise to internal microcracks and extended impurity atmospheres; the latter arise due to strain-stimulated diffusion of some components of glass, such as potassium, copper and antimony, into the domains with a high density of the precipitated clusters, denuding the rest of the volume of the bead and introducing chemical

Figure 6. LSM images (a), (b) of the cleavage surface of a segmented bead shown in the panel (c); numerous foreign microinclusions are spread throughout the spall area and aggregation of the inclusions is observed in the centres of the images (a) and (b); cracks of various sizes are also observed everywhere on the surface (some of them are marked by the letter ‘S’) which indicate the presence of a strong strain.
inhomogeneity into the glass. Bead granulation during the last phase of corrosion seems to result from this inhomogeneity. The precipitates responsible for the internal strain in the glass presumably consist of some chemical compound of antimony.

Concluding the article we would like to mention that in past decades optical techniques based on Rayleigh scattering of light were often used for the characterization and imaging of microdefects in various materials such as single-crystalline semiconductors [14–17] or leucosapphire wafers [18], etc. This article demonstrates that such methods are informative in the investigation of historical or archaeological glasses and glassware, usually subjected to different kinds of volumetric and surface corrosion.

Acknowledgments

The research was carried out under the Collaboration Agreement between the State Research Institute for Restoration and the A M Prokhorov General Physics Institute of RAS. The Center of Collective Use of Scientific Equipment of GPI RAS supported this research by allowing the use of its instrumentation. We cordially thank Professor Victor Loschenov and especially Dr Anastasia V Ryabova for examining the samples of beads by means of the laser scanning microscope. We express our appreciation to Mr Ilya B Afanasyev of the Forensic Science Center of the Ministry of the Interior of the Russian Federation for the XRF measurements and the elemental analysis. We also thank Mr Nikolay Yuryev for his help in making and assembling the microspectrometer.

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