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INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

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Interaction of Graphite with Hydroxide–Salt Melts

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Received December 8, 2005

Abstract—The mechanism and kinetics of graphite dissolution in melts based on sodium hydroxide were studied. The effect of various salt additives on the intensity of the occurring reactions is considered. A method recommended for removal of graphite in the form of remainders of molds and mold cores from titanium casts is described.

DOI: 10.1134/S1070427206040033

The existing industrial methods for cleaning the surface of machine and equipment parts to remove operational contaminations are imperfect: they are, as a rule, low-intensive, fail to always provide a satisfactory quality of cleaning, involve manual labor, and cannot rule out health hazard and occurrence of dangerous situations, e.g., inflammation [1]. This, in particular, refers to cleaning of titanium alloy casts to remove remainders of graphite molds and mold rods. Commonly, graphite is removed from casts of this kind manually, with auxiliary cutting tools, with these tools frequently broken; this procedure fails to always provide the due quality of surface cleaning and may cause mechanical damage to articles so that they go to scrap.

The aim of this study was to develop a high-temperature procedure for cleaning the surface of titanium alloy casts to remove graphite rods.

There is no published evidence about systematic studies of the interaction between graphite and hydroxide–salt melts. There have only been reports describing the behavior of carbon electrodes and structural elements in electrochemical processes [2].

EXPERIMENTAL

A derivatographic study of processes occurring in binary C–NaOH, C–KOH, C–NaNO₃ systems and ternary mixtures C–NaOH–NaNO₃ was carried out. The molar ratio of the components was varied from 5 : 1 to 1 : 4 for the first two systems and from 2 : 1 to 15 : 1 for the third. The molar ratios for the ternary system were 5 : 1 : (0.7, 2.5), 1 : (2–4) : 2, 1 : 2 : 1, and 1 : 1 : 0.5. The measurements were performed

on an OD-102 derivatograph at a heating rate of 5.1 deg min⁻¹. The weighed portions of the starting substances were in the range from 0.2 to 1.8 g.

An interaction between the components in mixtures of graphite and sodium and potassium hydroxides is observed even at low temperatures. For example, release of a certain amount of heat begins in the C–2NaOH mixture at approximately 160°C. The process is enhanced as the alkali melts. The quantitative characteristics of the effects observed strongly depend on the ratio of the components. It is noteworthy that oxidation of powdered graphite by atmospheric oxygen begins only at temperatures exceeding 400°C. The processes occurring in C–NaOH mixtures are accompanied by slight changes in the sample weight: the weight loss is due to moisture removal, and the weight gain upon melting of the alkali is associated with oxygen absorption. The thermal and gravimetric effects are considerably more pronounced for mixtures of graphite with potassium hydroxide.

In the C–NaNO₃ mixtures, the components interact at a temperature markedly exceeding the melting point of the nitrate. Depending on the component ratio, the beginning of a vigorous reaction is observed in derivatograms at 380–420°C. In mixtures with component ratios of 2 : 1 to 10 : 1, the interaction is markedly enhanced on reaching a temperature of 450°C. At large nitrate contents, the reaction proceeds in a moderate mode.

As follows from the experimental data obtained, the interaction of graphite with sodium and potassium hydroxides is considerably weaker than that in mix-

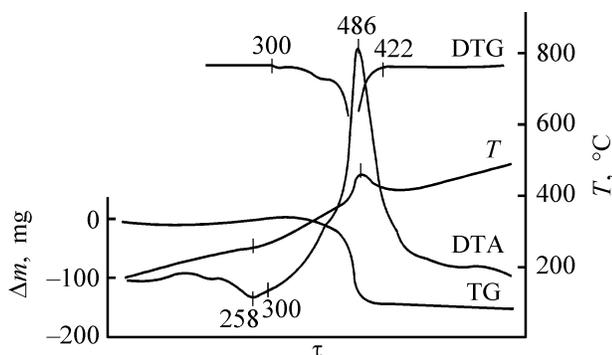


Fig. 1. Derivatogram of the 2NaOH–2NaNO₃–C mixture. (Δm) Weight loss, (T) temperature, and (τ) time.

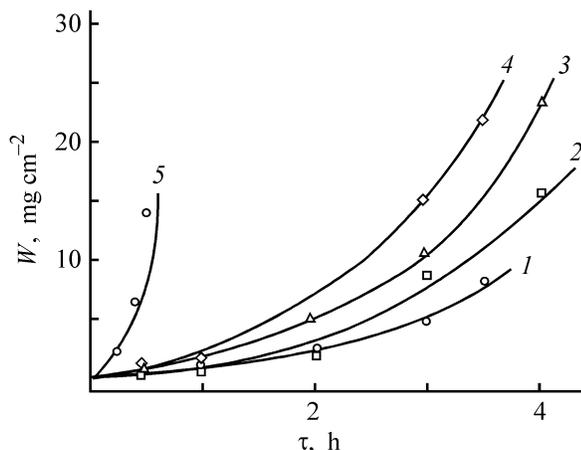


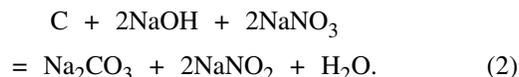
Fig. 2. Amount W of graphite etched away in melts of (1) NaNO₂, (2, 3) NaOH, and (4, 5) NaNO₃. Temperature (°C): (1, 2, 4) 450 and (3, 5) 500. (τ) Time.

tures of graphite and sodium nitrate. Apparently, atmospheric oxygen is involved in reactions after the melting of the alkali:



In the C–NaOH–NaNO₃ mixtures, the components intensively interact with carbon at temperatures 80–100°C lower than those in the mixture with sodium nitrate (Fig. 1) and this interaction is accompanied by a considerable weight loss. The values of the weight loss, experimentally determined for the C–2NaOH–

2NaNO₃ (initial weighed portion of the mixture 1.867 g), correspond to the occurrence of the reaction



It is noteworthy that the rate of reaction (2) strongly depends on the component ratio. For example, its intensity in the C–4NaOH–2NaNO₃ mixture is considerably higher, which can be judged from the abrupt weight loss and a more pronounced rise in temperature.

In addition to carrying out a derivatographic study, the kinetics of graphite etching in molten sodium hydroxide, nitrate, and nitrite and NaOH–NaNO₃, NaOH–NaNO₂, and KOH–KNO₃ mixtures was examined. The method of isothermal gravimetry of a sample under free-convection conditions was used. Graphite samples (99.9% C) in the form of rods (6–8 cm²) or plates (10–18 cm²) were treated in melts at 450 and 500°C. The mass of the melt was 120–140 g. The samples were preliminarily polished to obtain the same surface quality in each case. After treatment in the melt, samples were cooled to room temperature, washed in boiling distilled water for 15–20 min, and calcined at 200°C. In determining the rate of graphite etching in molten NaOH–NaNO₃ and NaOH–NaNO₂ mixtures, the time of experiment was limited to 20 min and the average value was calculated.

The kinetic curves of graphite etching in the individual melts under study have a shape typical of autocatalytic processes (Fig. 2), which is caused by an increase in the reaction area with time. The kinetic dependences are described by a power equation whose constants are listed in Table 1.

The rate of graphite etching in molten NaOH–NaNO₃ and NaOH–NaNO₂ mixtures depends to a greater extent on the component ratio. The isotherms of etching rate in these mixtures pass through a maximum (Fig. 3) at a nitrate content of approximately 35% (500°C) and 45% (450°C) in the first system and a nitrite content of 20% at both temperatures in the second system. It is noteworthy that the data for the NaOH–NaNO₃ system are in agreement with the results of a derivatographic study of processes in the ternary mixture C–NaOH–NaNO₃ in relation to the ratio of the components of the hydroxide–salt phase.

A number of alkaline formulations used to process titanium alloys, namely, to remove scale, are known [3, 4]. However, preliminary experiments demonstrated that formulations of this kind are ineffective or at all unacceptable for removal of graphite present

Table 1. Constants of the power equation $d_0\tau^n$, g cm^{–2} h^{–1}

Melt	T , °C	d_0	n	τ
NaOH	500	1.08	2.3	0–4
NaNO ₃	500	99.1	3.3	0–1
NaNO ₂	450	2.02	0.9	0–4

Table 2. Results of industrial tests of the method for cleaning of titanium casts to remove remainders of the graphite-based mold mixture in a melt based on alkali metal hydroxide

Kind of cast	Rod characteristics			Number of simultaneously processed casts	T, °C	Time of complete rod removal, h	Average rate of rod removal, mm h ⁻¹
	shape	shape in cross-section, mm	length, mm				
Turbine blade	Straight	5 × 20	120	1	560	7.5	8.0
Pipe	90° bend	d = 8	55	5	540	3.0	9.2
connection	The same	d = 10	40	5	560	2.0	10.0
Adapter		d = 10, 6	70	3	520	4.2	8.3
Flange (6 rods)	Straight	d = 5	10	3	500	0.5	10.0
Base (12 rods)	90° bend	Oval: a = 13, b = 35	27	1	520	1.75	7.7

in the form of remainders of molds and mold rods from titanium casts. It was found experimentally that the intensity of graphite removal in such melts at temperatures lower than 500°C is insufficient, in particular, for long rods. At the same time, treatment at above 500°C may lead to inflammation of articles. For comparison, a melt patented in a number of countries was used [5–7]. The melt contained (wt %): 50–78 sodium hydroxide, 8–20 potassium hydroxide, 9–15 sodium nitrate, and 5–15 sodium chloride. The intensities of graphite (rod) removal and types of corrosion behavior of the titanium alloy were compared for a particular alloy containing the above components in close to the middles of the indicated ranges. The optimal parameters of the process of cast cleaning were found for the VT5 alloy.

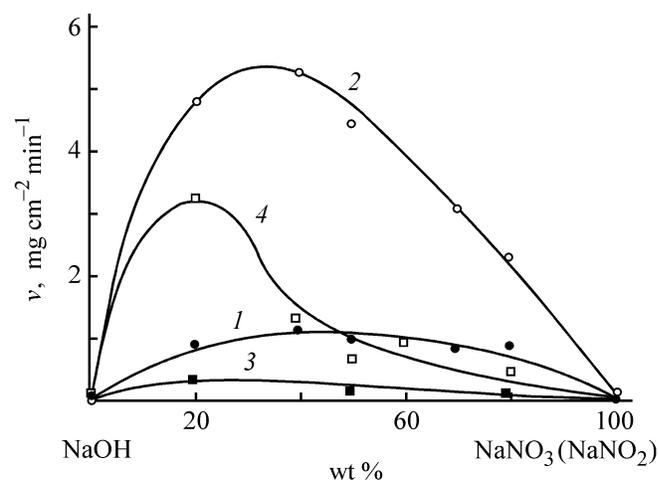
The results obtained in the study served as a basis for suggesting a melt containing four components. The melt is based on sodium hydroxide and nitrate. Potassium chloride contained in the melt improves its technological properties and, in addition, serves to prevent inflammation and explosion of potassium nitrate; KCl was introduced in an amount of 4–10 wt %. Making its content higher is undesirable because of a pronounced decrease in the dissolution rate of graphite. New properties are imparted to the melt by sodium orthotitanate. This additive to the alkaline melt exerts the strongest inhibiting influence on the corrosion of titanium. Also, the thermal stability of titanium and its alloys substantially increases. The solubility of sodium orthotitanate in molten sodium hydroxide is limited. For example, it is somewhat higher than 6 wt % at 550°C. The advantage of this salt is that Na₄TiO₄ can be obtained from a titanium waste, and, provided that certain conditions are satisfied, this can be done directly in the alkaline melt.

Comparative experiments demonstrated that the composition containing sodium hydroxide, nitrate,

and orthotitanate and potassium chloride has a higher (by a factor of 2.5–10) reactivity toward graphite, and no inflammation is observed at 550°C and a treatment duration providing complete removal of a rod.

The experiments performed suggested as the optimal melt for removal of graphite in the form of remainders of molds and mold rods from titanium casts the following formulations (wt %): sodium nitrate 40–55, potassium chloride 4–10, sodium orthonitrate, 2–6 and sodium hydroxide the rest.

Industrial tests of the technique suggested were carried out at a titanium casting shop of a machine-building plant in an industrial thermal furnace. The melt prepared in a rectangular steel bath had the following composition (wt %): sodium nitrate 48, potassium chloride 5.5, sodium orthotitanate 2.05, and sodium hydroxide the rest.

**Fig. 3.** Isotherms of etching rates v of graphite in molten (1, 2) NaOH–NaNO₃ and (3, 4) NaOH–NaNO₂. Temperature (°C): (1, 3) 450 and (2, 4) 500.

On melting the mixture and removing moisture at 400–500°C in the course of 1 h, the temperature was elevated to the working point. Casts of a VT5L alloy with remainder of molding sand and graphite rods of variously intricate shapes were cleaned. The removal of rods was periodically monitored in the course of processing. The results of the tests are listed in Table 2. A high rate of rod removal (8–10 mm h⁻¹) was achieved in the tests. A metallographic analysis demonstrated that the surface of the casts remains unchanged, with no corrosion etching occurring, and the mechanical properties of the alloy satisfy the standard requirements.

The advantage of the chemical method for removal of graphite from titanium alloy casts consists in that there is no need for manual labor, the output capacity significantly increases, cutting tools are saved, and the cleaning quality is improved.

CONCLUSIONS

(1) The mechanism and kinetics of graphite dissolution in hydroxide–salt melts and the effect of various salts (NaNO₃, NaNO₂, KCl, NaCl, Na₄TiO₄, KNO₃) were studied. As a result, an efficient method for removal of graphite in the form of remainder of molds and mold rods from titanium casts was sug-

gested. The optimal melt composition is as follows (wt %): sodium nitrate 40–55, potassium chloride 4–10, sodium orthotitanate 2–6, and sodium hydroxide the rest. The working temperatures of the method are in the range 500–550°C.

(2) The new technique was successfully tested in industry. The tests demonstrated the advantages of the chemical method for removal of graphite from inner hollows of titanium alloy casts.

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