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Fractional gas analysis method for non-metallic inclusion control

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The content, nature, size and distribution of oxide inclusions significantly influence the quality of tyre cord, railway, bearing and stainless steel grades. The control of non-metallic inclusions allows predicting steel properties but modern methods of non-metallic inclusions evaluation are highly labor and time-consuming. Fractional Gas Analysis (FGA) method developed is a modification of oxygen determination method, under non-isothermal conditions^[1]. It provides a possibility to separate and identify the oxides in steel. Low carbon steel killed with aluminum, railway steel, tyre cord steel, bearing steel and a number of commercial steel grades were carried out by FGA. The difference in temperature thermodynamic stability forms the basis of the fractional separation of oxides. The modern analyser is computer controlled and contains measurement cells along with supporting software to perform the fractional analysis. However, a wide application of this method is limited by the absence of well-established fractional analysis performance, software for peak separation and oxide identification.

Basing on the physicochemical analysis of non-isothermal carbon reduction of oxides and taking into account the gas dynamic phenomena in gas system of analyzer, a novel FGA procedure and software package for peaks separation and oxides identification have been developed^[2].

The real fractional analysis performance using the modern analyzer's possibilities consist of the ramping analysis procedure optimized from the maximum peaks resolution point of view and provides sufficient signal to noise ratio for peaks separation data processing, and oxides identification procedure uses characteristic parameters of dedicated oxides peaks.

The fractional analysis procedure differs from the total one in a feature ramps the furnace (heating rate) temperature and enlarged analysis time. The analysis proposed a good temperature control. The double wall crucibles heater and inner have to use in fractional analysis procedure because of temperature control requirements.

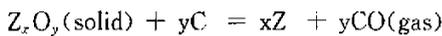
The sample is fused in the graphite crucible when the temperature reaches the sample melting point. Different oxygen forms of the sample interact with carbon forming carbon monoxide. The sample melting begins in the metal-graphite contact zone. A melt saturated with carbon is formed. It is caused by the fact that Fe-C and Ni-C phase diagrams have metal-carbon eutectics with melting points 1426 K and 1593K, respectively, being 350-380 K lower than melting temperatures of pure metals. Experimentally obtained that

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carbon concentrations in iron melt is close to saturation of pure iron with carbon according to the Fe-C and Ni-C equilibrium phase diagram. The sample begins to melt at a small overheating ($\Delta T = 30-50\text{K}$) above eutectic temperature and the sample melting is completed at the temperature that is 100-120K higher than the melting temperature. These values depend on the heating rate (ramp).

Thus, thermal reduction of oxides during the fractional analysis process with non-isothermal conditions can be divided into three periods. The reduction conditions for these periods differ substantially. These periods are illustrated in Fig. 1: (1) Temperature interval from the sample dropping into the carbon crucible up to the beginning of sample fusion. (2) The melting period up to the end of sample fusion. In this case, oxide reduction rate has a complex kinetic control. Proper separation and oxides identification during this period are impossible. (3) The period of FGA begins when the melting is completed. The kinetics of the process is controlled by the slowest stage, and is similar for each oxide reduction during the analysis temperature interval. Identification and separation of oxides within this period can be performed.

During the sample heating in carbon crucible, oxides are reduced with carbon and oxygen leaves the melt as carbon monoxide according to the following reaction:



$$K_p = \frac{a_Z^x \cdot p_{CO}^y}{a_C^y \cdot a_{ZxOy}}, \quad (1)$$

Where Z is the oxide forming element; x, y are the stoichiometric coefficients, K_p is the reaction equilibrium constant; a_C, a_{ZxOy}, a_Z are carbon, oxide and deoxidizer activities, respectively; p_{CO} is the partial pressure of carbon monoxide.

Basing on the equilibrium constant for considered reaction it is feasible to evaluate actual temperatures of carbon oxide reduction beginning in melt. In so doing we suppose; the sample heating rate to be low, there are no temperature and concentration gradients in melt and there is a thermodynamic equilibrium at every moment of time. If there is not an oxide-metal mutual solubility then basing on Gibbs energy equation we can directly estimate the temperature where carbon monoxide vapor pressure achieves a desired value:

$$\Delta G_1 \equiv y(\Delta G_{CO}^0 + RT \ln P_{CO}) + RTx \ln(x_2 \gamma_2) - \Delta G_{oxide} = 0, \quad (2)$$

Where x_2, γ_2 are mole portion and Raul activity coefficient of deoxidizer in melt; ΔG_{CO}^0 is the change of standard free energy of CO formation, J/mole; ΔG_{oxide} is the standard free energy of oxide formation from pure liquid metal and gaseous oxygen, J/mole. Activity coefficient of deoxidizer in melt saturated with carbon can be expressed in the terms of interaction parameters.

Substituting deoxidizer activity coefficient into (2) and taking into account temperature dependencies of formation free energy of oxides, interaction parameters and carbon solubility parameters we obtain a transcendental equation. The beginning reduction temperature of oxide Z_xO_y can be estimated solving Eq. 2 for corresponding alloy composition.

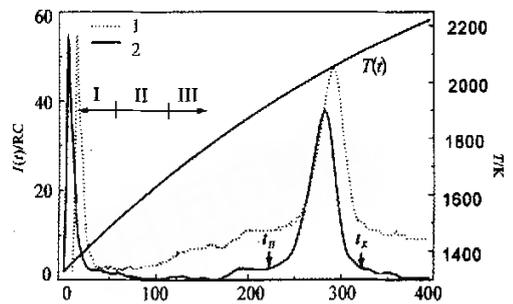


Fig. 1 Periods of the thermal reduction of oxides during fractional analysis
dashed line 1—the experimental FGA data curve; solid line 2—the OxSeP result after blank subtraction and time-delay correction

The next fundamental principle of the fractional oxide separation and identification can be proposed;

Every oxide has its own temperature interval of the reduction by carbon for the given melt composition. The lower temperature of this field when the heating rate (RAMP) $\rightarrow 0$ is the thermodynamically calculated temperature of the oxide reduction beginning (T_{beg}). The oxygen content in sample and heating rate can influence the shape and fractional analysis results

The shape of the FGA peaks was especially investigated using the different steel and model alloy samples. The similarity of the different peaks don't depends on aluminum and silica concentration was established. The software Ox-Id for oxide identification is based on this thermodynamic model of carbon reduction of oxide inclusions and owns experimental results. It is an important part of the FGA performance.

The thermodynamic estimation of the T_{beg} for FGA carbon reduction of silica, alumina and titanium oxide inclusions in iron melt depending on deoxidizer concentration can be illustrated with the next figure (Fig. 2) The calculated T_{beg} increase with increase of Si, Al and Ti concentrations in sample melt. Comparison of experimental (points) and calculated by OxId software (curve) results shows a good correspondence. The temperatures of oxide reduction beginning (T_{beg}) significantly depend on the deoxidizer concentration.

Low carbon steel killed with aluminum, rail steel, tyre cord steel, bearing steel and a number of commercial samples were carried out by FGA. The use of OxSeP software for carbon steel killed with aluminum, rail steel, tyre cord steel, etc. is characterized by the same accuracy of the oxide separation results as for standard steel samples and model materials. OxSeP software can be successfully used in different fields of metallurgy and material control.

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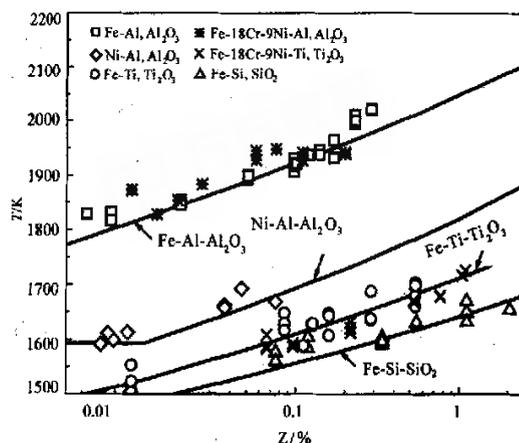


Fig. 2 The thermodynamic estimation of the T_{beg} for FGA carbon reduction of silica, alumina and titanium oxide inclusions in iron melt depending on deoxidizer concentration. Comparison of the experimental and calculations results.