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## CORROSION OF METALS BY MOLTEN SALTS IN HEAT-TREATMENT PROCESSES

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Molten salt baths are widely used in industry for various types of heat and thermochemical treatments of metal parts, tools in particular [1].

However, along with advantages, the application of molten salts has some drawbacks. For instance, due to the high activity of their ions and groups of ions at high application temperatures (300–1300°C), they can cause surface corrosion of the metal parts.

The objective of the present work, on the basis of literature studies and many years of experience by the author, is to analyze the reasons for the corrosive action of molten salts on metal parts during heat treatment.

The corrosive effects of various molten salt components were assessed on the basis of the corrosive rates of technical iron and "iodide" zirconium specimens exposed in molten chlorides of alkali and alkaline-earth metals used in industry. Iron was chosen because it is the main constituent of steel, while zirconium was studied because it is one of the most electronegative metals, which allows a very good comparison of the oxidation capacities of various components of the molten salts. To eliminate the effect of accidental factors, the experiments were carried out under strictly controlled conditions. The molten salts were free from such contaminants as water, oxidizing gases, and foreign ions, and an inert atmosphere (purified argon or helium) was maintained over the molten bath. The experiments were conducted in crucibles with external heating.

### Salt Components as Metal Oxidizers

Oxidation of metals by molten chlorides is an electrochemical process of ion exchange between the metal and the salt [2]:



These reactions take place under conditions close to equilibrium with respect to the salt layer adjacent to the electrode. Even in the absence of oxidizing contaminants (oxygen, water, etc.) the salt cations which can be reduced to the elemental state, or to a lower valency state, can act as metal-depolarizers. Cations of the alkali and alkaline-earth metals are the weakest oxidizers of metals. The corrosion rates of iron and steel exposed to such salts are negligible (less than 1 mm/yr [3]). However, the rates can grow if iron ions transferred into the molten salt bath react with anions of the salt to form stable complex anions. For instance, additions of fluoride ions (e.g., as a rectifier), which are themselves not oxidizers, increases the corrosion rates of iron and zirconium (Fig. 1a), due to the formation of  $[FeF_4]^{2-}$  and  $[ZrF_6]^{2-}$  anions, which are more stable than the respective chloride ions [4].

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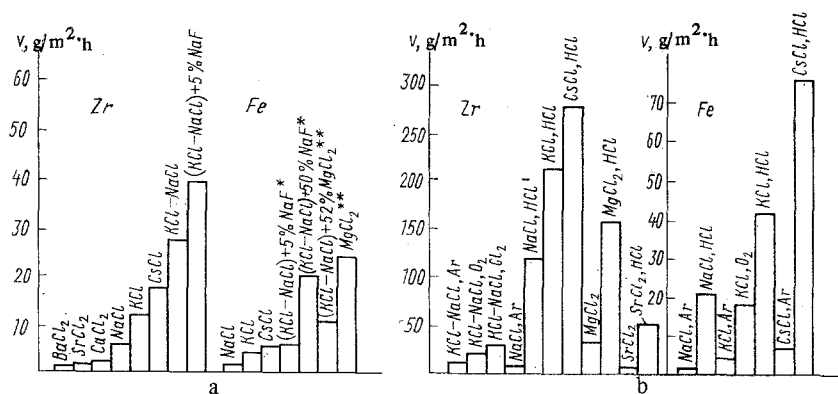
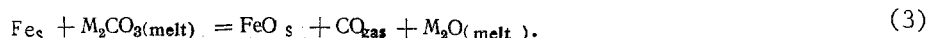
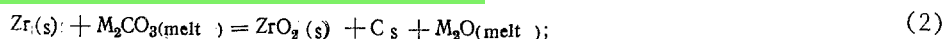


Fig. 1. Iron and zirconium corrosion rates ( $v$ ) during heating at  $900^{\circ}\text{C}$  for 4 h as a function of the molten bath composition (inert atmosphere over the bath) (a) and as a function of the composition of the atmosphere above the molten chloride bath (b). The data drawn from the literature are marked with asterisks.

The cations of polyvalent metals with a higher oxidizing power, i.e.,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Cr}^{6+}$ , etc., are stronger oxidizers than the alkali and alkaline-earth metals. Thus, the presence in a molten bath of  $\text{Fe}^{3+}$  ions can cause intensive corrosion of parts being heat treated [5].

Results of the iron and zirconium corrosion-rate measurement shown in Fig. 1a reflect the oxidizing activity of the alkali and alkaline-earth metal cations.

In molten baths of oxygen-containing salts — carbonates, nitrates, sulfates, and alkalis — the metal oxidizing agents are the following anions:  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{OH}^-$ . Their oxidizing characteristics and the products of their reduction vary depending on the chemical activity of the metal in the parts being heat treated. Thus, the more active zirconium reduces carbonate ions to elemental carbon, while iron (steel) reduces them only to carbon monoxide. The oxygen ions liberated by this reaction combine with the metal ions to form low-solubility, heat-resistant oxides ( $\text{FeO}$ ,  $\text{ZrO}_2$ , etc.)



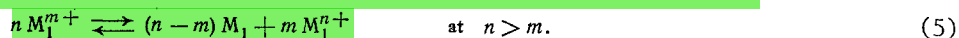
Therefore, the presence of oxygen-containing anions as impurities in a molten bath intensifies the corrosion of heat-treated parts and causes the formation of sludge in the molten bath.

#### Effect of Container Material

At high temperatures, not only the salt components but also the container (crucible) material can act as metal oxidizers, even if there is no direct contact between the crucible and the heat-treated parts. In molten alkali and alkaline-earth chlorides metal corrosion can proceed by the nonelectric transfer of the lower valence ions of electronegative metals to electropositive metals if the original elemental metals can form alloys with each other. The nonelectric transfer in molten salts was studied in detail in [6] and is widely used for nonelectric liquid zinc plating, borating, aluminizing, chromizing, siliconizing, and other steel surface-hardening methods. It has to be mentioned that the formation of metal alloys through molten salts goes in a strictly defined direction: the more chemically active metal  $\text{M}_1$  (electronegative) corrodes in the molten bath:



The low-oxidizing-level ions  $\text{M}_1^{m+}$  of that metal transfer by convection towards the more electropositive metal  $\text{M}_2$ . On the surface of that metal they disproportionate:



The atoms of the active metal  $\text{M}_1$  formed in this way produce an alloy  $\text{M}_1\text{-M}_2$ , while the  $\text{M}_1^{n+}$  ions (at a higher oxidation level), reaching the surface of  $\text{M}_1$ , accelerate its corrosion:

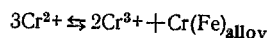
TABLE 1

| Temp.,<br>deg C | Crucible material | Mass<br>change,*<br>g/m <sup>2</sup> | Zr concentration in<br>molten bath, % | Remarks   |
|-----------------|-------------------|--------------------------------------|---------------------------------------|---|
| 900             | Quartz            | +21                                  | $3,1 \cdot 10^{-4}$                   | ZrSi <sub>2</sub> layer on specimen surface                       |
| 900             | Alundum           | -2                                   | $4,0 \cdot 10^{-4}$                   | Light etching marks on specimen surface                           |
| 950             | Glass-carbon      | -266                                 | 0,176                                 | Specimen is etched; finely dispersed ZrC particles in molten bath |
| 950             | Molybdenum        | -229                                 | 0,142                                 | Specimen is etched; 0.02-cm-thick Zr-Mo layer on crucible surface |

Note. The plus sign indicates increasing specimen mass; the minus sign indicates specimen mass decreasing.



For instance, the corrosion rate of a Cr specimen in molten NaCl at 900°C increases 30 times if an alundum crucible (inert with respect to the salt) is replaced by an iron crucible. In the latter case Cr corrodes,  $\text{Cr} - 2e \rightarrow \text{Cr}^{2+}$ , while on the crucible surface the following reaction takes place:



As a result of that reaction the  $\text{Cr}^{3+}$  ions enter into solution, accelerating the corrosion of Cr. The rate of this type of corrosion process increases with temperature, with intensified stirring of the molten bath, and with increasing surface area of the electronegative metal.

In the process of a nonelectrical transfer in a molten salt, nonmetallic materials (such as quartz  $\text{SiO}_2$ , alundum  $\text{Al}_2\text{O}_3$ , graphite C, and others) can take part provided they are soluble in the molten bath. Table 1 presents the results of mass change measurements of Zr specimens exposed for 4 h in molten  $\text{SrCl}_2$  (similar to  $\text{BaCl}_2$ ), as a function of the crucible material [7]. The increased mass of the Zr specimens in the quartz crucible is caused by reaction of the metal with silicate anions ( $\text{SiO}_3^{2-}$  or  $\text{SiO}_4^{4-}$ ) formed when quartz dissolves in the molten salt:



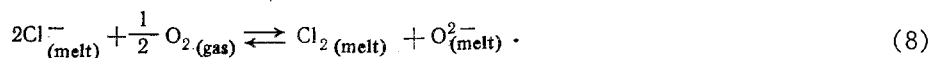
Alundum ( $\text{Al}_2\text{O}_3$ ) crucibles are most stable in alkali and alkaline-earth chlorides, the corrosion rate of Zr is lowest in such crucibles. The use of glass-carbon or molybdenum crucibles accelerates the dissolution of specimens because of the transfer of Zr through the molten bath with consequent formation of its alloy with the more electropositive molybdenum or carbon particles which come into the molten chloride bath due to contact with carbon-graphite materials [8].

Metal corrosion by nonelectric transfer can also proceed due to the temperature gradient in the molten salt bath, since the equilibrium of the reaction between a metal and its ions changes with temperature [6]. Because of this, either the metal corrosion will increase, or the metal will precipitate in the melt as finely dispersed particles. This characteristic of a molten salt bath has to be taken into consideration when choosing a crucible metal: such metal must either have a chemical activity equal to that of the heat-treated part, or it should not form alloys with the heat-treated metal. Special attention should be given to the lining of molten salt baths. Thus, chamotte lining (50-65 mass %  $\text{SiO}_2$ , 30-45 mass %  $\text{Al}_2\text{O}_3$ ) can cause pronounced corrosion of cutting tools during their heating in barium chloride baths at 1000-1250°C before quenching [1]. Such baths should be lined with a high-alumina refractory of MKO-72 type or with a chromomagnesite refractory.

#### Oxidation of Metals by Gases Dissolved in Molten Salts

Oxygen, chlorine, hydrogen chloride, and water vapor possess a low solubility in molten alkali and alkaline-earth chlorides. The solubility constant  $K_g$  of chlorine in such environment at 650-950°C is  $(0.03-4.62) \cdot 10^{-6}$  mole of the gas/cm<sup>3</sup> of the gas atmosphere,  $K_g$  of hydrogen chloride in the same conditions is  $(0.19-3.16) \cdot 10^{-6}$  mole/cm<sup>3</sup>, while for oxygen it approxi-

mately equals  $10^{-8}$  mole/cm<sup>3</sup>. The solubility constant  $K_s$  of water vapor in nitrates at 265-337°C, and in LiCl-KCl mixture at 390-480°C, is of the same order [9]. However, the oxidizing gases dissolved in molten chlorides cause a significant metal corrosion even if the metal has no direct contact with the gas medium. Chlorine, in addition, can be present in molten chloride as a result the following reaction of oxygen (air) with chloride ions:



It is known [2] that the equilibrium constant of (8) at 700-900°C is  $10^{-25}$ - $10^{-20}$  and that the concentrations of chlorine and of oxygen ions in the molten bath have to be very low. However, if such cations as  $\text{Fe}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Ni}^{2+}$ , etc., which can form low-solubility oxides with oxygen ions, are present in the molten bath, they will move the equilibrium in the direction of  $\text{Cl}_2$  evolution, which will be more intensive the higher is the concentration of cation-impurities in the molten salt.

For instance, chlorine can form as a result of the reaction between  $\text{FeCl}_3$  in a molten chloride bath and atmospheric oxygen in the following way:



or as a result of this molten salt being heated in vacuum to  $\geq 500^\circ\text{C}$ , when  $\text{FeCl}_3$  dissociates to  $\text{FeCl}_2$  and  $\text{Cl}_2$  [10].

Hydrogen chloride forms as a hydrolysis product of some chlorides during their melting. Hydrogen ions can be introduced into molten salts from atmospheric moisture, from the bath lining, or it can be present in incompletely dried salt. Molecules of water, when present in the molten bath, dissociate to  $\text{H}^+$  and  $\text{OH}^-$  ions. The equilibrium of this reaction depends on the molten salt composition. In molten salts containing high-valence cations the  $\text{OH}^-$  ions react forming heat-resistant, low-solubility oxides. Therefore, the water dissociation equilibrium of this reaction depends on the molten salt composition. In molten salts containing high-valence cations the  $\text{OH}^-$  ions react forming heat-resistant, low-solubility oxides. Therefore, the water dissociation equilibrium moves towards formation of hydrogen ions, which are metal oxidizers. A vast series of works by V. P. Kochergin [2] is dedicated to that problem.

Technical errors in the preparation of salts, prior to their loading into the bath, might be one of the main reasons for the increased corrosion of metal during heat treatment. Thus, chlorides of the alkali and alkaline-earth metals should be dried (calcined) at suitable temperatures before loading into the bath. The most hygroscopic salts (for instance,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ , etc.) can be treated by ammonium chloride at 200-220°C. The influence of the atmosphere above the molten bath on iron and zirconium corrosion rates in molten alkali-metal chlorides is demonstrated in Fig. 1b.

## CONCLUSIONS

1. When choosing the composition of a salt for metal heat treatment, it is necessary to consider the corrosion activities of the molten salts in relation to the metal being heat treated.

2. Corrosion activity of the molten bath can be decreased by strictly following the rules required for their operation, i.e., storage and preparation (drying) of the salts and the rectifier prior to their loading.

3. Particular attention should be given to the selection of the bath (crucible) material: chemical activity of the crucible metal and of the heat-treated metal must be the same (or nearly the same), while the crucible lining material must be as chemically stable as possible in the molten salt used.

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#### DIRECTIONS IN RATIONALIZATION OF THE USE OF ENERGY IN HEAT TREATMENT OF METALS\*

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From the moment of intense development of industry in all countries of the world an uninterruptedly increasing demand for energy has been observed. In 2000 the world demand for fuel and primary energy will be about 2.5 times greater than in 1975 (Fig. 1). It should be noted that in the different countries of the world the demand for energy is increasing dissimilarly.

This is accompanied by a decrease in the energy consumption for production operations as the result of their improvement. For example, to melt 1 ton of steel in the Middle Ages 100-150 etp<sup>†</sup> was necessary, in 1800 10 etp, during the Second World War about 2 etp, and at present less than 1 etp.

At the same time, as a rule, the energy consumption of industrial production (in relation either to the amount of this production or to the national income) is higher in countries with a medium level of industrial development and especially in developing countries than in countries with a high level of industrial development. A higher energy consumption accompanies a higher material consumption of production and the national economy in general.

For at least the last 10 years the necessity of decreasing the rate of growth in the requirement for energy in all areas of the activity of mankind has become increasingly clear on a world scale. The largest consumer of energy is industry. In 1975 66.6% of energy was consumed for the needs of industry, and in 2000 more than 71% of energy will be consumed for it (the world average).

At present rationalization of the use of energy in industry for the purpose of providing the minimum consumption of energy in production operations without negative technical, economic, and ecological consequences is a very acute problem [9].

Rationalization of the use of energy in industry makes it possible:

- 1) to improve the balance of fuel and other energy resources by decreasing their consumption;
- 2) to improve industrial production by abandoning obsolete production operations and highly energy consuming equipment and replacing them with improved and less energy consuming ones;

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<sup>†</sup>1 etp = 1 equivalent ton of petroleum = 1600 kWh.

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