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METALOTERMICKÝ PROCES V LIATINE – „MIMOPECNÉ SPRACOVANIE“

METALLOTHERMY IN THE CAST IRON “OUT OF THE FURNACE TREATMENT” PROCESS

Výroba vysokoakostných liatin v malých množstvách sa stáva v súčasnosti aktuálnym problémom. Existujuce technológie tavenia liatiny sú málo progresívne.V práci sú prezentované teoretické základy získania legovanej liatiny (Cr,Ti) pri použití metalotermie. Zdrojom týchto prvkov sú ich oxidy. Proces metalotermického spracovania prebieha bez zníženia teploty tekutého kovu, dochádza k zvýšeniu obsahu pridaných prvkov a zníženiu obsahu uhlíka a síry.

Production of high-quality cast irons in a batch production is topical current problem. Existing technologies of melting cast iron are not very progressive. The basic theoretical knowledges of obtaining of alloyed cast iron (Cr, Ti) by using metalothermy are presented in this work. The oxides are sources of this elements. The metalothermy treatment process is running without decrease of liquid metal temperature, comes to increase of quantity addition elements and reduction of quantity of carbon and sulphur.

1. A theoretical basis of aquiring metals from their oxygen compounds

A process of aquiring metals or their alloys is connected with a course of chemical reactions. The course interlocks many internal factors (e.g. quantity of reacting factors), concentration of reacting substances, an aggregation state of reacting substances and reaction products, thermal effect as well as external factors, (e.g. presure and reaction rates).

Metals, as acquired results of metallurgical processes, according to a purity grade, may be monophase, while alloys are usually multiphase and determine a part of a structural constituents mixture. An occurance range of individual phases or their mixtures is shown on adequate equilibrium system diagrams *(heterogeneous systems).*

In metallurgical processes, according to the mutual interaction of the system and its environment, which is a conversion of mass and energy between them, there are two *types of the system*[1]:

- *“an open system”* – a conversion of both mass and energy between the system and its environment is possible;
- *“a closed system”* – only a conversion of energy between the system and its environment is possible. There is no conversion of mass between them.
  A state of the examined chemical reaction may be defined, with the aid of a collection of thermodynamic variables that can be divided into two main groups:
- *thermodynamic variables;*
- *a state quantity.*

To the *first* group belong: temperature T, pressure P, volume V and concentration c. To the*second* group belong: internal energy U, entrophy S, entalphy H, chemical potential μ and free energy F.

A connection between enthalpy, entrophy and temperature may be described as a formula below:

$$G = H - TS \tag{1}$$

where: G - Gibbs free entalphy or thermodynamic potential or Gibbs free energy.

A thermodynamic potential, during a spontaneous process proceeded in a permanent temperature and under a permanent pressure, tends to approach its minimum value. Reaching this minimum value determines achieving the equilibrium state.

In practice, knowledge of S, H, G value changes (not their absolute values) is sufficient. Then the formula (1) is as follows:

$$\Delta G = \Delta H^0_{298} - T\Delta S^0_{298} \tag{2}$$

where: ΔH- the enthalpy change of the reaction while = const. and T = 298 K;
ΔS - the entrophy change of the reaction while T = 298 K, T - temp. in Kelvin.

It is more convenient to use this quotation because ΔH^0_{298} and ΔS^0_{298} can be found in tables.

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Acquiring metals or their alloys as results of exothermic reactions between metal (a reducer) and metal compounds (mainly oxygen compounds) is a process called *methallothermy* [2]. If we use aluminium as a reducer - then the process is called *aluminothermy,* silicon - *silicothermy,* calcium - *calciothermy.* Except for pure metals, alloys can be used for reduction, eg. $Ca-Si$, $Al-Ca-Si$, $Al-Fe-Si$. The metal oxide reduction process is presented as an underneath formula:

$$Me'O + Me'' \rightarrow Me' + Me''O \qquad (3)$$

The reaction proceeds in an easier way when a difference in a propinquity to them between a metal Me″ reached from reduced oxide and metal – the reducer is more significant. The thermodynamic potential, also called the oxygen potential, terms the estimation of oxides durability. The estimation is presented as follows:

$$\Delta G^0_T = -RT \ln p_{o_2} \qquad (4)$$

where: R - universal gas constant,
p_{o_2} - oxygen pressure in equilibrium with metal oxide at a particular temperature.

A thermodynamic potential change that occures during the formation of a few oxides from their chemical elements, (depending on the temperature values) is shown on Fig. 1.

Reduction conditions may be defined as a temperature dependence on the thermodynamic potential ΔG^0_T. The reaction can be initiated at $\Delta G^0_T < 0$. The superior the depreciating (detrimental) ΔG^0_T values, the easier the reaction runs. A reciprocal course of thermodynamic potential changes determines that the magnesium reduction of aluminium oxides as well as silicon, chromium and iron oxides is possible. The aluminium reduction is suitable for silicon oxides as well as for chromium and iron oxides. Silicon, however, reduces chromium oxides and iron oxides only. Under the pressure of 98,07 kPa it is not possible to apply the aluminium reduction for magnesium oxides, because ΔG^0_T for this reaction is > 0. A metalthermic reaction initiates if in any place of the mixture the ignition temperature is achieved. Heat emission creates a reaction around the ignition place. Exotermic mixtures lighting up is caused by dint of *initiators* (igniting mixtures), e.g. magnesium with sodium nitrate or aluminium with barium peroxide. The reaction initiators, in the metal or alloy production process from metalthermic methods, are situated in the proper place of charge and lighten up with a glowing bar. The igniting mixtures satisfy requirements by dint of a low ignition temperature as well as a great thermal effect.

Using the enthalpy values ΔH^0_{298} it is possible to determine which metalthermic reactions will spontaneously proceed (without the heat from the outside).

German research [2] angles that the quantity of emitted heat for 1g of the charge shouldn't be lower than 2300 J. A unitary thermal effect can be counted as follows:

$$H^0_{298} = \frac{\Delta H^0_{298}}{molMe'O + molMe''} \qquad (5)$$

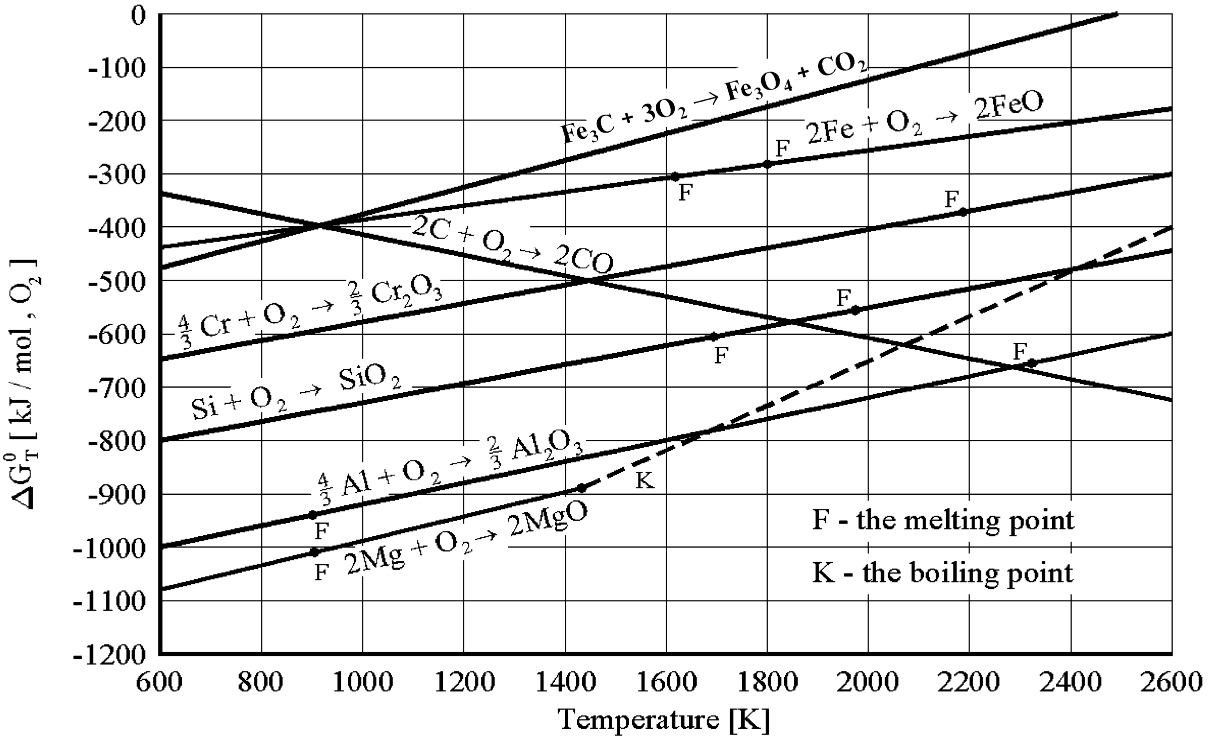

Fig. 1 The temperature values of the thermodynamic potential change of the creating oxides Mg, Al, Si, Cr, Fe [2]

Russian research [3] angles that for a proper metalthermic reaction course a unitary thermal effect, not lower than 2700 J is required. Metalthermic processes run spontaneously if $-\Delta H^0_{298} > > 300$ kJ/g – atom of the reductor. A great output and purity of the diminished element can be obtained. As an example the *enthalpy value* for a mole of the reaction reducer – aluminium or silicon has been posed.

$${}^{3}/_{4}\,SiO_2 + Al \rightarrow {}^{3}/_{4}\,Si + {}^{1}/_{2}\,Al_2O_3 \qquad (6)$$
$$\Delta H = -\ 158.7 \text{ kJ/mol Al}$$

$${}^{1}/_{2}\,Cr_2O_3 + Al \rightarrow Cr + {}^{1}/_{2}\,Al_2O_3 \qquad (7)$$
$$\Delta H = -\ 272.2 \text{ kJ/mol Al}$$

$${}^{3}/_{8}\,Fe_3O_4 + Al \rightarrow {}^{9}/_{8}\,Fe + {}^{1}/_{2}\,Al_2O_3 \qquad (8)$$
$$\Delta H = -\ 418.3 \text{ kJ/mol Al}$$

$${}^{1}/_{4}\,K_2Cr_2O_7 + Al \rightarrow {}^{1}/_{2}\,Cr + {}^{1}/_{2}\,Al_2O_3 + {}^{1}/_{4}\,K_2O \qquad (9)$$
$$\Delta H = -\ 419.1 \text{ kJ/mol Al}$$

$${}^{1}/_{2}\,CrO_3 + Al \rightarrow {}^{1}/_{2}\,Cr + {}^{1}/_{2}\,Al_2O_3 \qquad (10)$$
$$\Delta H = -\ 547.2 \text{ kJ.mol Al}$$

$${}^{3}/_{7}\,KMnO_4 + Al \rightarrow {}^{3}/_{7}\,Mn + {}^{1}/_{2}\,Al_2O_3 + {}^{3}/_{14}\,K_2O \qquad (11)$$
$$\Delta H = -\ 564.8 \text{ kJ/mol Al}$$

$${}^{2}/_{3}\,Cr_2O_3 + {}^{4}/_{3}\,Al \rightarrow {}^{4}/_{3}\,Cr + {}^{2}/_{3}\,Al_2O_3 \qquad (12)$$
$$\Delta H = -\ 151.2 \text{ kJ/mol Al}$$

$${}^{1}/_{3}\,K_2Cr_2O_7 + Si \rightarrow {}^{2}/_{3}\,Cr + SiO_2 + {}^{1}/_{3}\,K_2O \qquad (13)$$
$$\Delta H = -\ 345.4 \text{ kJ/mol Si}$$

$${}^{1}/_{2}\,Fe_3O_4 + Si \rightarrow {}^{3}/_{2}\,Fe + SiO_2 \qquad (14)$$
$$\Delta H = -\ 346.3 \text{ kJ/mol Si}$$

$${}^{2}/_{3}\,CrO_3 + Si \rightarrow {}^{2}/_{3}\,Cr + SiO_2 \qquad (15)$$
$$\Delta H = -\ 521.3 \text{ kJ/mol Si}$$

$${}^{4}/_{7}\,KMnO_4 + Si \rightarrow {}^{4}/_{7}\,Mn + SiO_2 + {}^{2}/_{7}\,K_2O \qquad (16)$$
$$\Delta H = -\ 542.2 \text{ kJ/mol Si}$$

Recent research indicated that the reactions marked as (6), (7) and (12) do not run spontaneously.

A question if these reactions courses can be accomplished appears.

Training indicates some ways of the *heat effect extention.*

The most important ways are presented below:

1. *An electric energy lead.* The process may also be called *electrosilicothermy* in case of silicon oxides reduction. This alternate design cannot be used in the "out-of-klin" treatment.
2. *An addition of iron oxide and aluminium oxide mixture to the charge – ferromit mixtures* (reaction 8). A heat excess helps the right reaction. The method is suitable for iron alloy productions because, in case pure metals are obtained, iron pollutes them.
3. *Using an oxide of a higher oxidation number as a part of the charge,* e.g. in the chromium production a portion of Cr_2O_3 should be replaced by CrO_3 (reactions 10 and 15).
4. *Using oxy-salts of the reducing element instead of the oxides.* For example one can use $K_2Cr_2O_7$ instead of Cr_2O_3 (reactions 9 and 13). If manganum presence in a product is acceptable then $KMnO_4$ can be a part of the charge (reactions 11 and 16).
5. *An addition of peroxides to the charge.* You can use barium or calcium that in connection with aluminium, silicon or magnesium emit a great heat quantity. The reaction products (barum oxide or calcium oxide) and a reducer run to the metallurgical slag and do not pollute metals.
6. *Making addition of a great oxygen amount salt to the charge.* These salts, in addition with aluminium, set a prominent heat value (e.g. chromates, dichromates, permanganates, nitrates, chlorates, perchlorates). Nitrates, chlorates and perchlorates, in connection with aluminium, set products as well as heat effect as follows:

$$6\,NaNO_3 + 10\,Al \rightarrow 5\,Al_2O_3 + 3\,Na_2O\uparrow + 3\,N_2\uparrow \qquad (17)$$
$$\Delta H = -\ 623.9 \text{ kJ/mol Al}$$

$$NaClO_3 + 2\,Al \rightarrow Al_2O_3 + NaCl\uparrow \qquad (18)$$
$$\Delta H = -\ 783.0 \text{ kJ/mol Al}$$

$$3\,NaClO_4 + 8\,Al \rightarrow 4\,Al_2O_3 + 3\,NaCl\uparrow \qquad (19)$$
$$\Delta H = -\ 783.0 \text{ kJ/mol Al.}$$

Reaction products run to the slug (Al_2O_3) or they leave the reaction environment, being in a gaseous state.

7. *The charge heating.* During this reaction, for every 100 K the heat effect grows for 125,6 J/g of the charge. This procedure is not suitable for the low ignition temperature mixtures, because during the heat process self-ignition can happen.

Temperature of metalthermic processes. It's quite difficult to measure metalthermic processes' temperatures. The most often an optical pyrometer is used during the measurements. A basic difficulty arises from the fact, that a temperature of a system surface in a short time equals the reaction temperature. The surface is covered with the oxygen of the reducer [3].

The burning temperature of the thermite mixture was measured pyrometrycaly at the temp. of 2200 − 2400 °C. The measurements pose that this temperature should reach 3200 ± 200 °C. Photometric measurements however pose that it reaches the temperature of 3200 ± 50 °C. The temperatures achieved during the metalthermic reactions exceed the melting temperatures of the reduced metals. So one can put forward a proposal that there will be no heat losses during the "out of the furnace treatment" reaction.

2. A chromium oxides reduction with aluminium - chromium output

There is another parameter describing metalthermic processes (except for the heat effect). It's their *efficiency* measured by an output of the reduced metal in the aluminothermic process. The output is connected with *the equilibrium constant,* which, for the reaction (7), is shown as follows:

$$K_p = \frac{a_{Cr}^2 \cdot a_{Al_2O_3}}{a_{Al}^2 \cdot a_{Cr_2O_3}} \tag{20}$$

where: a - activity of chemical elements and molecules of the system.

For the system, created by chromium aluminium trioxides as well as the products of their reactions, for the measurements mole fractions of the slag products as well as reacting substances instead of the activity can be used. After their replacement to the formula (20) the equation will be given as follows:

$$K_p = \frac{n_{Cr}^2 \cdot n_{Al_2O_3}}{n_{Al}^2 \cdot n_{Cr_2O_3}} \tag{21}$$

where: n - an amount of substantial moles for the reaction (7) in the state of equilibrium related to 1 mole of Cr_2O_3.

The system created by the reaction (7) consists of two phases: a metal phase (Cr) and the slag (Al_2O_3). At the stable pressure the state of quotation can be determined by the metal bath temperature as well as by one of the factors *concentration.* The concentrations of the other system factors are presented as follows:

$$n_{Cr} = 2(1 - n_{Cr_2O_3})^2 \tag{22}$$

$$n_{Al_2O_3} = 1 - n_{Cr_2O_3} \tag{23}$$

$$n_{Al} = 2n^2{}_{Cr_2O_3} \tag{24}$$

so:

$$K_p = \frac{(1 - n_{Cr_2O_3})^3}{n^3{}_{Cr_2O_3}} \tag{25}$$

Making an assumption that the reaction (7) runs almost to the end (when $n_{Cr_2O_3} << 1$ and $n_{Cr_2O_3} \approx 1$) we get:

$$K_p = 1/n_{Cr_2O_3}^2 \tag{26}$$

Resisting on the temperature and a state of chemical equilibrium, a Cr_2O_3 mole account can be calculated:

$$n_{Cr_2O_3} = \sqrt[3]{\frac{1}{K_p}} \tag{27}$$

$$\lg K_p = \Delta G_T^0 / 19{,}55T \tag{28}$$

The formulas (22 - 28) allow to calculate K_p, n_{CrO}, n_{Al}, as well as the chromium output in the equilibrium state of the reaction (7) at the temperatures of 2000, 2250 and 2500 K.

A chromium output was calculated from the formula as follows:

$$U_{Cr} = \frac{100 n_{Cr}}{n_{Cr} + n_{Cr_2O_3}} \tag{29}$$

Findings were compiled in the chart below:

Temperature [K]	2000	2250	2500
K_p	$1.4 \cdot 10^{11}$	$3.7 \cdot 10^{9}$	$2.1 \cdot 10^{8}$
$n_{Cr_2O_3}$	$1.9 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$
n_{Al}	$3.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$
A chromium output [%]	99.98	99.93	99.83

The received results indicate two facts: *first* – a theoretical chromium output in its aluminium trioxide reduction process is very high and in the temperatures of industrial conditions equals over 99 %. *Second* a chromium output decreases as the temperature increases.

Under the industrial conditions a chromium output from the aluminothermic process equals 88 %. A question "where is the source of the conciderable divergence in the chromium output" appears.

The above problem can be considered resisting on the thermodynamic potential change during the process of chromium receiving, using the aluminothermic method (Fig. 2).

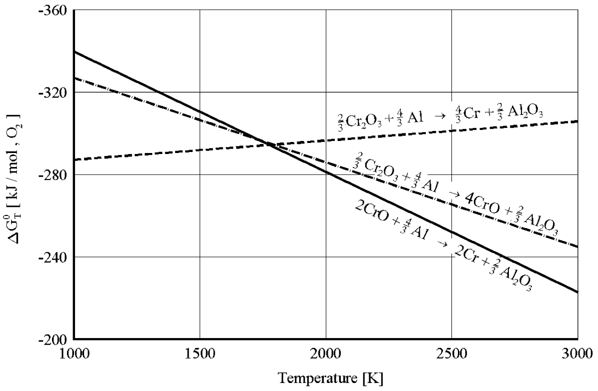

Fig. 2 Thermodynamic potential change for aluminium reduction process of chromium oxides depending on the temperature [3].

At the temperature of over 1835 K the reduction process should run as follows: $Cr_2O_3 \rightarrow CrO \rightarrow Cr$. Probability of this course rises with the temperature growth. A forming chromium oxide CrO passes into the slag, giving a durable complex $Cr^{2+} - AlO^{2-}$. A slag search shows that chromium presented in the complex is not only in the combined state, but pure metal drops, bounded by the slag, determine its great majority. The chromium losses are the main cause of its low output in industrial conditions.

As a counteraction of chromium oxide CrO forming which, at the temperature of 1800 K, is more durable than Cr_2O_3, calcium oxide is added to the charge. Presence of this compound boosts the system reactivity, chromium trioxide becomes more active and the reaction (7) shifts to the right.

The reaction course (7) is presented as follows:

$$\begin{aligned} &{}^2/_3\, Cr_2O_3 + {}^4/_3\, Al + {}^2/_3\, CaO \rightarrow \\ &\rightarrow {}^4/_3\, Cr + {}^2/_3\, (CaO \cdot Al_2O_3) \end{aligned} \tag{30}$$

A thermodynamic potential change of this reaction is presented as a formula below (31):

$$\Delta G^0{}_T = -\ 385390 + 31{,}11\ T \qquad (31)$$

and for the reaction (7) – the formula (32):

$$\Delta G^0{}_T = -\ 372600 + 42{,}50\ T \qquad (32)$$

Comparing both formulas (31) and (32) we can notice that for the same temperature value a thermodynamic potential value for the reaction (30) will always be greater than the reaction (7). $\Delta G^0{}_T$ increases when the temperature rises.

Taking full advantage of the presented theoretical deliberations, chromium production technology has been developed. There are two methods developed: *"a period procedure"* and *"a semi-period procedure"*, using a draining - off slag or the slag itself. In the second method liquid metal as well as slag taps the heat after the specified time of the mixture burning up.

3. Chromium oxides reduction under conditions of cast iron "out of furnace" treatment

As far as the recent research is concerned, a chromium oxides reduction process proclaims a closed system. How a complex system of the liquid cast iron and the exothermic mixture is going to behave burning up on its surface?

A reaction analysis that can proceed between a chromium trioxide and cast iron elements, should be investigated from the analysis of thermodynamic potential changes of $Cr-O-C$ system, depending on temperature values - Fig. 3.

Cr_7O_3, Cr_2O_3, $Cr_{23}C_6$, Cr are the reaction products, having their thermodynamic potentials greater than the reaction (7) thermodynamic potential at the temperature value greater than 1600 K. A reaction giving a chromiun trioxide as a product is undesirable because in this case a proceeding process is reverse to the required process.

The product with the highest $\Delta G^0{}_T$ Cr_7C_3 values determines the result of the reaction as follows:

$$^{14}/_5\ Cr_3C_2 + O_2 \rightarrow {}^{6}/_5\ Cr_7C_3 + 2\ CO\uparrow \qquad (33)$$

Chromium carbide Cr_3C_2 as a substrate determines the result of the reaction as follows:

$$^{2}/_3\ Cr_2O_3 + y\ C \rightarrow y\ Cr_3C_2 + 2\ CO\uparrow \qquad (34)$$

The reaction thermodynamic potential is greater than the basic reaction (7) thermodynamic potential only at 2100 K. This temperature can be reached by the system, but only for a short period of time and an inconsiderable volume, because the contact of the mixture with a liquid slag is limited. This fact estimates that the reaction (34) course as well as the reaction (33) course is

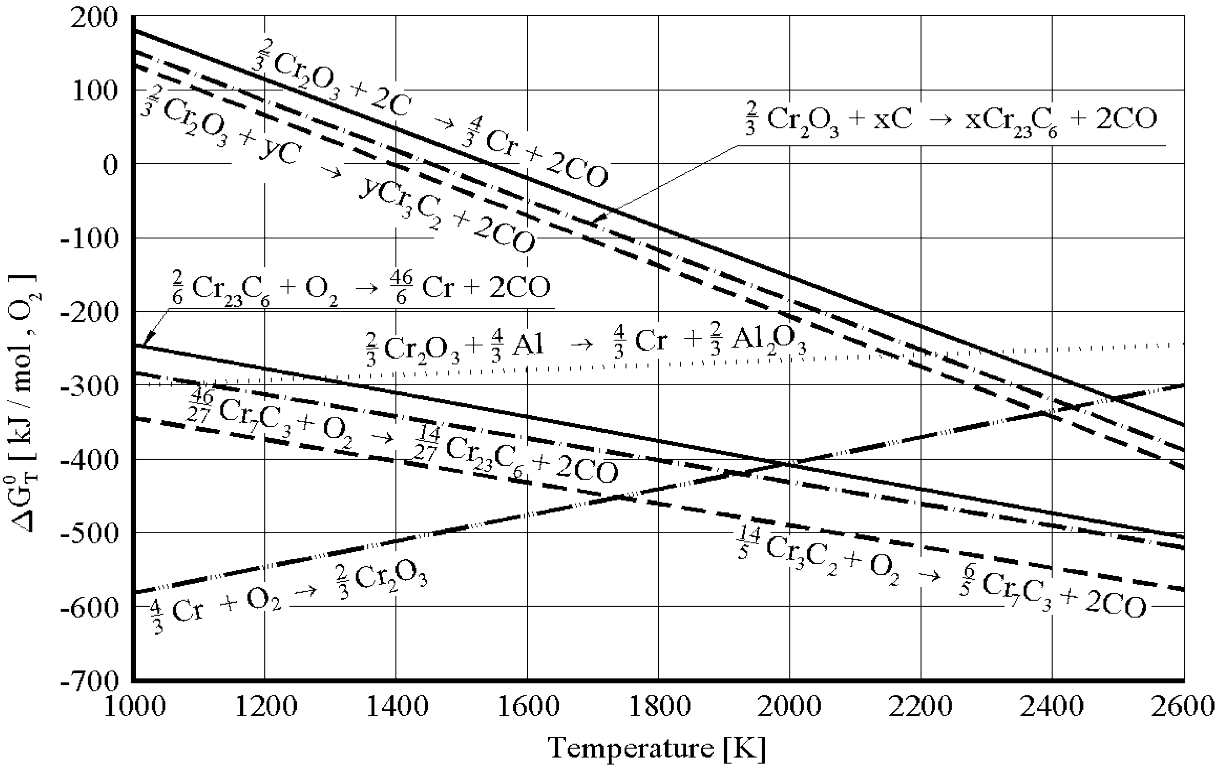

Fig. 3 A thermodynamic potential of Cr-O-C system (in the temperature range of 1000 - 2600 K) [3].

imperceptible. The other carbide $Cr_{23}C_6$ determines a result of the reaction as follows:

$$ {}^{46}/_{27}\, Cr_7C_3 + O_2 \rightarrow {}^{14}/_{27}\, Cr_{23}C_6 + 2\, CO\uparrow \qquad (35)$$

Cr_7C_3 is a substrate of the reaction whose amount is regulated by the (33) and (34) reactions. Forming the $Cr_{23}C_6$ carbide doesn't decrease a chromium output, because free chromium determines the result of its reaction with oxygen, according to the reaction (36) as follows:

$$ {}^{2}/_{6}\, Cr_{23}C_6 + O_2 \rightarrow {}^{46}/_{6}\, Cr + 2\, CO\uparrow \qquad (36)$$

$Cr_{23}C_6$ carbide also becomes the result of the reaction below:

$$ {}^{2}/_{3}\, Cr_2O_3 + x\, C \rightarrow x\, Cr_{23}C_6 + 2\, CO\uparrow \qquad (37)$$

Reaching the temperature over 2200 K determines the reaction course condition. From Fig. 3 one can specify a direct chromium trioxide reduction reaction with carbid, according to the reaction as follows:

$$ {}^{2}/_{3}\, Cr_2O_3 + 2\, C \rightarrow {}^{4}/_{3}\, Cr + 2\, CO\uparrow \qquad (38)$$

Thermodynamic conditions of the reaction are more beneficial than the (7) reaction only at over 2300 K. The possibilities of Cr_3C_2, $Cr_{23}C_6$ and Cr formation shouldn't be excluded from the thermodynamic analysis of $Cr-C-O$ system. A probability of their formation decreases as they are listed.

Carbide oxide is one of the (33) ÷ (38) reactions product which as gas simply leaves the reaction environment. Forming the carbid oxide involves a carbid contents decrease in the system.

Silicon, following carbid, and oxygen, is another chemical element to analyse. The thermodynamic potential change during a silicon reduction of chromium trioxide is shown as below:

$$\Delta G^0{}_T = -\,49200 + 7{,}5\ T \qquad (39)$$

Comparing both formulas: (33) and (40) an inference that, for every temperature value the (7) reaction is more justifiable than reaction (15) appears.

During the Cr-C-O system and the (15) reaction analysis, carbid and silicon were considered in a solid state, while oxygen was concidered in a gaseous state. In the slag carbid and silicon are in a dissolved state, while oxygen is in an ionized state. It causes an increase in activity of these elements, activity of oxygen in particular. There is a lack of data for the liquid iron - exothermic mixtures system analysis.

Some other reactions may run between carbid and chromium trioxide. Reaching the temperature of 2100 K determines a condition of their course. A high temperature is reached by the system as a result of reaction (7) course mainly.

Nascent metallic chromium may react with slag oxygen and mixture oxygen. Chromium trioxide determines the product of the reaction. The course of the reaction is objectionable because there is a lack of aluminium and a forming product (Cr_2O_3) may pass the slag, decreasing a chromium output. That's why free oxygen in the slag or mixture is harmful. Free oxygen in the mixture estimates liquid oxygen in a binding material, which is used for integrating mixture elements.

Burning exothermic chromium mixture in contact with a liquid slag creates an open system, because it gives the heat and chromium away to the slag and absorbs mainly carbon from it.

4. Exotermic mixture elements for the "out of the furnace" treatment

Making full use of the professional literature [2, 3], small publications [4, 5] as well as personal experiments [6, 7] in the above field, exothermic alloy mixtures contain:

- *a source of an alloy element;*
- *an oxidizer* - nitrates, chromates, dichromates, chlorates, perchlorates, sodium, silicon or calcium permanganates;
- *a reducer* - aluminium, calcium, silicon, manganate or their alloys;
- *a binder* - water-glass, cement, an organic binder;
- *a reaction initiator* - a burning up mixture - magnesium dust and sodium nitrate or barium peroxide with aluminium;
- *a flux* - calcium oxide or calcium fluoride.

Pure metals, ferroalloys or chemical compounds are *sources of alloying elements.* In case of exothermic chromium mixtures-chromium sources may be: ferrochromium, chromium concentrate (60 % Cr_2O_3, 14% FeO), chromium trioxide, chromates, dichromates.

As a reducer an aluminium power is used. It should fulfill two conditions:

- its grains' dimension should not transgress 0.3 mm;
- its' oxygen contents is max. 0.05 %.

A process of alloying elements conversion from the exothermic mixture to the liquid slag is connected with a chemical reaction course. The right effect requires a great surface of mixture factors, an uniform composition.

To get a mixture factors contact, its composition contains a binder which is the main source of smoke and dross coming to the slag.

Because of these reasons some other ways of factors connection are used where possible. In this work [2] agglomeration was applied. A salt recrystalization process can be used as well. In each method of exothermic mixture factors connection water is added as well as drying at the temperature range of 383 - 413 K is used.

A point lay-out initiator is also used. That procedure doesn't bring positive results to the reaction initiation. A volume lay-out initiator is used to reduce the mixture burning time [4]. Magnesium alloys can also be applied as factors of burning mixture. The burning of the exothermic mixture during the "out of the furnace" treatment succeeds as a result of its contact with liquid metal.

Not every mixture contains flux. In this work [8] the flux (fluorite) was added to accelerate a modifier assimilation grade of the liquid metal. Fluorite is also a factor of the self-fusible ferrochromium [9]. However, no flux is added to the mixture that consists of chromite.

Making full use of the above facts we can ascertain that the flux presence in the exothermic mixtures proclaims an open problem.

The exothermic mixtures composition should be assorted to have the exothermic reactions' thermal effect between the alloying element's oxygen compounds and the reducer, the oxidizer and the initiating factor greater enough to cover the heat losses for the mixture heating up as well as for some of its factors fusion. The too great heat effect causes an impetour reaction course which aggravates the industrial safety. However, the insufficient amount of emitted heat causes the temperature decrease of the melt as well as the decrease of the inserted elements' output [10].

Reviewed by: T. Liptáková, A. Sládek

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