Predicting of Reactions During Carburization and Decarburization of Steels in Controlled Atmospheres

Napovedovanje reakcij, ki potekajo med naogljičenjem in razogljičenjem jekla v kontroliranih atmosferah

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Prejem rokopisa - received: 1996-10-01; sprejem za objavo - accepted for publication: 1996-11-04

The knowledge of the thermodynamics of complexe systems consisting of gases and metal should be valuable for the control of industrial processes. The Gibbs energy minimization model has been implemented in the software program GPRO® and associated with a powerfull and reliable database. The computer package can perform computation of the equilibrium composition in very complex chemical and metallurgical systems. Some examples in this paper illustrate the simplicity of the computation and the use of the program in the field of some typical metallurgical applications.

Key words: equilibrium reactions, NO_x modelling, combustion of fossil fuels, active gas-atmospheres, decarburizing of non-oriented electrical steels, carburizing of alloyed steels with in situ produced atmospheres

Poznavanje termodinamičnih odnosov v kompleksnih sistemih plin - kovina ima lahko izreden pomen za kontrolo industrijskih procesov. Gibbsov model o minimizaciji energije je implementiran v programsko opremo GPRO®, ki mu služi kot osnova močna baza verificiranih termodinamičnih podatkov. Programska oprema omogoča izračunavanja ravnotežnih sestav v zelo kompleksnih kemijskih in metalurških sistemih. Navedeni primeri v tem članku ilustrirajo enostavnost izračunavanj in način uporabe programa na področju metalurških reakcij, ki jih večinoma izvajajo strokovnjaki na tem področju.

Ključne besede: ravnotežne reakcije, tvorba NO_x, zgorevanje fosilnih goriv, aktivne plinske atmosfere, razogljičenje neorientirane elektropločevine, naogljičenje legiranih jekel

1 Introduction

The application of thermodynamics to a system gas/solid enables to calculate the composition at equilibrium, direction and extent of change which can take place under specified conditions.

Rapid developments have taken place in recent years in efficiency of thermodynamics in the engineering as thermodynamic can be defined as being the meeting point between physical - chemical principles and practical applications[1]. In this paper an attempt has been made to demonstrate use of a personal computer software program as an ellegant and sensitive method for numerous metallurgical applications especially for the analysis of gaseous systems. It is hoped, that users of this method will be in a good position to go more deeply into learning thermodynamic laws.

2 Principles of the Gibbs method

In the fields of heat treatment of metals like *annealling, carburizing, decarburizing, nitrocarburizing and many other operations*, the metallurgist is concerned not with the pure gases but with the mixture of various species (gaseous and solids) which form the atmosphere in the furnace.

The thermodynamics of such complex systems can be treated by two methods:

- The classical method of numerical solution of an equilibrium problem when the equilibrium constant (K_r) or free energy change $\Delta G°$ of the involved reactions are known.
- The general Gibbs method for the numerical solution of an equilibrium. The problem is to determine the values of the species which minimize the state of total free energy at the given temperature and pressure.

Both treatments are thermodynamically equivalent, however, it seems that the later method has significant advantages for calculating the equilibrium conditions in complex systems, in mixtures containing both gaseous and condensed species.

During the last 20 years, SOLGASMIX computer program, as the method of attacking chemical and metallurgical problems, has influenced our approach to the study of a branch of scientific knowledge in physical chemistry.

There can be no doubt that to attack such a complex application of thermodynamics is only possible with the use of computer technology.

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3 Description of the method used for the calculation of complex equilibrium conditions

Several excellent software programs for calculating equilibria reactions at high temperatures, have been developed in the last two decades (SOLGASMIX, THERMOCALC, FACT, CHEMSAGE...)[2,3]. However, most of them are designed and written in a complex form using very strong computer units, while few are intented as a simply a tool to be applied for the purposes of solving practical problems. Therefore, it seemed worthwile to develop a program which would combine these two computer program designs. The new software program, called GPRO is based on the method of free energy minimization and extended to systems containing numerous gaseous and condensed phases in accordance with SOLGASMIX-principles. GPRO-program is dimensioned for 16 elements and 100 species. If necessary, this figure can be increased or new included datasets, which if necessary are written by the user (private databases are open and can be easily included also).

3.1 Thermodynamical approaches to the Gibbs-method

The power of Gibbs method energy minimization lies in its simplicity for the description of chemical reactions in complex systems, and its ability to facilitate the determination of the effect, on equilibrium state, of changes in the external influences which can be brought to bear on the system. In our software program, the user needs only to specify the type, the species present and the conditions (for example: *temperature of the system*) for the calculation. The program will automatically perform equilibrium thermodynamic computions typically associated with complex chemical equilibria from a defined database. With the aid of the GPRO-program, a user is able to perform most of the following operations:

1. The energy for pre-heating the initial mixture from the initial temperature T_o to the reaction temperature T,
2. The reaction heat,
3. The computation of the complex chemical equilibria in gaseous mixtures and activity of solid compounds,
4. Displaying and printing data for compounds and solutions at selected temperature and composition.

An additional scientific and engineering benefit of this program is the software able to develop a more basic understanding of chemical equilibria at high temperatures and its applications. Although the power software program will automatically perform the thermodynamical computation (no danger of pluging wrong numbers in wrong equations), however, the user must have some knowledge of the chemical nature of the considered system. In this paper the attempt is made to demonstrate the breadth and diversity of the modern software program in simple way so that a user may be able to understand the thermodynamical method and apply it to metallurgical problems. Most of the examples are chosen with the aim to show superiority of the computer program, over traditionally manual methods, which are particularly stressed for the engineers and students.

3.2 Databases associated for the equilibrium thermodynamic comptutations

From many excellent standard treatises on thermodynamics it is known, that without reliable thermodynamic data most equations are ineffective and the numerical answers will be therefore wrong. GPRO software program is based on the use of both the expressions for calculations of the standard Gibbs energies of the formation of a selected phase:
in the form:

$$\Delta G^\circ_T = \frac{A}{T} + B + CT + DT^2 + ET^3 + + FT\ln T$$

or using thermodynamical data on enthalpy ΔH°_T, entropy ΔS°_T and heat capacity $C_p(T)$:

$$\Delta G^\circ_T = \Delta H^\circ_{298} + \int_{T_o}^{T} C_p(T)dt - T\Delta S^\circ_{298} - T\int_{T_o}^{T} \frac{C_p(T)}{T} dT$$

Both methods used from the database involve the search for a minimum value of free energy ΔG of a system and give an equivalent result. However, the last method using enthalpy ΔH°_T, entropy ΔS°_T and heat capacity $C_p(T)$ has more advantages because it combines heat and equilibrium calculations. A typical example is the determination of the adiabatic flame temperature, where enthalpy of reaction serves as the criterion of the heat balance.

4 Exploiting the GPRO-program for complex equilibria calculations

Modelling Mechanism of Formation Nitrogenous Oxides by the Combustion of Fossil Fuels

Modern combustion processes of fossil fuels meet the relevant requirements for cost-effective operation and avoidance of enviromental pollution. In article some results of the basic study of the formation and reduction NO_x in high temperature combustion processes are presented. The obtained results demonstrate the use of the sophisticated methods of thermodynamics as one of the most important tools by the study of the combustion processes for a better understanding of the mechanism of formation of nitrogen oxides, one of the most important pollutants in combustion of fossil fuels[8-16].

Example 1:

In this example is a demonstration of the use of the GPRO-software program as method for prediction of complex combustion reactions and equilibrium gas composition including NO-oxydes formation.

The high temperature furnace is fired with natural gas and air (no air preheating). The question was: calculate

Table 1: Results of GPRO-analysis of the natural gas combustion by different air - index and without air preheating

Equilibrium data for methane combustion (λ=0,74...2,2)[1]										
$CH_4 + 2\lambda O_2 + 7{,}52\lambda N_2$										
Air index	0,74	0,84	0,94	1,00	1,10	1,30	1,60	1,80	2,00	2,20
CO (%)	6,90	4,44	1,95	0,95	0,30	0,04	0,002	0,0	0,0	0,0
CO_2 (%)	4,77	6,29	7,69	8,49	8,40	7,44	6,16	5,51	4,99	4,71
NO (%)	0,0021	0,017	0,112	0,23	0,345	0,334	0,200	0,130	0,087	0,066
H_2O (%)	18,09	18,99	19,01	18,52	17,28	14,94	12,32	11,03	9,98	9,42
O (ppm)	1,04	14,20	133	258	282	111	15	5	1	0
O_2 (%)	0,00	0,00	0,127	0,53	1,75	4,32	7,28	8,75	9,93	10,56
N_2 (%)	64,97	67,79	70,02	70,89	71,78	72,90	74,03	74,58	75,02	75,25
H_2 (%)	5,27	2,47	0,81	0,37	0,11	0,02	0,00	0,00	0,00	0,00
$\Sigma_{(input)}$ (mole)	8,04	9,00	9,25	10,52	11,47	13,37	16,23	18,14	20,04	21,24
$\Sigma_{(output)}$ (mole)	8,56	9,32	10,10	10,59	11,49	13,37	16,23	18,14	20,04	21,24
T_{adb} (K)	2023	2143	2233	2231	2151	1955	1712	1584	1482	1421

[1] air index

the equilibrium gas composition and the adiabatic flame temperature for the air-index in range $0{,}74 \leq \lambda \leq 2{,}2$ and compare the obtained results of the flame temperature with similar reference data known in the literature (normally presented in graphically form).

In **table 1** and **figure 1** the computed values for the gas equilibrium are given. The adiabatic flame temperature calculation show values slightly above the compared data.

Thermodynamic evaluation of carburizing atmospheres

The accuracy of the gaseous atmosphere control in the steel carburizing furnaces has been remarkably improved owing to the application of the computer control system and the development of new measuring techniques, for example: oxygen and/or carbon sensors. The atmosphere in carburizing furnaces are consists of: air + methane or other hydrocarbons and involves the gases CO, CO_2, H_2, H_2O, N_2. The four first gases are interdependent in a reversible reaction, commonly called the water-gas reaction:

$$CO + H_2O = CO_2 + H_2$$

The ratio:

$$K_w = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} \qquad (1)$$

is a constant, the value of which depend on the temperature.

The carburizing of steel, i.e. carbon content increasing on the steel surface, occurs through the reaction:

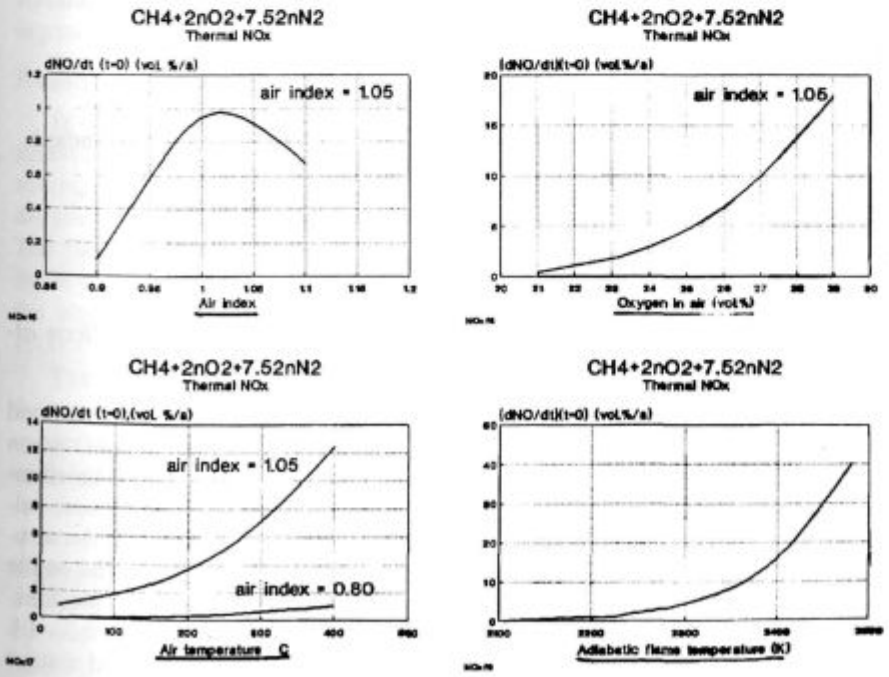

Figure 1: The formation of the nitrogenous oxide NO (model simulation)
Slika 1: Tvorba dušičnega oksida NO (modelne simulacije)

$$2CO = C + CO_2 \quad (2)$$

For any given temperature, the coresponding equilibrium constant of Boudouard's reaction will determine the carburizing potential of the atmosphere:

$$K = \frac{a_c}{p_{CO} \cdot (p_{CO}/p_{CO_2})} \quad (3)$$

The carbon potential of on atmosphere is simple to determine if the partial pressure of CO and ratio (p_{CO}/p_{CO_2}) is known. From EMF measurement (**e**lectro-**m**otive **f**orce) with the oxygen probe, considering the furnace temperature (p_{CO}/p_{CO_2}) or (p_{H_2}/p_{H_2O}) and measuring the CO - content in the atmosphere is possible to ensure the control of the carburizing process.

Example 2:

The carbon activity in a steel depends on the content of alloying elements, thus every steel composition will have determined carbon potential which corresponding to the atmosphere composition.

In next example three type steels were treated with air + methane atmosphere with the aim to obtain a constant carbon content near the surface of about 1 wt.% C).

Data in **table 2** show, that small deviations in the gas atmospheres (or the change of air + methane ratio) have a remarkable effect on the carbon activity. This model simulation is in good agreement with practical data.

Table 2: Influence of the steel chemistry on the process parameters (Simulation made by GPRO programme by T = 1223K)

Chemistry (%)	Fe+1%C+ 1%Si	Fe+ 1%C	Fe+1%C+ 1%Cr
CO	19.27	19.25	19.24
CO_2	0.0629	0.0717	0.078
H_2O	0.199	0.227	0.248
CH_4	5.17	5.15	5.13
N_2	36.83	36.88	36.92
H_2	38.46	38.42	38.38
O_2 (bar)	$9.4\ 10^{-21}$	$1.16\ 10^{-20}$	$1.46\ 10^{-20}$
EMF(mV)	1173	1167	1162
T_{dp}*)(°C)	-13	-11	-10
a_C	0.818	0.715	0.654
%C	1.03	1.06	1.08
$Q_{gas}(m^3/h)$	1.1	1.1	1.1
$Q_{air}(m^3/h)$	2.094	2.100	2.1045

*) T_{dp} = Dew point temperature

Example 3:

The carburizing of steel is a continuously process within which - due to the kinetics of various reactions - damming up effects may occur leading to non equilibrium CH_4-contents in the furnace atmosphere.

In this case the carburizing reactions under non-equilibrium conditions are modelled.

A mixture of natural gas and air at 1 bar total pressure is introduced into the carburizing furnace heated to 1223 K[5]. The quantity of natural gas and air are $3,1.10^{-4}$ m^3/s and $4,2.10^{-4}$ m^3/s. Calculate the gaseous equilibrium composition in the furnace atmosphere and the carbon activity assuming graphite as standard state. If the air flow suddenly increased from $4,2.10^{-4}$ m^3/s to $5,8.10^{-4}$ m^3/s by constant natural gas flow $3,1.10^{-4}$ m^3/s in the inlet mixture, determine the new gas equilibrium composition and carbon activity!

Table 3 shows the computed results for gas non-equilibrium composition and obtained energy changes, the preheating energy $H°_T - H°_{289}$, the heat of reaction $H°_R$ and $H°_{total}$ the total heat of the system.

Table 3: Example of input and output of a non-equilibrium composition by the production of endothermic gas from methane and air by T = 1223 K

	$1,1CH_4 + 2\lambda O_2 + 7,52\lambda N_2$			
Air/ methane (m^3/s)	$\lambda = 0,157$ $4,2.10^{(-4)}/3,1.10^{(-4)}$ $\alpha^{1)}_{methane} = 0,575$		$\lambda = 0,221$ $5,8.10^{(-4)}/3,1.10^{(-4)}$ $\alpha^{1)}_{methane} = 0,795$	
	X_{inp} (mole)	X_{out} vol.(%)	X_{inp} (mole)	X_{out} vol.(%)
CO	0,0000	17,58	0,0000	19,25
CO_2	0,0000	$4,28.10^{-2}$	0,0000	$7,19.10^{-2}$
CH_4	1,1000	13,40	1,1000	5,80
H_2O	0,0000	0,135	0,0000	0,227
HCN	0,0000	$3,76.10^{-3}$	0,0000	$2,65.10^{-3}$
H_2	0,0000	35,29	0,0000	38,41
N_2	1,1890	33,33	1,6590	36,22
O_2	0,3150	$(5,45.10^{-21})^{2)}$	0,4410	$(1,28.10^{-20})^{2)}$
a_C 3)	.....	1,0000	.....	0,714
Σ(mole)	2,604	3,5397	3,200	4,4962
$(H_2/C)^{4)}$	2,00	2,00	2,00	2,00
$H°_T - H°_{298}$ (kJ/mol)	92,95		116,77	
$H°_R$ (kJ/mol)	- 14,79		- 22,24	
$H°_{total}$ (kJ/mol)	78,15		94,53	

1) $\alpha_{methane} = \frac{CH4(c)}{CH4(t)}$, $CH_{4(c)}$ = fully cracked CH_4 and $CH_{4(t)}$ = total CH_4

2) p_{O2} in bar,

3) a_C = carbon activity referred to graphite as standard state

4) $\frac{H_2}{C} = \frac{H_2 + H_2O + 2CH_4}{CO + CO_2 + CH_4}$, λ = air index

Calculation of the decarbirization process of silicon alloyed steels

The use of gaseous atmospheres with a well-defined oxygen potential for the decarburization of low carbon iron-silicon steels in continuous furnaces can be simulated using a thermodynamical model. Equilibrium calculations and practical measurements show that the solubility and carbon activity in Fe-C-Si steels depend on the gaseous atmosphere, temperature and steel composition.

Silicon-iron alloys containing 1 - 3% Si and 0,3 - 1% Al are typical steels for non-oriented sheets and a strict

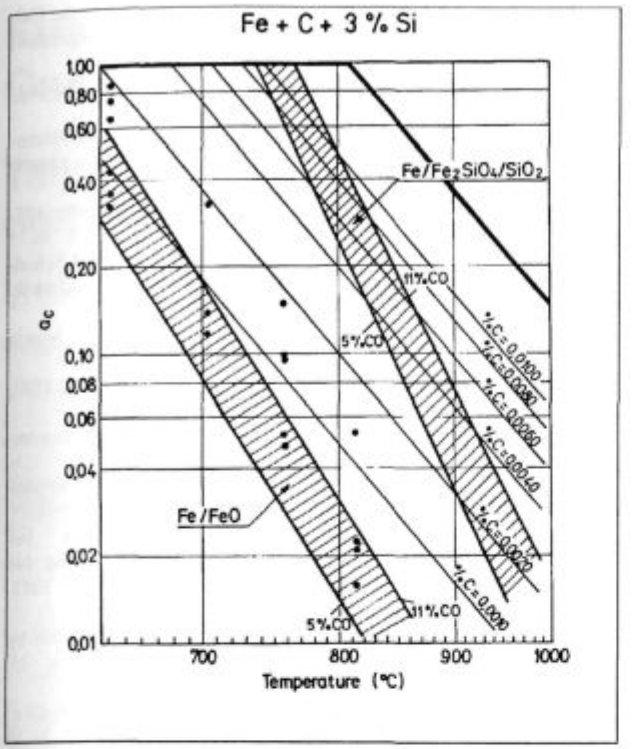

Figure 2: Plot of thermodynamical data for Fe_2SiO_4 as a function temperature calculated with GPRO-program

Slika 2: Diagram termodinamihnih podatkov Fe_2SiO_4 kot funkcija temperature izrahunano s GPRO-programom

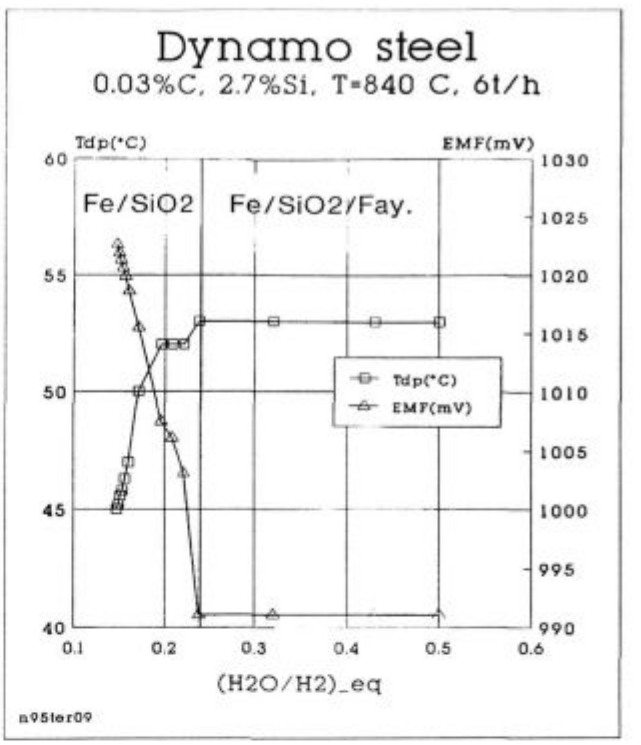

Figure 3: Equilibrium oxide-formation by the decarburization of non-oriented electrical sheets in gaseous atmosphere $H_2 + H_2O + N_2$ (T_{dp} - dew point temperature, EMF (mV) = electromotive force, $(H_2O/H_2)_{eq}$ = equilibrium pressure ratio)

Slika 3: Ravnotežni pogoji tvorbe oksidov med razogljičenjem neorintitane pločevine v plinski atmosferi $H_2 + H_2O + N_2$ (T_{dp} - točka rosišča, EMF (mV) = elektromotorna napetost, $(H_2O/H_2)_{eq}$ = ravnotežno razmerje plinov)

control of the decarburization and surface reactions is required. The optimum properties for an electrical steel normally include high permeability with low core loss and minimal aging effects. An important factor in a process control is the formation of a high quality glassy film which is developed through a complex series of processing steps.

Example 4:

In order to clarify the relation between the decarburization atmosphere for the carbon removal during the annealing, the thermodynamical reactions and formation of different oxide phases in the scale have been studied. The first task was the determination of the carbon activity in the decarburization gas atmosphere containing at the start $H_2 + N_2 + H_2O$ in temperature range 600 - 1000°C.

The mathematical model GPRO allows an easy use of thermodynamical data to predict the equilibrium carbon content in electrical steels. It is convenient to use the carbon activity in the gas atmosphere by different partial pressures of CO to present the conditions for the formation of FeO and Fe_2SiO_4 by the different temperature. **Figure 2** shows the results obtained. Having these curves available, it is possible to determine the dew point temperature as the function of the partial pressure ratio H_2O/H_2.

As shown on **Figure 3**, the ratio of H_2O/H_2 at which the formation of fayalite actually disappeared is near $H_2O/H_2 = 0,24$ at 840°C.

It is obvious that the pressure ratio H_2O/H_2 and CO_2/CO is interchangeable with the partial pressure of oxygen - p_{O_2} and finally also by means of the relation:

$$\log p_{O_2} = \log\left(\frac{p_{CO}}{a_c}\right)^2 - \frac{11854}{T} - 9{,}090 \qquad (4)$$

which allows the application of the oxygen (carbon) sensor signal (EMF).

5 Conclusions

The use of thermodynamic predictive model offers many advantages over conventional gas atmosphere calculations because of the simplicity for description of chemical reactions in complex systems, the automatic performance of equilibrium computations, of the avoidance plugging wrong numbers in wrong equations and so on. The rational and theoretical basis for the Gibbs energy model used was presented elsewhere[5,17-19]. To summarise, the key features of model calculations for the nitrocarburizing atmospheres are as follows:

- Modern combustion processes of fossil fuels meet strict requirements for cost-effective operation and avoidance of enviromental pollution. This article presents the first results of study into formation and reduction NO_x in high temperature combustion processes.
- The obtained results demonstrate the use of the sophisticated methods of thermodynamics as one of the most important tools for the study of combustion processes to understanding better the mechanism of formation of nitrogen oxides, as one of the most important pollutants in fossil fuels combustion.
- Little is given in disponible references on use of thermodynamical models in the field of active atmospheres. Such mixtures containing both gaseous and condensed components for example: Fe + C + O + H + N are extremly complicated for the numerical calculations. Detailed experimental studies are difficult and also thermodynamical results are mostly presented in the graphical form, which are very useful in research work but of little effectivness in searching solutions for a current practical operation.
- To obtain equilibrium compositions in the real gaseous mixtures by high temperatures, taking into account both energy and material balances, the development of new approaches are strongly required.

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