

THERMODYNAMIC MODELING OF CHEMICAL AND PHASE TRANSFORMATIONS IN A WAE LZ PROCESS-SLAG – CARBON SYSTEM

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Chemical and phase transformations in a Waelz process-slag – carbon system in the range 1700 – 2100 K at a pressure of 0.1 MPa are modeled. It is established that the maximum degree of iron transferred into condensed Fe_3Si is from 34.7 % at 1800 K to 99.9 % at 2100 K, and into Fe_5Si_3 from 47.7% at 1900 K to 45.6% at 2000 K. With a further increase in temperature iron starts to be transferred into the gas phase. Silicon, in comparison with iron, is more difficult to recover and with an increase in temperature starts to pass into the gas phase. The degree of nonferrous metal Zn, Cd and Pb transfer into the gas phase is 99.99 % over the whole temperature range. Modeling makes it possible to analyze the possibility of obtaining ferrosilicon from technogenic non-ferrous metallurgy waste by electric melting in an electric arc furnace.

Keywords: Waelz process-slag, carbon, thermodynamic modeling, chemical and phase transformations, ferrosilicon, non-ferrous metal sublimates.

INTRODUCTION

In the last forty years on Earth 11 billion tons of metal have been produced (of 16 billion tons of metal produced by humanity for the last 6600 years) [1 – 7]. However, world reserves for metal production are not unlimited. Proceeding from the index for resource utilization [1 – 7] nonferrous metal reserves in the first half of the XXI century are being exhausted in the following sequence: Au, Sn, Zn, Pb, W, Cu, and Sb. The in the second half of the XXI century there will be exhaustion of Mo, Ni, Mn, Co, Al, Ti, and Fe. Currently the raw metal problem of metallurgy cannot be resolved solely by comprehensive redevelopment of natural raw material drawing into the production sphere technogenic and secondary raw material. In this case the duration for exhaustion of Cu reserves for example increases by a factor of 4, for zinc by 5.6, and for Ag by a factor of 7.2. Concerning comprehensive processing of natural raw material it should be noted that within the nature single-mineral raw material is hardly encountered; this may also be said about technogenic raw

material. Therefore, the complicating classification of raw material with respect to an industrial principle does answer entirely the task of its comprehensive usage. In metallurgy quite often (in the last quarter of the XX century) there is use of an understanding of a single raw or technogenic raw material with whose treatment it is possible to obtain not only for example nonferrous metals, but also products for ferrous metallurgy [1 – 7].

Today the new technological revolution suggests use of a rational approach to utilization of natural and technical resources with maximum effective energy saving, and also comprehensive secondary processing of all industrial waste and preparation from it of new production, raw material, or energy. Correspondingly, SMART-technology will make it possible to find optimum ways for preserving the environment [8].

However in this case it should be considered that technogenic mineral raw material has complex mineral and chemical compositions and requires an individual approach to finding the newest methods for treatment. Wastes from enrichment and metallurgical conversion form as a result of specific production processes and are subsequently subjected to secondary changes during weathering, oxidation, leaching, reprecipitation, etc. Technogenic raw materials cannot be treated effectively by means of traditional technology, based

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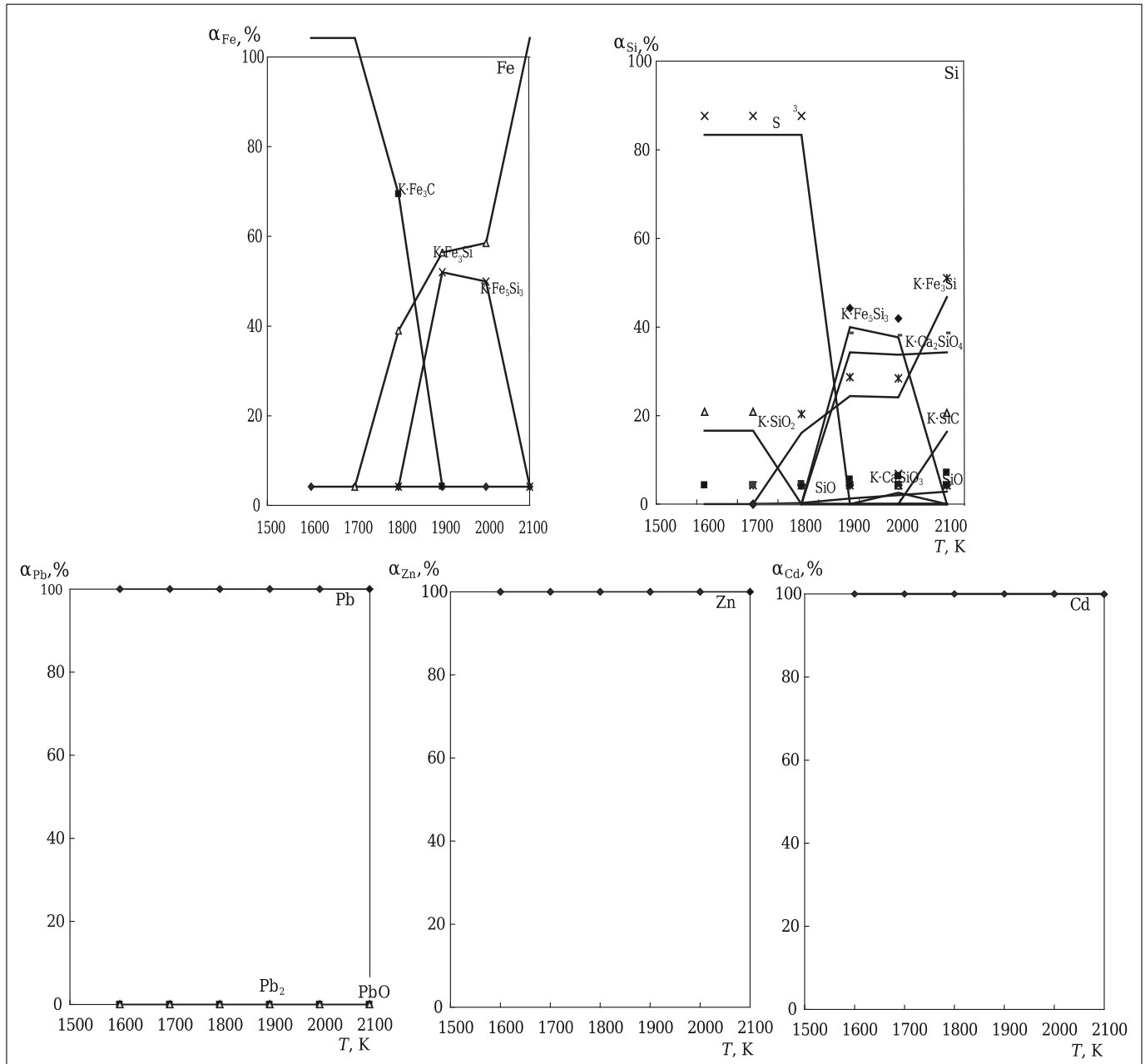


Fig. 1. Effect of temperature T on degree of distribution of α -Fe, Si, Pb, Zn, and Cd in a Waelz process-slag – carbon system.

on separation features and on the contrasting nature of mineral properties, since they contain mineral formations that are impossible to separate into mineral phases, and consequently to enrich [9].

Therefore priority scientific and technological studies aimed at treating waste from mining and processing of economic minerals becomes: development of methodology for mineral-technological prediction of an estimate of the enrichment capacity of technogenic raw materials that are difficult to treat, a combination of methods of contemporary technological mineralogy with improved reliability of analysis of non-traditional forms of metal compounds in new forms of

mineral raw material; substantiation and development of effective production processes for extracting valuable components from technogenic raw material based on a combination of mechanical enrichment methods (gravitation, flotation, etc.) with chemical-metallurgical methods (pyro- and hydrometallurgy, autoclave leaching, electrochemical and biological oxidation) with application energy action intensifying processes for separation of mineral complexes; substantiation and development of production processes for preparing additional finished product from the non-ore part of waste for secondary utilization [10].

Proceeding from this it is possible to refer to this category of a single technogenic raw material slags from Waelz oxidized zinc ores of the Achisai lead-zinc deposit, containing apart from Zn, Pb, and Cd also important elements for ferrous metallurgy such Fe and Si. In spite of the existing experience of processing and utilization of slags the task of their comprehensive treatment has not been resolved entirely. During slag treatment from Waelz oxidized ores Zn and Pb are hardly extracted and pass into tailings. Therefore it is necessary to find innovative technology and rational scientific approaches.

Ferroalloys are of considerable importance in order to improve the quality of structural steels. Development of the theory and technology for producing ferroalloys is an important area in special steel metallurgy. The efficiency of ferroalloy production is mainly determined by the cost of raw materials and reducing agent. Use of technogenic metal- and carbon-containing wastes will make it possible to utilize their conversion with preparation of cheap product [11 – 18].

The possibility is considered in this work of forming ferrosilicon iron silicide from slag from Waelz treatment based on thermodynamic modeling in the range 1700 – 2100 K at a pressure $p = 0.1$ MPa. Modeling of chemical and phase transformations in the system was performed by means of Astra-4 multipurpose software developed in the N. E. Bauman MGTU. The composition of phases and equilibrium characteristics were calculated from properties of individual substances using a reference database. The information base of the Astra-4 software comprises thermodynamic, thermophysical, and thermochemical properties of individual substances that have been systematized in the High Temperature Institute of the Academy of Sciences of the USSR and the USA national Standards Bureau. Data have been published in the periodical press and monographs, references, and also treated and calculated in the N. E. Bauman MGTU [19 – 23].

Within the system of slag from Waelz treatment – carbon reaction has been considered for the chemical composition of slag with carbon. The effect of temperature on distribution of iron, silicon, carbon, zinc, and lead within the system is characterized by formation of more than six elements and compounds: Fe, Fe₃C, Fe₃Si, Fe₅Si₃, Si, Si₂, Zn, ZnO, Pb, PbO, Cd, CO, and CO₂. It follows from Fig. 1 that the degree of transfer of Fe into Fe_mSi_n in a slag system from Waelz treatment-carbon comprises for compounds Fe₃Si 34.7% at 1800 K, then 52.3% at 1900 K, and 99.9% at 2100 K, and for compound Fe₅Si₃ 47.7% at 1900 K and 45.6% at 2000 K.

The degree of transfer of Si into Fe_mSi_n comprises for Fe₃Si compound from 2.44% at 1800 to 46.6% at 2100 K, and for Fe₅Si₃ compound up to 40.09% at 1800 K. The degree of transfer of nonferrous metals Zn, Cd, and Pb into the gas phase over the whole test range from 1700 to 2100 K comprises almost 100% (see Fig. 1).

Therefore, within the slag system from Waelz treatment – carbon it is possible to form groups of silicides of silicon with a maximum silicon content from 19.0 to 27.% (which

corresponds to ferrosilicon grade FS20 and FS25 according to GOST 1415–93). The degree of extraction of silicon into alloy α_{Si} is from 24 to 46%, and for iron α_{Fe} from 34.7 to 99.9%; nonferrous metals (Zn, Cd, and Pb with sublimation into the gas phase) 100% in the temperature range 1800 – 2000 K. Therefore, from technogenic waste, i.e., slag from Waelz treatment by electromelting with a reducing agent, it is possible to extract Fe and Si into ferroalloy, in particular into ferrosilicon, which may be used in the metallurgical, oil, and gas industries [24 – 26], and sublimation of Zn, Cd, and Pb into collective sublimes. The slag formed, which is mainly 90% of the total of calcium, silicon, and aluminum oxides may be used as an adjustment additive to a raw material mixture in order to prepare cement clinker [27 – 29] with subsequent milling into Portland cement.

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