Causes and mechanism of destruction of heat-resistant concrete in an aggressive reducing gas environment of carbon monoxide at high temperatures

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Abstract. Scientific and technological progress in a number of industries has led to the need to create new types of thermal aggregates in which high-temperature production processes occur in the presence of highly aggressive media towards lining materials. The medium with a high concentration of carbon monoxide (CO) reducing gas can be considered as an example.

For the lining of such thermal aggregates in practice, special piece refractory were used, therefore, the available literature data on the resistance of materials under these conditions are mainly related to them, and for fundamentally different heat-resistant concretes this question is not well studied.

It should be noted that heat-resistant concrete is a relatively new type of lining material, which has proven high technical and economic efficiency of use. They are non-fired materials, the stabilization of the structure and properties of which occurs during drying and first heating of the structures, which are made from the latter - directly in the constructed thermal aggregate.

In view of the circumstances, in comparison with pre-fired refractory items, have a number of features, and question arose on the way to creating similar heat-resistant concrete, which require thorough studies. A variety of heat-resistant aggregates, binders and concrete on their base with different chemical and mineralogical compositions, structures and physical and mechanical properties were studied through various laboratory tests.

As a result of physical and mechanical, physical and chemical and electron-microscopic complex studies, the causes and the mechanism of their destruction in these conditions are identified and all the initial requirements for the components and technologies for preparing and using such concretes are established.

The correctness of the established criteria is proved by the long-term reliable operation of lightweight heat-corrosion-resistant perlite concrete, developed on high-alumina cements in monolithic linings of a number of thermal aggregates of Oskol Electrometallurgical Plant of the Russian Federation. In the presented article, only part of the results is presented, which relates to the causes and mechanisms of destruction of heat-resistant concrete in afore-mentioned conditions.

Introduction
The development of metallurgical, chemical and a number of other industries, along with other problems, also necessitates the creation of new, more reliable and durable heat-corrosion-resistant lining materials for industrial thermal aggregates.
Such materials include both special refractory piece items, and heat-resistant concretes, simultaneously stable in an aggressive gas environment of carbon monoxide (CO) at high temperatures.

In practice, for these purposes, piece refractory items has traditionally been used and the available literature data on the resistance of materials under these conditions mainly related to them [1 ... 4], and this problem has been not well studied in heat-resistant concretes. It should be noted that heat-resistant concretes are non fired materials and stabilization of their structure and properties occurs during drying and first heating of structures made from them directly in the constructed thermal aggregate. Therefore, in comparison with precast piece refractory, these concretes have a number of features, as a result of which in this case there were questions requiring detailed studies. On the other hand, it is well known that compared to small-piece refractories, heat-resistant concrete has a number of advantages: as non fired material has a relatively low cost, they can reject highly skilled manual labor on masonry and mechanize and industrialize the construction, having completed the required structures in both monolithic and prefabricated and precast-monolithic versions from enlarged prefabricated elements, it is easy to create any complex forms of structures, significantly reduce duration and cost of construction, in many cases, increase the reliability and service life of constructed aggregates etc. [5].

In this aspect, the expansion of the nomenclature and areas of application of heat-resistant concrete by creating new types, including the most complex heat-corrosion-resistant varieties [6], is a significant scientific and technical task. In particular, in order to obtain heat-and-corrosion-resistant concrete suitable for use in the specified aggressive environment, it is necessary to completely determine the causes and destruction mechanism of the lining materials under these conditions and then establish all the initial requirements for the components and technologies for preparing and using such concrete materials.

**Methodology**

Taking into consideration non-availability of standard methods and equipments for testing materials in a gaseous environment of CO at high temperatures in the country, the studies were carried out by analogue with the American standard method ASTMS-288, designed for refractory products. For this, a pilot test plant of the Eastern Institute of Refractories of the Russian Federation (Yekaterinburg) was used. After loading the test samples into the working chamber, it was hermetically sealed and previously purged with an inert gas (nitrogen or helium). Hereafter, taking into consideration that the most hazardous for the destruction of materials in this environment is a temperature of 500 °C, the temperature of the working chamber is increased to 500 ± 10 °C and at the same time the chamber was filled with CO gas to the content of ≥95%, which was controlled by a gas analyzer. CO gas was obtained chemically, as a result of decomposition of formic acid in the presence of heated sulfuric acid:

$$CH_2O_2 \xrightarrow{H_2SO_4} CO + H_2O$$  \hspace{1cm} (1)

According to this method, the test samples were continuously kept under this conditions for 500 hours, and then the resistance of the material evaluated by the relative weight loss of the sample, which should not exceed 10%.

Considering that this standard method relates to refractory materials, as to use them for heat-resistant concrete, we have made some changes resulting from the specifics of the latter. Refractory products in production undergo preliminary high-temperature firing; therefore, at a temperature of 500 °C they no longer undergo thermal transformations. The situation is different with concrete, which, as noted above, is an non fired material and, in this experiment, in addition to possible transformations occurring under the influence of aggressive gas, thermal transformations of drying and stabilizing first heating will also take place at the same time.

To eliminate this factor, the test samples of aggregates (in the form of grains 10 ... 20 mm in size), cement stones and concrete (in the form of cubes with sizes of edges 20 and 70 mm, respectively, of 28 day normal hardening) are pre-dried and calcined at 600 °C with keeping under this temperature for 4 hours.
Nevertheless, taking into account that, usually thermal transformations often also occur during prolonged heating, so for exclusion of this factor, in another furnace at the same temperature conditions, but in a normal atmosphere conditions, control samples of the test samples are subjected to parallel continuous heating.

As a result, the stability of the samples in the reducing aggressive gas environment of CO was evaluated taking into account the mentioned factors. As an evaluation criterion, along with the mass loss characteristics, required by the mentioned standard, the residual compressive strength of the processed samples were also used. Along with this, in order to determine the influence of a longer stay of this materials in this aggressive environment, another batch of samples were tested for a double period - 1000 hours. To identify the possible phase and other physical and chemical transformations during the tests, the samples were studied by X-ray diffraction, electron microscopy, and differential thermal methods.

**Results and conclusions**

The problem of developing concretes that are resistant in an aggressive gas environment of carbon monoxide (CO) at high temperatures, heat-resistant concrete and structures were assigned tasks for NIIZhB Gosstroy of the USSR in the early 1980s, for lining a number of thermal units under construction at the time, the largest in Europe Oskol electrometallurgical plant for the production of high purity iron. Moreover, along with durability under these conditions, for the simultaneous solution of the problem of insulation of this thermal aggregates, it was necessary to develop a lightweight heat-insulating corrosion-resistant concrete with an average density of not more than 1000 kg/m³ and an application temperature of up to 900...1000 °C. At that time, there were no such concretes in the country's practice and, moreover, there were no standards and methods for testing materials in such conditions, as well as regulatory provisions, recommendations and requirements for the development of concretes. As a result of this, in a plant, which was under construction by the German company Khimi-Lurgi, for this purposes, extremely expensive foreign special dry concrete mixtures were planned to use, the compositions and production technologies of which were kept secret for obvious reasons.

Considering these circumstances, activities on the development of similar concrete on local materials was planned to start with identifying the causes and mechanisms of destruction and establishing the foundations of the durability of materials in these operating conditions.

Comprehensive study in the laboratory of heat-resistant concrete and structures of the NIIZhB was started in 1982. under the guidance of prof. KD Nekrasov and was one part of my dissertation [7]. Considering the lack of standard methods and testing equipment in the country, as mentioned above, the basis of a number of other research organizations were also used.

In studies of concrete components for the implementation of monolithic structures, 7 varieties of binders were included: Portland cement with target additives, alumina cement, ultrapure high-alumina expensive cement of brand Talum and having 4 to 5 times lower prime cost of 4 varieties of high-alumina cement compared to the latter industrial waste: slag from smelting of aluminothermic production of ferrochrome, the same ferrotitanium, slurry of organic synthesis, production of ethyl isopropylbenzene and exhaust catalysts IM-2201 of petrochemical industry.

To identify the causes of destruction of heat-resistant concrete under these conditions, various varieties of chamotte and claydite, expanded perlite and foam corundum were studied as aggregates.

As a result of the researches in early 1984 the main aspects of the resistance of materials under given conditions were established [8]. Later, guided by these criteria, experimental compositions of the required lightweight heat-resistant concrete were developed and tested.

Based on the studies, the optimal compositions of concrete were selected, which starting in October 1984, with high technical and economic efficiency were introduced into the construction of thermal aggregates of Oskol Electrometallurgical Plant, instead of expensive imported concrete [9,10,11].

Subsequently, for establishment of the influences of a number of other technical and technological factors on the resistance of heat-resistant concrete in these conditions, research has been continued in details and some of the results are summarized in this article.
The research results allowed us to state that the main factor affecting the concrete durability in an aggressive reducing gas CO\textsubscript{2} is their chemical composition, which is due to the chemical composition of their initial materials and possible pollution by inclusions during concrete works.

According to the single opinion of many authors [1...4], which is also confirmed by our researches, the cause of concrete destruction under these conditions is the presence of iron particles and its oxides in the material, which usually serve as a catalyst for decomposition of carbon monoxide by the following reaction:

\[ 2CO \rightarrow CO_2 + C \] (2)

However, there are number of contradictions regarding the mechanism of destruction of materials under these conditions between the authors of [2,4] and [1,3]. Taking into consideration these opinions, we mentioned that in each of them there are quite convincing separate explanations, however, based on the results of our research, we can put forward our generalized version, which confirms some approaches of both sides, but has its own interpretation, substantiated by experiments. Visual inspection of a large number of samples disturbed during testing using the above methodology showed that there are many carbonaceous releases of different sizes — soot precipitates, from which, upon careful examination, individual points with larger and denser precipitates can be identified (Fig. 1). Studies of the nature of the mechanical destruction of the tested samples shows that it was precisely at these points that the internal bursting destructive stresses were applied, so we will call these points the mature decisive centers of destruction.

Figure 1 shows typical cases of specimens destructions, among which in cases “a” and “c” the decisive centers of fracture are closer to the surface and, as a result, the specimen has local shear and ongoing cracks on the surfaces.

In the second characteristic case “b”, the decisive foci in the depth of the sample, which led to the separation of the sample into two parts. In cases “d” and “e”, the samples simultaneously had several crucial foci in the body of the material, which led first to severe cracking (d), and then to complete fragmentation (e) of the sample. In all cases, on the separated pieces of the samples, on one piece is a clear pyramid-shaped protuberance with large black accumulation at the top, and on the opposite other, the corresponding slot with a black trace at the bottom. This is especially clearly seen in Figures 1a and 1b.
Figure 1. Typical examples of the destruction of failed samples in a CO medium at a temperature of 500°C: a, c-local shears near the edges (decisive foci are closer to the surface of the sample), b-division into 2 parts (decisive focal point is in the depth of the sample), d-cracking (several critical foci in the body of the material, not yet leading to fragmentation of the sample) e-fragmentation (several critical foci in the body of the material, leading to destruction of the sample)

The nature of the mechanical fracture presented is also confirmed by electron microscopic studies of mature decisive foci, an example of which is shown in Fig. 2. Here, the same source with a pyramid-shaped configuration and accumulated black dense discharge on the top (a, b) is shown by various magnifications, which more clearly shows the nature of the destruction, i.e. the fact that the undoubted point of application of bursting destructive stresses is precisely this point, which is also indicated by clearly formed sliding surfaces of the separated parts.

As mentioned above, in any destroyed sample, in addition to the matured centers of bursting stresses, there are also many other, relatively small black soot accumulation points. Microscopic studies showed that soot carbon deposits at these points and foci of destruction are very different from each other. In small points, they have a loose, fragile structure, and here we can agree with the opinion of the authors of [3], who claim that they are not able to be a source of destructive stresses.
Figure 2. Micrographs of the characteristic decisive core of destruction of the tested sample: a-general view of the core, b-fragment of the core in close shot, showing the sliding surfaces of the separated parts during the destruction of the material.

However, such statement is true only for the mentioned small points (immature foci of destruction) and it is impossible to disseminate it for all cases.

In mature foci of destruction with a large accumulation of black mass, it is densely packed, densely clogged the nearby pores of the main material and created the so-called dense core in the body of this material, the borders of which are clearly visible in micrographs of Fig. 2.

In this case, the question arises - what is the material of the formed core and what is the source of internal bursting destructive stresses.

The process of soot formation from the decomposition of CO gas by reaction (2) cannot be a source of such internal stresses, and we can agree with the authors of [3] that this reaction is reversible and the conditions are determined by the Le Chatelier rule.

Formation of tensions in the material as a result of CO decomposition, it is necessary that the reaction proceeds only in the direction of carbon release, i.e., an increase in pressure in the system, which would contradict this rule.

On the other hand, it is impossible to explain the destruction of samples according to the mechanism proposed by the authors of [3], because there are number of contradictions between it and the pattern of destruction of materials that we observed.

Firstly, they reject the possibility of compaction of soot carbon deposits and their role in the destruction of the material, considering it to be a secondary stage, masking the destructive nature of another, the previous process of chemical interaction of CO with the iron-containing phases of the material. In addition, in the considered mechanism the time factor doesn’t mentioned, while we have established that this is one of the decisive factors. Our studies showed that after a 500-hour test cycle, many samples that were not destructed, after a repeated 500-hour cycle, are decomposed. This suggests that the formation of a dense core of destruction is a long process.

On the other hand, the formation of foci of soot carbon accumulation and the rate of their growth to the focal point of destruction of the material directly depend on the possibility of penetration of CO gas into these locations of iron-containing particles. As a result, all points with soot carbon release do not turn into foci of destruction at the same time.

An analysis of X-ray phase studies [7] showed that the same materials tested in parallel in a CO medium and in an ordinary atmosphere are almost identical in terms of the main phase composition.

To establish the processes in the foci of destruction, special samples were prepared enriched with the products of the of destruction. The X-ray diffraction patterns of these samples showed only weak reflections of iron carbide (FeC), which indicates its low content in the tested material. X-ray diffraction
patterns also revealed some lines of Fe$_3$C and Fe$_2$C. Carbon was present in the amorphous state, in the form of soot carbon, and its emission in the form of strong dense crystalline pyrocarbon was missing.

As a result, based on a comprehensive analysis of the available literature and the data obtained, it can be definitely stated that the main cause of the destruction of heat-resistant materials in an aggressive reducing gas medium of carbon monoxide is the presence of iron and its oxides in it, and other factors only enhance or retard the destruction process.

Thus, the mechanism of destruction can be represented as follows. In the presence of iron particles and its oxides, which usually serves as a catalyst, the process starts with the simultaneous decomposition of carbon monoxide according to above reaction (2), with the formation of gas CO$_2$ and C (in the form of soot carbon) and with the chemical interaction of CO with the iron-containing phases of the reduced material iron (Fe) from its oxides. Further, the reduced iron interacts with CO in the carbide formation reaction:

$$Fe + 2CO = FeC + CO_2$$ (3-process of primary carbide formation)

After this, the following subsequent reactions occur:

$$2FeC + 2CO = Fe_2C + CO_2 + 2C$$ (4-process of carbon content increase),

$$3Fe_2C + 2CO = 2Fe_3C + CO_2 + 2C$$ (5-process of carbon content increase),

Along with these, a further alternating reaction is also possible [2]:

$$2Fe_3C + 2CO = 3Fe_2C + CO_2$$ (6-process of the reverse transition of Fe3C to Fe2C, after which the reaction proceeds with an increase in carbon content according to reaction 5).

The mentioned transformations occur slowly and at a given point of the presence of iron-containing phases a mass of soot carbon gradually accumulates. According to the authors of [3], the reactions of formation of iron carbides, as well as the possible re-oxidation of iron, are accompanied by a multiple (up to 100%) increase in volume. At the same time, as a result of reactions (2) and (4), new portions of soot carbon are added to the system in a loose form, but at the same time during carbide formation reactions and their transformations (3,4,5), which are accompanied by an increase in volume (crystallization pressure), the formed friable mass of soot carbon gradually thickens.

At the same time, due to the compression of the soot carbon crust around the iron-containing phases, the rate of these reactions gradually decreases. However, in a certain period, destructive processes from crystallization pressures again contribute to the penetration of CO gas to iron-containing particles. Thus, the processes of accumulation and compaction of soot carbon around the iron-containing phases create dense nuclei gradually increasing in volume, consisting of a compacted mechanical mixture of soot carbon, iron carbides and the main material.

An increase in the core volume is accompanied by a gradual increase in bursting stresses that are formed in the structure of the material and the appearance of cracks in it (for example, Fig. 1a, c, d), through which aggressive gas enters the deeper layers of the material and intensifies similar decomposition processes, i.e. formation of new centers of soot carbon.

Accumulation around other iron-containing phases that were not previously available for CO gas.

When reaching bursting stresses in the early core of the sublevel that increases the strength of the base material, mechanical destruction of the sample occurs, which, depending on the location of this core or several cores at the same time, develops itself in the form of local shear, separation, or complete fragmentation, visual examples of which are shown in Figure 1.

The complete absence of particles of iron and its oxides can be a guarantee for the resistance of heat-resistant concrete in an aggressive reducing atmosphere of CO at high temperatures. In the presence of
these particles in concrete, the resistance of the material to CO is determined mainly by their percentage, with an increase in which the probability of concrete destruction increases.

It should be noted that the low content of these components cannot serve as a criterion for the concrete resistance, because it can only be determined by taking into account other factors, such as structural defects in concrete, moisture content, porosity, gas permeability, operating temperature, volume distribution of harmful particles, pores and defects, physical and mechanical properties of the binder component and aggregates, etc. The issues of the influence of these factors on the durability of concrete in this medium are sufficiently studied, but are a subject of a particular discussion and should be presented in other article.

The advanced versions of the causes and mechanism of destruction of heat-resistant concrete in an aggressive gaseous environment of CO at high temperatures allowed us to establish the basics of the resistance of heat-resistant concrete in these conditions [8], the evidence of which is the long-term successful operation of light heat-resistant concrete developed by these criteria in monolithic linings of a number of thermal units of Oskol electrometallurgical plant in the Russian Federation [9,10].

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