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Prospects for recycling leather industry waste as a source of chromium-containing raw materials: physicochemical analysis of the Fe–Cr–P–O system

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Перспективи рециклінгу відходів шкіряної промисловості як джерела хромовмісної сировини: фізико-хімічний аналіз системи Fe–Cr–P–O

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Abstract. The paper considers thermodynamic and physicochemical regularities of phosphorus behavior in multicomponent systems of Fe–Cr–P, Fe–Cr, Fe–P, Cr–P and Fe–Cr–P–O when using chromium-containing man-made raw materials, in particular substandard ores and leather industry wastes. The analysis of the current state of the raw material base of chromium in Ukraine is carried out and the expediency of attracting alternative sources of chromium-containing raw materials is substantiated. The literature data on phase equilibrium, thermodynamic properties and features of the formation of phosphide and oxide-phosphate phases in these systems is summarized. It has been established that the main problem of the use of man-made raw materials is the increased content of phosphorus, which negatively affects the properties of the metal. It is shown that solid-phase reduction creates favorable conditions for controlling the distribution of phosphorus between the metal and slag phases. The influence of temperature, charge composition and interatomic interaction on the stability of phosphide phases and the efficiency of dephosphorization has been determined. Particular attention is paid to the role of the magnetic state of iron and the conditions for the formation of solid solutions and intermetallics in the Fe–Cr–P system. The results obtained can be used to develop energy-efficient technologies for the processing of chromium-containing waste and substandard ores in order to reduce import dependence and increase the environmental safety of metallurgical production. **The purpose of the work** is to study the thermodynamic and physicochemical patterns of phosphorus behavior in the Fe–Cr–P, Fe–Cr, Fe–P, Cr–P and Fe–Cr–P–O systems when using complex chromium-containing raw materials (substandard ores and leather industry wastes), as well as to substantiate the possibility of controlled phosphorus removal in order to improve the quality of the obtained metals and alloys. **Research methodology:** A systematic analysis of the scientific and technical literature on phase equilibrium and thermodynamic properties of Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O systems was carried out. composition of the charge and reducing medium for the distribution of phosphorus between phases. **Scientific novelty:** The relationship between the parameters of the interatomic interaction (ZY , d , tga , pl) and the thermodynamic stability of phosphide phases has been established. **Practical significance:** The expediency of using leather industry waste as an alternative source of chromium for metallurgy has been substantiated. Approaches to reducing the phosphorus content in the pro-



cessing of complex raw materials, which allows to improve the quality of steel and ferroalloys, have been proposed. The optimal temperature and thermodynamic conditions for the implementation of dephosphorization processes have been determined. The results can be used in the development of energy-efficient technologies for solid-phase recovery and recycling of waste. It helps to reduce Ukraine's import dependence on chromium-containing raw materials and increase the environmental safety of production.

Keywords: waste recycling, leather industry, chromium-containing raw materials, Fe–Cr–P–O system, thermodynamic modeling, ferrochrome, chromium utilization, phase transformations.

Анотація. У роботі розглянуто термодинамічні та фізико-хімічні закономірності поведінки фосфору в багатоконпонентних системах Fe–Cr–P, Fe–Cr, Fe–P, Cr–P та Fe–Cr–P–O при використанні хромовмісної техногенної сировини, зокрема некондиційних руд і відходів шкіряної промисловості. Проведено аналіз сучасного стану сировинної бази хрому в Україні та обґрунтовано доцільність залучення альтернативних джерел хромовмісної сировини. Узагальнено літературні дані щодо фазових рівноваг, термодинамічних властивостей і особливостей утворення фосфідних та оксидно-фосфатних фаз у зазначених системах. Встановлено, що основною проблемою використання техногенної сировини є підвищений вміст фосфору, який негативно впливає на властивості металу. Показано, що твердофазне відновлення створює сприятливі умови для керування розподілом фосфору між металевією та шлаковою фазами. Визначено вплив температури, складу шихти та міжатомної взаємодії на стабільність фосфідних фаз і ефективність дефосфорації. Особливу увагу приділено ролі магнітного стану заліза та умовам утворення твердих розчинів і інтерметалідів у системі Fe–Cr–P. Отримані результати можуть бути використані для розробки енергоефективних технологій переробки хромувмісних відходів і некондиційних руд з метою зниження імпортозалежності та підвищення екологічної безпеки металургійного виробництва. **Метою роботи** є дослідження термодинамічних і фізико-хімічних закономірностей поведінки фосфору в системах Fe–Cr–P, Fe–Cr, Fe–P, Cr–P та Fe–Cr–P–O при використанні комплексної хромовмісної сировини (некондиційних руд і відходів шкіряної промисловості), а також обґрунтування можливості керованого видалення фосфору з метою підвищення якості отриманих металів і сплавів. **Методика дослідження:** Проведено системний аналіз науково-технічної літератури щодо фазових рівноваг і термодинамічних властивостей систем Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O. Застосовано метод оцифрування графічних даних (діаграм стану, залежностей) для формування репрезентативних вибірок. Виконано аналіз міжатомної взаємодії на основі концепції спрямованого хімічного зв'язку з використанням параметрів (Z^* , d , tga , ρ). Проведено порівняльний аналіз впливу температури, складу шихти та відновлювального середовища на розподіл фосфору між фазами. **Наукова новизна:** Встановлено взаємозв'язок між параметрами міжатомної взаємодії (Z^* , d , tga , ρ) та термодинамічною стабільністю фосфідних фаз. **Практична значимість:** Обґрунтовано доцільність використання відходів шкіряної промисловості як альтернативного джерела для металургії. Запропоновано підходи до зниження вмісту фосфору при переробці комплексної сировини, що дозволяє підвищити якість сталі і феросплавів. Визначено оптимальні температурні та термодинамічні умови для реалізації процесів дефосфорації. Результати можуть бути використані при розробці енергоефективних технологій твердофазного відновлення та рециклінгу відходів. Сприяє зменшенню імпортозалежності України щодо хромовмісної сировини та підвищенню екологічної безпеки виробництва. **Ключові слова:** рециклінг відходів, шкіряна промисловість, хромовмісна сировина, система Fe–Cr–P–O, термодинамічне моделювання, ферохром, утилізація хрому, фазові перетворення.

Introduction

The current state of ferrous metallurgy is characterized by the search for innovative solutions to increase profitability and minimize man-made impact on the environment. The global market situation causes the transformation of the production structure and changes in the positions of key players in the segments of high-quality metal and pig iron [1-3].

One of the promising areas is the attraction of non-traditional materials, in particular waste from the leather industry, as well as substandard ores containing chromium. The choice of chromium is motivated by its irreplaceable role in the production of high-alloy and specialized steels - such as stainless, Cr–Mo alloys, heat-resistant materials and tool alloys, which are in demand in the domestic market. Chromium is one of the most important alloying elements in ferrous metallurgy, which increases the corrosion resistance, heat resistance, wear resistance and hardness of steel. Chromium-containing steels are widely used in power engineering, aviation and automotive industries, chemical engineering, as well as in the production of stainless steels. Chromium-containing steels are of particular importance due to their advantages, namely: increased corrosion resistance in aggressive environments; stability of the structure at high temperatures; increasing the durability of parts and struc-

tures; the possibility of reducing the weight of structures due to higher strength characteristics.

Ukraine is experiencing a shortage of its own raw material base of chromium due to limited reserves of deposits [4]. The main manifestations of chromite mineralization are concentrated in the massifs of the Middle Buzhzhia (interspersed ores, lenses, chromium-nickel weathering crusts). The development of the Kapitanovske deposit [5], which can partially meet the needs of metallurgy, with chromite ore is promising. At the same time, the deposits available in Ukraine (in particular, the Middle Buzhzhia) are characterized by a low content of Cr_2O_3 (9–25 %) and an increased amount of impurities of iron, nickel and silicates [5]. This creates significant technological barriers. In particular, traditional beneficiation methods (gravitational, magnetic) are effective only at a content of $\geq 30\text{--}35\%$ Cr_2O_3 . An additional problem is the fine-grained structure of ores, which complicates separation even when using modern equipment.

One of the promising wastes containing a significant amount of chromium oxide, about 70%, is ash from leather production waste [6]. These wastes are considered as potential raw materials for the production of ferrochrome [7, 8].

It has been established [9, 10] that ash of leather production, due to its biogenic origin, is marked by a

high concentration of phosphorus-containing compounds. The use of such raw materials within the framework of traditional ferroalloy production technologies will lead to the inevitable transition of phosphorus into the melt, which will lead to its increased content in finished alloys [11].

Despite the need to solve the problem of phosphorus removal, the involvement of leather production waste in recycling has a comprehensive positive effect. In particular, this contributes to increasing the level of occupational safety and health, reducing the environmental burden on industrial regions, as well as minimizing environmental pollution, which generally improves life safety indicators [12].

Thus, although waste can replace part of the traditional raw materials, its use in classic smelting schemes has significant limitations.

One of the most promising areas is the use of technologies for solid-phase reduction of complex charge containing waste. The essence of the technology is that the reduction of chromium and iron oxides occurs not in melt conditions, but in the solid phase, at temperatures lower than the melting point of the charge. For iron oxides ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$), the initial stages of transformation usually begin as early as $\sim 300\text{--}400\text{ }^\circ\text{C}$ (especially in hydrogen reduction), intensive conversion to metallic iron often occurs in the range of $\sim 500\text{--}900\text{ }^\circ\text{C}$ depending on the reducing agent (H_2 , CO or carbon agents), particle size, and charge porosity [13]. For chromium oxides (Cr_2O_3 and chromite), solid-phase (carbothermal or gas-phase) reduction usually requires higher temperatures: the initial stages of reduction and formation of chromium carbides/carbonitrides are observed at $\sim 800\text{--}1100\text{ }^\circ\text{C}$, and the complete reduction of Cr_2O_3 to metallic chromium in a "pure" carbothermal process often begins to occur closer to $1200\text{ }^\circ\text{C}$ and above [14]. The main advantages of solid-phase recovery should be attributed [15-17]:

- the ability to control diffusion processes and create conditions for the oxidation of phosphorus;
- reducing the transition of unwanted impurities, in particular phosphorus, to the metallic phase and directing it to the slag phase;
- reduced energy consumption due to lower process temperature;
- the possibility of processing substandard ores and leather industry waste.

Thus, solid-phase recovery allows you to combine environmental and economic advantages – rational use of waste, reduce the burden on the environment and at the same time obtain a precursor, followed by the production of steel and ferroalloy.

Materials and methods of research. A significant number of scientific studies have been devoted to the study of multicomponent systems Fe–Cr–P, Fe–Cr–P, and Fe–Cr–P–O [18-25]. The accumulated array of data on phase equilibrium and physicochemical properties of these systems has become the basis for modern technology of steel smelting and optimization of their chemical composition.

At the same time, despite the in-depth study of the main phases, a number of complex compounds potentially formed in such systems remain insufficiently studied. In particular, the study of their physical and chemical nature in the context of phosphorus removal from melts is of particular relevance, since a deep understanding of the mechanisms of formation of these compounds is critically important for the development of effective methods of dephosphorization and obtaining high-quality metal products.

As the accumulated scientific and practical experience of scientists [18-25] shows, the study of complex multicomponent systems in metallurgy, such as Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O, requires the use of a whole range of experimental and analytical methods. The main features and factors that are the key to successful experimental phosphorus reduction in these systems include:

1. High temperatures and reactivity. Iron, chromium and phosphorus in melts actively interact with oxygen, nitrogen and crucible materials. Experiments require the creation of an inert or reducing atmosphere (argon, vacuum, hydrogen), which complicates the design of equipment and increases the cost of research. High temperatures (more than $1500\text{ }^\circ\text{C}$) lead to intensive evaporation of phosphorus and its compounds, which makes it difficult to accurately determine concentrations [18, 19].

2. Fragility of phosphide phases. Compounds such as Fe_3P and $(\text{Fe,Cr})_3\text{P}$ often have a brittle structure and can be destroyed during machining of samples, and such fine phosphides are difficult to fix during quenching due to their tendency to dissolve during rapid cooling [19, 20].

3. Problems of fixing the phase composition. To construct phase diagrams, it is necessary to fix equilibrium structures, but metastable phases often occur in multicomponent systems. Slow cooling allows to achieve equilibrium, but causes segregation of impurities and isolation of secondary phases. In the work of Bernhard et al. [18] it has been shown that even for relatively simple binary and ternary Fe–P and Fe–C–P systems, there are significant discrepancies between experimental phase fields and predictions from thermodynamic models. The authors note that with slow cooling, a coarse-crystalline structure is formed with pronounced segregation of phosphorus along the grain boundaries, which complicates the fixation of equilibrium phases. Rapid quenching, on the other hand, results in the preservation of metastable phosphide phases (e.g. Fe_3P or Fe_2P), which should not be present in real equilibrium. Thus, the data obtained depend on the method of fixing the structure, which complicates the construction of reliable phase diagrams. In a study by Cao et al. [19] it is emphasized that even when using CALPHAD modeling, the Fe–P system requires adjustment due to the difficulty of obtaining pure experimental data. The authors note that equilibrium phase ratios are highly dependent on the cooling rate and in a number of experiments phases are recorded that are the product of

non-equilibrium crystallization. This confirms that thermodynamic optimization should take into account the possibility of fixing metastable structures and adjust experimental data using model calculations.

4. Complexity of working with oxygen in the Fe–Cr–P–O system. In the presence of oxygen, complex oxide-phosphide inclusions are formed, the composition of which is difficult to predict. When studying such inclusions in laboratory conditions, their change in the analysis process is often observed (especially in an electron microscope due to heating with an electron beam) [21-23].

5. Chromium in the Fe–Cr system forms solid solutions in iron in a wide range of concentrations. Experimental difficulties are associated with **the high temperature of liquidus and the tendency of chromium to oxidation**, however, vacuum melting or melting in an inert gas atmosphere is necessary to obtain pure samples [24, 25].

6. Phosphorus in the Fe–P system is limited soluble in α -iron, which leads to segregation at grain boundaries. In experiments, **it is difficult to reproduce the uniform distribution of phosphorus, especially at high temperatures, due to its volatility** [18, 19].

7. Chromium phosphides in the Cr–P system are characterized by high hardness and thermal stability. Their synthesis requires temperatures above 1300 °C and strict control of the atmosphere, otherwise Cr oxidation and the formation of Cr_2O_3 occur [20].

8. In the triple system Fe–Cr–P, complex interactions between phases are observed, which depend on the ratio of elements. Obtaining pure three-component alloys requires a complex technology that excludes the ingress of carbon and oxygen

[20]. In particular, in the Fe–Cr–P–O system, the formation of multicomponent inclusions containing oxides and phosphates requires complex analysis – optical metallography, X-ray phase analysis, scanning electron microscopy.

9. The problem is the instability of some inclusions in contact with air or moisture [21-23].

Research results and discussions. The review of modern information on the behavior of phosphorus in Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O systems was aimed not only at collecting a theoretical scientifically grounded review, but also at forming reliable representative data samples, as an important component for modeling and predicting physicochemical interactions with an appropriate focus on the removal of phosphorus into the slag phase. As a result of the literature review, it was noted: that a significant amount of information is not in an unconventional format (tables of chemical compositions), but in graphic representations, dependencies and state diagrams. That is why to create a representative sample of data, the method of digitizing data was used while maintaining their initial accuracy of fixation by researchers (Table 3).

Based on the concept of directed chemical bonding [26, 27], the dependence of the standard enthalpy of formation (ΔH) of the Fe–P alloy on the phosphorus content at temperatures of 298 K and 900 K according to the data [28] was analyzed. This approach allows to identify correlations between thermodynamic parameters and phosphorus concentration in the Fe–P system, which is represented through the parameter of the interatomic interaction $\text{tg}\alpha$, which describes the gradient of change in the radius of the ion from its charge (Fig. 1).

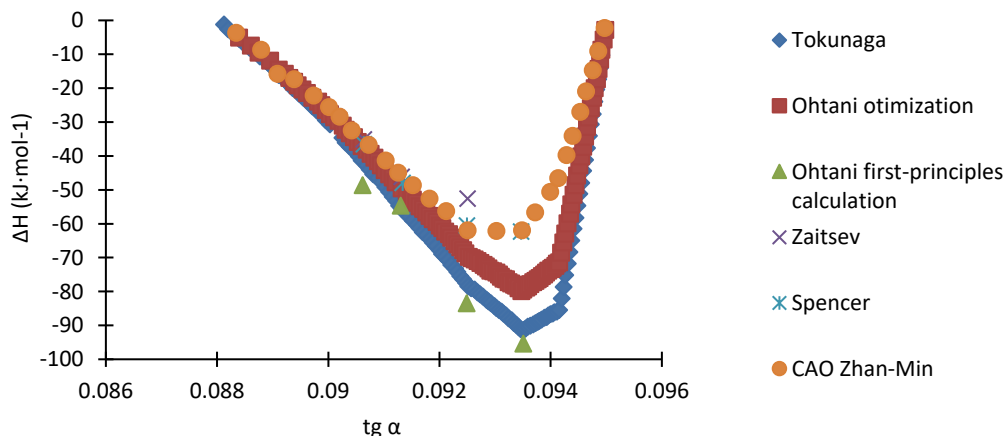


Figure 1 – Dependence of the standard enthalpy of formation (ΔH) of an alloy of the Fe–P system according to data [28] on the parameter of the interatomic interaction $\text{tg}(\alpha)$.

The high correlation between the results presented in the paper [28] and the obtained calculation data confirms the expediency of using the parameters of the interatomic interaction as criteria for the reliability of the results. In particular, *the $\text{tg}\alpha$ parameter* almost completely reproduces the course of the curves described by the authors [28]. Similar trends and de-

pendencies persist at a temperature of 900 K. It has been established that an increase in the absolute value of the negative enthalpy of the formation of a compound indicates its higher thermodynamic stability relative to the initial simple substances.

With an increase in the phosphorus content, its charge increases, which is reflected by the *parameter*

$\text{tg } \alpha$ in Fig. 2, at the same time, the weighted average internuclear distance of ions in the system, represented by the parameter d , is minimal at its maxi-

mum content, which testifies in favor of the formation of strong interatomic bonds with the partner, in particular iron.

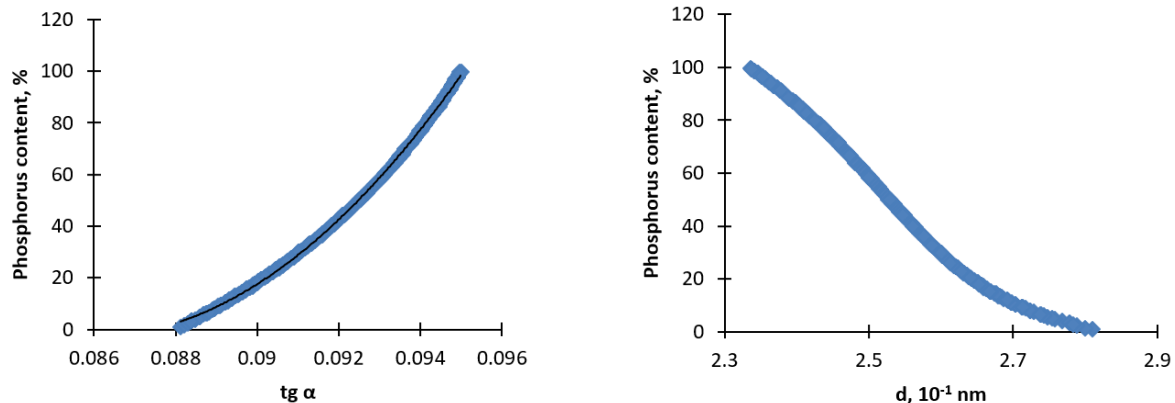


Figure 2 – Relationship between changes in phosphorus content and parameters of interatomic interaction.

The results obtained confirm that the regulation of the parameters of interatomic interaction in Fe–Cr–P–O systems allows creating thermodynamically grounded conditions for the effective reduction of iron and phosphorus. The formation of stable phases in the reduction process creates the necessary prerequisites for their further extraction from complex oxide systems.

The relevance of further developments is reinforced by the lack of comprehensive research in this area. In particular, in domestic scientific practice, the issue of disposal of leather production waste is usually considered only in the environmental aspect, which neutralizes their value as a source of chromium-containing raw materials for metallurgy. The analysis of world publications also confirms the lack of attention to the technological potential of such waste. Thus, the introduction of recycling of ash from leather production waste will not only partially provide enterprises with important chromium-containing raw materials, but will also lay the foundation for the formation of new global trends in the field of rational environmental management.

Conclusions

The analysis of literature data of domestic and foreign scientists made it possible to find a promising

way to obtain chromium, in particular, it is the use of leather production waste, but it should be noted a significant number of related issues that need to be solved for the successful implementation of the recycling scheme. Namely, the removal of a significant phosphorus content by directing it to the slag phase.

The limiting factors that should be taken into account for conducting experimental studies on phosphorus removal in Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O systems (high temperatures and reactivity, fragility of phosphide phases, problems of fixation of phase composition, and others) have been described and systematized.

A representative sample of data has been created, including data on Fe–Cr–P, Fe–Cr, Fe–P, Cr–P, Fe–Cr–P–O systems using the technique of digitizing graphic data while maintaining their initial accuracy of fixation.

The relationship between enthalpy at temperatures of 298K and 900K and phosphorus content has been investigated through the prism of the concept of directed chemical bonding. A significant discrepancy between the presented authors and the dependencies obtained by us was revealed, which testifies in favor of using the parameters of interatomic interaction to assess the reliability of the data obtained.

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