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Thermogravimetry in the Studies of Ancient Technical Ceramics

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Abstract

The technical ceramics of the Bronze Age Krotovo culture of the Baraba forest-steppe (the end of the III – the beginning of the II millennium BC) were analysed. Samples of internal and external surfaces of casting molds and crucibles were measured by thermogravimetric analysis. Good and very good quality of firing was identified. Reliable differences in the mass loss were identified between the inner and outer surfaces of the crucibles, which allows determining the type of fire installation (open or closed), the direction of air injection onto the crucible, and the period of use. Other processes occur in a mold. During metal pouring, a large gradient of temperature arises: at the surface of contact with the casting, mold temperature approaches the temperature of the melt. At the outer surface, temperature is equal to the initial level at this moment. However, the time of temperature action is short-term and limited by the period of metal solidification. The difference in the mass loss between the inner and outer surfaces can get accumulated only in the case of a long-term use of the mold, and thus it provides evidence of how many times the mold was used. Determination of the functional differences between technical ceramics, crucibles, and molds can be made on the basis of differences in mass losses for the inner and outer surfaces. The results of thermogravimetric analysis add essential objective data to the solution of the question of the multiple uses of forms and, as a result, the reconstruction of the technology of the ancient bronze casting production in Eurasia.

Key words: technical archaeological ceramics, thermogravimetric analysis, mass loss

INTRODUCTION

The modern stage of the development of archeology is essentially connected with the multidisciplinary approach to the investigation of archaeological sites and artefacts. The significance of analytical methods in modern archeological science cannot be overestimated: the area of the application of these methods is diverse and includes almost all the stages of investigation from

Fig. 1. Technical ceramics. Unbroken species: *1* – scoop, view from above, from the side and from below; *2*, *3* – simple crucibles, view from above and from the side, respectively; *4* – complex crucible, views from the side, working chamber and the view from above; *5*, *6* – single-winged molds, view from the side, the working chamber and the view from above respectively; *7* – double-winged mold, view to the cutoff point and the working chamber, view from above. *1*–*3*, *5*–*7* – burial ground Sopka-2; *4* – settlement Vengerovo-2.

the search for archeological objects to their cameral treatment [1, 2]. The methods used today in natural sciences get gradually involved also into the set of tools for the investigators of ancient ceramics [3–5]. In addition to principally new information which cannot be obtained using only archeological (historical) methods, thus obtained results are objective, reproducible, and allow carrying out thorough reconstructions of the phenomena under study [6], in the case under consideration – bronze foundry.

In the present work, we publish the results of the studies of technical ceramics. We understand the term 'technical ceramics' as a set of special metallurgical equipment including molds, nozzles, crucibles, scoops made of foundry mass based on clay materials. Technical ceramics are most frequently found by archeologists in the form of fragments, which does not allow them to reconstruct its initial shape and destination. Discovery of intact or archeologically intact molds, crucibles and other tools are very rare (Fig. 1). It was established experimentally that visually detected traces of thermal action may be not conserved after long-term presence in the ground in the case of an insignificant number of fusions [7]. The Researchers often have some doubt whether a find had been ever used in production, and wonder whether an article is defective, half-finished product or a thing that had served its time. It is also difficult to determine the functional purpose of the fragments of technical ceramics. It is difficult to establish the fact of repeated (multiple) uses of the found articles or their use for an indirect purpose. For example, molds made of the fragments of household ceramics were often used in a foundry in the cultures of the Bronze Age [8]. The cases of the use of crockery as crucibles are known [9, 10].

Researchers from the Institute of Archeology and ethnography of SB RAS and from the Research and Education Centre Molecular Design and Ecologically Safe Technologies of the Novosibirsk State University working within the integration project for the investigation ancient household crockery proposed a complex of methods including petrography, X-ray phase analysis (XPA), and thermogravimetry (TG). It should be stressed that the studies of this kind have been carried out for the first time in the world practice.

The goal of the present work was to study the technical ceramics of two kinds (crucibles and molds) by means of TG.

EXPERIMENTAL

A crucible (see Fig. 1, samples *2–4*) is a special vessel used to heat, roast or fuse various materials. The whole design of this vessel is meant for the above-listed tasks, so it often has thickened walls and sink. Petrographic studies show that the foundry mass of these articles is made of the same oversanded clay and loam as household ceramics, but the additives were not only chamotte (crushed fragments of ceramics) but the fragments of bones, and crushed rocks (granitoids) also occur.

A mold (see Fig. 1, samples *5–7*) is a specially manufactured vessel intended for obtaining a foundry by filling the cavity with liquid metal and keeping it untill complete solidification [11]. As a rule, in addition to the working cavity, the mold has additional (so-called service) cavities: risers, feeders, pouring basins, ingates, feeding channels, and represents a complicated technical structure. According to the petrographical data, foundry masses are most often represented by composite mixtures.

Relying on the results of the studies of ancient household vessels by means of TG, a procedure was proposed to prepare the samples of ancient ceramics, to carry out analysis, and to interpret the results. As an alternative to the generally accepted approach directed at the evaluation of firing temperature, a method is proposed in which essential is the comparative analysis of the remnant quantity of clay components in the foundry masses of ceramics in order to determine the quality of vessel firing [12–18]. It was established that mass loss at the outer surface of household vessels is always larger than that at the inner surface [19].

The specific properties of technical ceramics are in its functional destination – it is a vessel for fused metal. Experiments on the thermal tests of technical ceramics were carried out according to the procedure mastered for household vessels.

One fragment (sample T4) of technical ceramics was taken from a settlement related to the Odinovo culture (early and middle III millennium BC) and six fragments (T1–T3, T5–T7) of the Krotovo culture of the Bronze Age (middle III – early II millennium BC) in the Baraba forest-steppe (Fig. 2).

The samples were studied using an instrument providing simultaneous thermal analysis STA 409 PC Luxx of Netzsch company within temperature range 30 to 850 °C at a heating rate of 20 °C /min. Platinum crucibles were used; measurements were carried out in the atmosphere of argon (40 mL/min). The resolution of the electronic balance was 0.002 mg. Sample mass ranged from 46.9 to 47.1 mg, the instrumental accuracy of mass loss measurements was ±0.05 %.

To carry out the measurements, the samples were separated (cut off) from the inner and outer surfaces of technical ceramics.

RESULTS AND DISCUSSION

Sample T1 (see Fig. 2, a) is a casting mold of a bushing tool (Abramovo-10 settlement). Mass loss after dehydration of the sample from the inner surface was 2.71 %, from the outer surface 2.13 %.

Fig. 2. Investigated samples with the photographs of the regions of petrographic slices.

One more sample corresponding to the middle part of the vessel wall was taken from fragment T1.

Its mass loss after dehydration was 2.51 % (Table 1 and Fig. 3, *a*). Differences in mass loss (0.58 %) exceed the measurement error, that is, they may be considered reliable and related to the features of mass loss by the region from which the sample was taken.

Mass loss in the region of hydroxyl decomposition was 1.17 and 1.46 % for the inner and outer surfaces, respectively, and 1.29 % for the middle part of the wall. It should be stressed that a decrease in mass loss during dehydration (from the outer wall to the inner one) is accompanied by an increase in the mass loss during the decomposition of hydroxyl groups.

Sample T2 (see Fig. 2, *b*) is a two-layer casting mold (Abramovo-10 settlement). In the region of dehydration, the mass loss observed for the sample from the inner surface was 1.43 %, from the outer surface 1.26 % (see Table 1 and Fig. 3, *b*). During heating, mass loss increases from the outer surface to the inner one, and the difference is 0.17 %.

Within the region of hydroxyl decomposition, mass losses were 0.63 and 0.62 %. The difference between these two values (0.01 %) is within the limits of experimental accuracy, in spite of the reliable difference in the region of dehydration. Mass losses in the region of hydroxyl decomposition are equal. One can see in Fig. 3, *b* that the slope of the curves of mass loss for the inner and outer surfaces within the temperature range 350–600 °C is the same.

Sample T3 (see Fig. 2, *c*) is a fragment of a casting mold (Abramovo-10). The mass loss after dehydration was 2.59 % for the inner surface and 2.29 % for the outer one (see Table 1 and Fig. 3, *c*). The difference is 0.3 %, and this is a reliable value. An increase in mass loss is similar to that for fragment T2, from the outer surface to the inner one.

Within the region of hydroxyl decomposition, the mass loss is 1.06 % from the inner surface and 0.92 % from the outer one. Similarly to the region of dehydration, an increase from the outer surface to the inner one occurs (by 0.14 %).

Sample T4 (see Fig. 2, *d*) is an upper edge of a crucible (Tartas-1, structure 4, Odinovo culture). Mass loss after dehydration was 0.83 % for the inner surface and 1.37 % for the outer one (see Table 1 and Fig. 3, *d*). For this fragment, an increase in mass loss after dehydration is also reliable (the difference is 0.54 %) and proceeds from the inner surface to the outer one similarly to fragment T1.

TABLE 1

Mass loss by the samples of technical ceramics within temperature ranges, %

No.	Sample code / sample position	Temperature, °C			
		30–350	350–600	600–850	30–850
1	T1H[1]	2.71	1.17	0.58	4.4
2	T1C[2]	2.51	1.29	0.71	4.51
3	T1B[3]	2.13	1.46	0.75	4.34
4	T2H	1.26	0.62	0.26	2.14
5	T2B	1.43	0.63	0.27	2.33
6	T3H	2.29	0.92	0.42	3.63
7	T3B	2.59	1.06	0.43	4.08
8	T4H	1.37	0.88	0.42	2.67
9	T4B	0.83	0.40	0.18	1.41
10	T5H	0.79	0.48	0.18	1.45
11	T5B	3.97	0.89	0.39	5.25
12	T6H	1.05	0.54	0.20	1.79
13	T6B	0.9	0.42	0.15	1.47
14	T7H	1.07	0.74	0.24	2.05
15	T7B	4.72	1.05	0.94	6.71

Note. H[1], B[3] – outer and inner surfaces of the species, respectively; C[2] – the middle of species fracture.

Within the region of hydroxyl decomposition, an increase in mass loss proceeds similarly to the region of dehydration, that is, from the inner surface to the outer one. Mass loss was 0.40 % for the inner surface and 0.88 % for the outer one. The difference is 0.48 %, and this is a reliable value.

Sample T5 (see Fig. 2, *e*) is a crucible with a drop of metal in the section (Abramovo-10). Mass loss in the region of dehydration was 3.97 % from the sample of the inner wall, and 0.79 % from the outer one (see Table 1 and Fig. 3, *e*). An increase in mass loss proceeds from the outer wall to the inner one, and the difference in mass losses is substantial: 3.18 %.

Within the region of hydroxyl decomposition, mass loss was 0.89 % for the sample of the inner wall and 0.48 % for the outer one. The difference is not so substantial in comparison with dehydration region but it is quite reliable: 0.41 %, mass loss increases from the outer wall to the inner one, similarly to dehydration region.

Sample T6 (see Fig. 2, *f*) is a crucible, the outer shell ring; two superimposed ribbons are seen in the fracture (Abramovo-10). Within the region of dehydration, mass loss was 0.9 % for the sample of the inner surface, and 1.05 % for the outer surface (see Table 1 and Fig. 3, *f*), the difference is 0.15 %, which is reliable.

Mass loss after hydroxyl decomposition was 0.42 % for the sample of the inner surface and

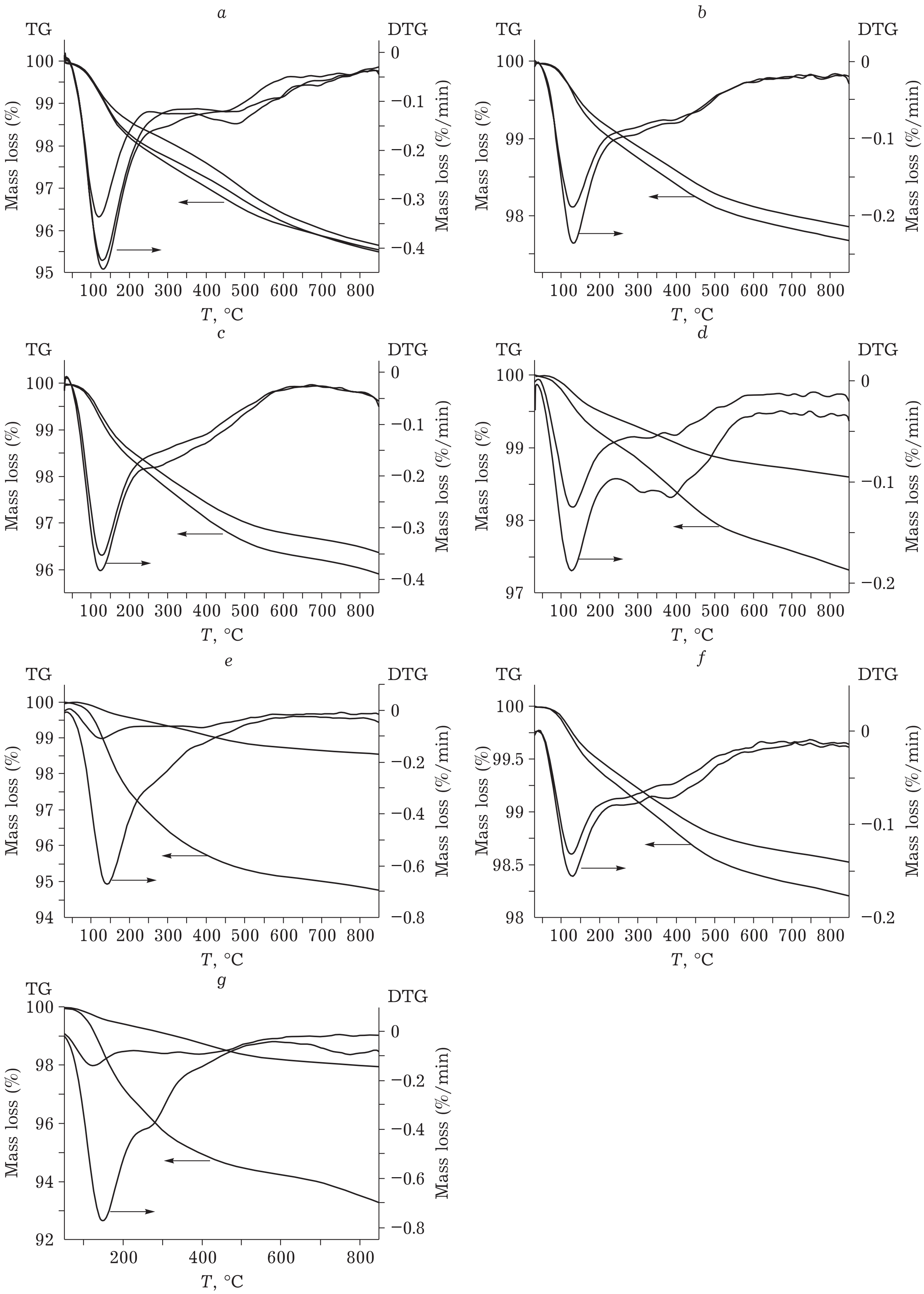

Fig. 3. TG – DTG curves for the fragments of technical ceramics: T1 (*a*), T2 (*b*), T3 (*c*), T4 (*d*), T5 (*e*), T6 (*f*), T7 (*g*).

0.54 % for the outer one. An increase proceeds from the inner surface to the outer one, similarly to the region of dehydration (the difference is 0.12 %).

Sample T7 (see Fig. 2, *g*) is a crucible with small drops of metal (Abramovo-10). Within the region of dehydration, mass loss was 4.72 % from the sample of the inner surface and 1.07 % from the outer one (see Table 1 and Fig. 3, *g*). The difference was 3.65 %, with an increase from the outer surface to the inner one.

Mass loss after dehydroxylation was 1.05 % from the sample of the inner surface and 0.74 % from the outer one. An increase by 0.31 % is observed from the outer surface to the inner one, similarly to the region of dehydration.

It is shown in Fig. 4 that all the samples, independently of their location on the species, have a good and very good quality of firing. If we compare the schematic positions of points related to the samples of household crockery and technical ceramics, we see that such a position is occupied by a small number of samples of the ceramics of the period of transition from the Bronze Age to the early Iron Age, but mainly those of Middle Ages and the Russian crockery [20].

A special position of samples T5 and T7 is observed. By their example, a large difference in mass losses from the inner and outer surfaces of the crucibles is manifested. Both samples are the fragments of the inner caps of complex sectional crucibles having an outer protective shell (see Fig. 1, sample *4*). In these cases, it may be assumed that a directed action of high temperature directly at the metal took place, which means air injection by the bellows into the cavity of the crucible. Sample T6 (see Fig. 2, *f*) is a crucible too, but it is an outer shell ring, which is an additional part to render more volume to the wall. A small mass loss was detected for both surfaces, but their high-quality firing is the evidence that the crucible was used many times. Evidently, an article that survived the directed action of high temperature at the metal and was used many times in production is sample T4 in spite of its earlier chronological position (it is a prototype of Krotovo complicated crucibles, see Fig. 1, sample *4*), the habit of its use and the technical installations involved do not differ from the hardware of the Krotovo culture.

The positions of the points related to the samples of casting molds better fits the positions of the points related to the samples of household ceramics. They are divided into two groups.

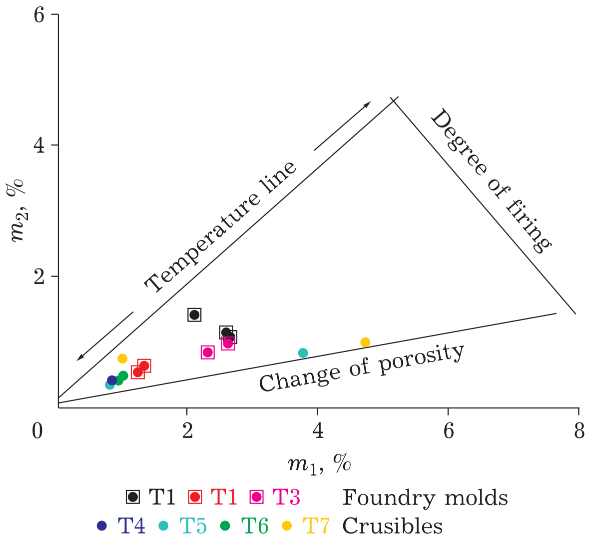

Fig. 4. Diagram of mass loss by samples T1–T7. m_1, m_2 – mass loss during dehydration and dehydroxylation, respectively.

Samples T1 and T3 are well fired. Copper melting occurs at a temperature of 1085 °C, so overheating by 200–300 °C is necessary to pour it into the mold, which is much higher than the usual temperature of ceramics firing in a bonfire. Metal pouring into a ceramic mold causes a large gradient of temperature: at the surface of contact with the foundry, mold temperature approaches the temperature of the melt, while at the outer surface it is equal to the initial temperature at that moment [21]. However, the time of temperature action is short, being limited by the time of metal solidification. The difference in the mass loss from the inner and the outer surfaces may be accumulated only in the case if the mold had been used for a long time, so it can be the evidence of how many times the mold was used. In our case, sample T2 was evidently used a minimal number of times.

CONCLUSION

Technical ceramics are a special kind of hardware connected with the bronze foundry. A small amount of attention has been paid so far to this category of finds, especially that found in a fragmented state. The studies of the foundry masses of technical ceramics of the Bronze Age from the population of the Baraba helped us to establish that special formulations of the foundry mass were used, with refractory additives for crucible molding: bones, crushed rocks, sand (clay materials account for only up to 25 % of the section area), unlike for household ceramics, for which the main formulation includes a mixture of clay with chamotte (crushed fragments of vessels).

The thermal analysis allowed us to detect reliable differences in mass loss from the inner and outer surfaces of the crucibles. This will allow us in some cases to determine the type of thermal installation (open or closed: high temperature is created within the whole structure or only in the inner part of the crucible), the direction of air injection at the crucible (from above directly at the metal or from the side to the wall), the time during which the crucible had been in use. In archeological practice, the multiplicity of use is established on the basis of visual observation of colour change and the state of the working chamber. The results of thermal analysis add objective data to these conclusions by detecting the difference in mass losses by different regions of the surface of the object under investigation. In addition, it appears possible to determine the primary functional destination of an artefact (a crucible or a mold) from a fragment of technical ceramics.

It is remarkable that the results of the thermal analysis may be used to distinguish household ceramics from technical ceramics. This will allow representing the objective proofs that the fragments of household ceramics had been used as molds to cast simple small species.

On the one hand, all the conclusions obtained in the study are objective and reproducible; on the other hand, it is impossible to obtain them using other methods, at least archeological ones. Further outlooks may include the studies of technical ceramics of other (later) epochs, followed by the correlation of the obtained data.

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