Creation of a Technological Path for Utilization of Waste Material from Iron Scale

Vladimir PETKOV, Radoslav VALOV

Bulgarian Academy of Science, Institute of Metal Science, Equipment, and Technologies
with Center for Hydro- and Aerodynamics "Acad. A. Balevski", Sofia, Bulgaria,
e-mail: vladimir2pe@yahoo.com

Abstract
A technology for utilization of iron scale from mechanical engineering and metallurgy has been developed. The aim of the research is the reduction of the scale to metallic iron. The chemical and granulometric composition of the waste iron powder has been determined. A tube furnace with a maximum operating temperature of up to 1350°C and a protective-reduction environment of $Ar + 35\%\ H_2$ was used. The temperature regimes at which partial and complete reduction of scale occurs have been established. The phases of the iron oxides depending on the temperature and the duration of the reduction process were studied by XRD analysis. The content of pure iron in the final product was determined as comparative X-ray diffraction analysis.

Keywords: utilization of waste iron powders, scale reduction

1. Introduction

In a long term, the initial resources of our planet are becoming more limited and the prices of the raw materials are constantly rising, which makes the utilization of waste materials economically feasible. The term waste material has been now replaced by the word by-product [1]. The composition and properties of waste materials are closely related to the development of new technologies and their recycling. As an example house hold waste glass becomes a raw material for expanded glass granules which are used in thermal insulation products [2]. Cinder ash from thermal power plants is successfully used in the ceramic and cement industries to obtain new composite materials applied in construction [3]. To develop a sustainable technology for utilization of iron waste powders from mechanical engineering and metallurgy, as well as to select an appropriate technology for recycling, it is necessary to assess the basic thermodynamic and kinetic processes for their formation. In general, waste iron powders contain the following iron oxides: wustite (FeO), hematite (α-Fe_2O_3) and magnetite (Fe_3O_4). The chemical composition of the scale varies depending on the type of steel and its processing. The iron content is usually about 70%, with traces of non-ferrous metals and alkali compounds and is contaminated with lubricants, oils and greases from related equipment [1].

For utilization of the scale material obtained after oxygenated cutting of steel products it is necessary:

1. To determine the phase and chemical compositions of the scale powder.

2. To determine the possibility to extract valuable materials from the provided iron powder mixture.

3. To establish an experimental regime for the extraction of iron from the provided waste powder mixture.

2. Experimental

2.1 Identification of the source material

The test powder scale was grinded in a planetary mill and sieved through a sieve 0.315 and then X-ray diffraction (XRD) and chemical analyzes were performed. The diffraction pattern of the starting material is shown in Fig. 1. It can be seen that the starting powder consists mainly of magnetite (Fe_3O_4) and wustite (FeO). According to the semi-quantitative analysis, the content of magnetite ($Fe_{2.92}O_4$) is 65.5 wt.%, and that of wustite ($Fe_{0.93}O$) is 34.5 wt.%. There are no alloying components in the starting powder. Its chemical composition corresponds approximately to that of low-carbon steels (Steel 20 and Steel 20K) and it is shown in Table 1.

Table 1. Chemical composition of Steel 20, Steel 20K

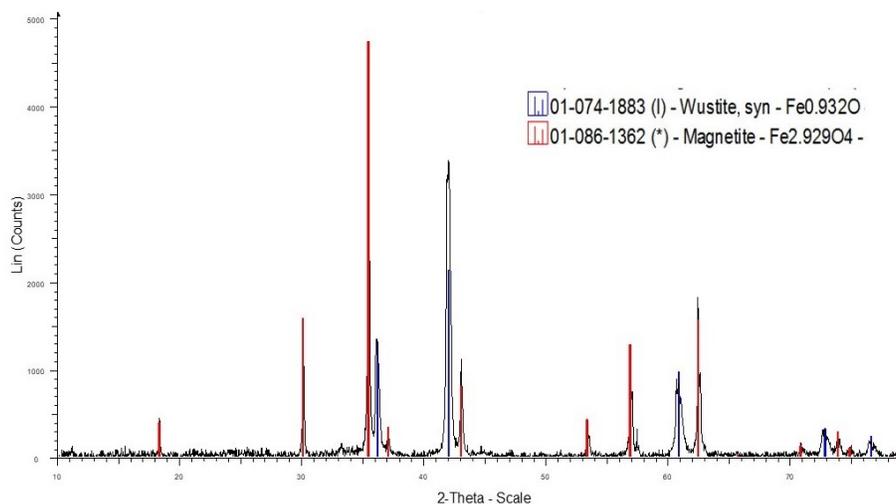| wt. %	C	Si	Mn	S	P	Cu	Fe
St. 20	0.18-0.22	0.17-0.37	0.4-0.8	≤0.015	≤0.02	≤0.3	balance
St. 20K	0.16-0.24	0.15-0.30	0.35-0.65	0.05	0.04	-	balance

Fig. 1. Diffractogram of the initial sample of waste iron dust (scale)

The granulometric composition of the initial sample of waste iron powder is shown in Table 2 and graphically presented in Fig. 2.

Table 2. Granulometric composition of the initial scale

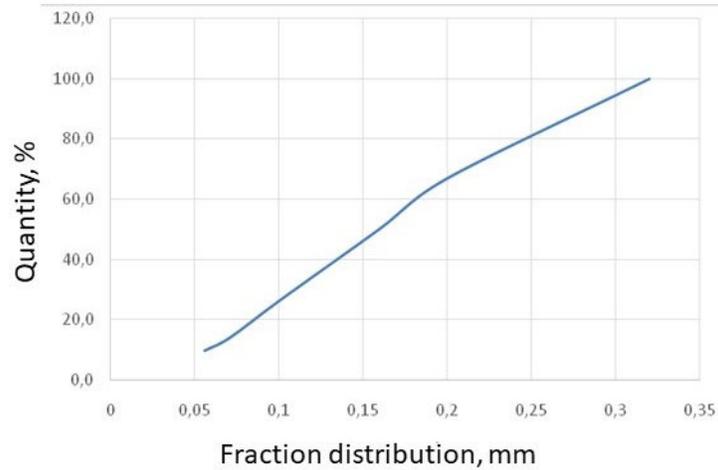| No, sample	№, Sieve	Size, mm	Quantity, g	Proportion, %
1	0,32	0.320>d>0.200	1594	33,0
2	0,2	0.200>d>0.160	807	16,7
3	0,16	0.160>d>0.100	1161	24,0
4	0,1	0.100>d>0.071	585	12,1
5	0,071	0.071>d>0.056	207	4,3
6	0,056	0.056>b (bottom)	474	9,8
Total	-	-	4.828	100

Fig. 2 Grain size distribution of the starting scale by fractions, %

2.2 Aim of the project

The subject of this research is the extraction of iron from waste iron powder (scale), consisting of magnetite and wustite, by reduction and to establish a technological regime. The most suitable reducing agent is H_2 or a gas mixture of H_2 and inert gas (Ar, N_2), and also dissociated ammonia - NH_3 (25% N_2 and 75% H_2).

2.3. Theoretical formulation of the reduction of iron oxides with hydrogen

The reduction of scale with H_2 (hydrogen) goes on according to three main reactions:

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O \tag{1}$$
$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O \tag{2}$$
$$FeO + H_2 = Fe + H_2O \tag{3}$$

Figure 3 shows the change in the isobaric-isothermal potentials (free Gibbs energy) of the temperature-reducing reactions of iron oxides with hydrogen.
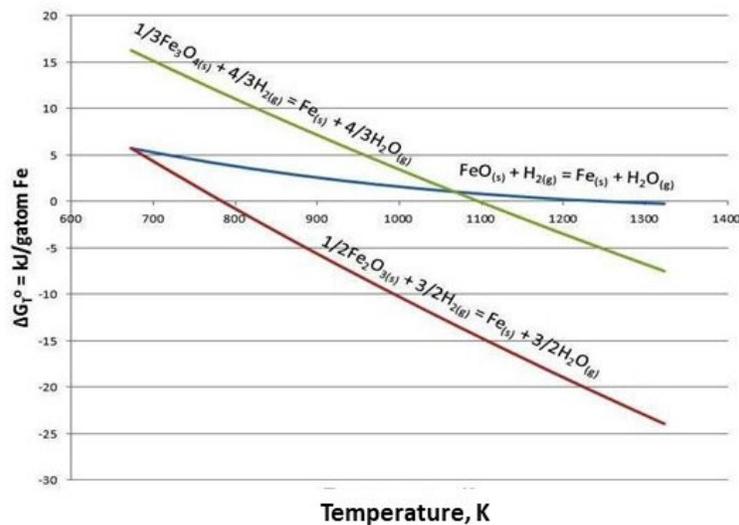

Fig. 3 Change in Gibbs energy of the reduction with hydrogen reactions, ΔG with temperature, K

297

It can be seen that Fe_2O_3 has the greatest tendency to reduction. It is reduced to metallic iron at temperatures above 500°C (773 K). The temperature of reduction with hydrogen of Fe_3O_4 is higher, about 827°C (1100 K). The most stable is FeO, which is reduced around 980°C (1250 K). Since the scale is a mixture of the above iron oxides, the temperature of reduction with hydrogen must be consistent with the highest temperature 980 - 1000°C. The mechanism of oxide reduction is complex, depending on the shape of the particles of the starting powder, their microporosity and others. During the reduction, oxygen atoms are separated from the oxide lattice, and pores are formed in their place, through which the other reaction product, water vapor, is released. At the beginning of the process, the rate of release of oxygen atoms is greater than the rate of conversion of the crystal lattice of the oxide in the lattice of the metal. The pores gradually close due to diffusion processes. Studies have found that after 15 - 20 hours of reduction, the velocities of the two processes become equal at a temperature of about 1050°C. This fact coincides with our thermodynamic conclusions [4].

2.4. Experimental setting

The scrap iron powder (scale) was placed in ceramic ladles and in refractory steel trays and then put in a tubular furnace in a protective-reducing environment of Ar + 35% H_2 or in a furnace with muffle in a protective - reducing environment. The heating rate is between 10 and 20°C/min to 1050 - 1150°C and hold from 1h to 2.5 h depending on the amount and type of waste scale.

3. Obtained results

The reduction processes were carried out on the same starting powder, delivered by the assignor scale from Steels 20 and 20K, at a temperature of 1050 - 1150°C. A gas mixture of argon + 35% hydrogen was used as a reducer. The thermochemical treatment was carried out at different temperature regimes.

3.1. Thermochemical treatment at temperature regime No 1 (Fe1)

Temperature mode - heating rate - 20°C /min and hold at 1050°C - 1 hour, free cooling.
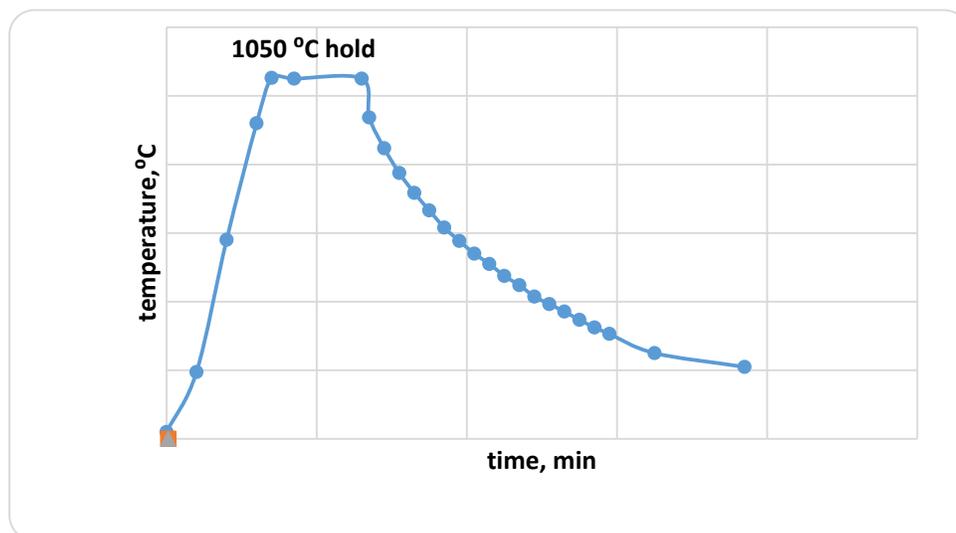

Fig. 3 Graphic temperature-time dependence of the reduction process of Fe1 at 1050°C and hold 1 h
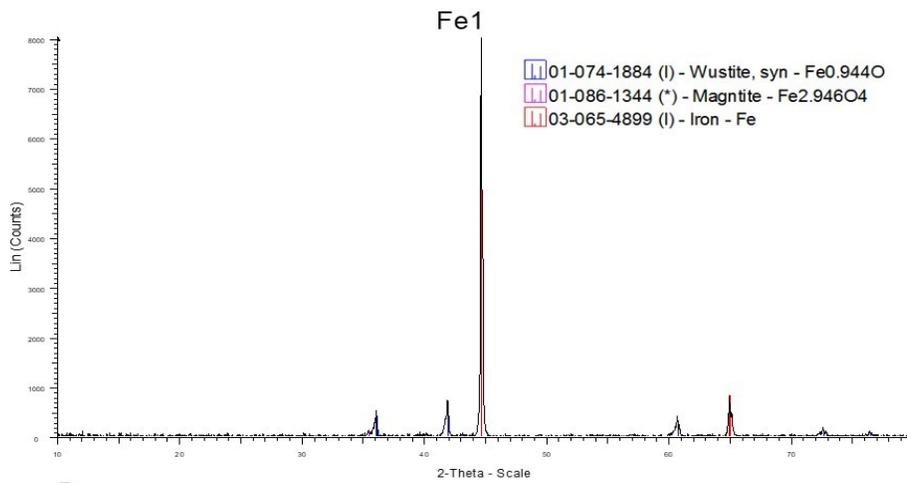
Fig. 4 Diffractogram of the phases obtained after reduction of scale at 1050°C and hold 1 h

Semi-quantitative analysis (wt.%) with an error of up to 5%:
Regime Fe1 (Fig. 3, 4):
    Fe = 79.7%,
    $Fe_{0.94}O$ = 16.8%,
    $Fe_{2.94}O_4$ = 3.5%.

3.2. Thermochemical treatment at temperature regime No 2 (Fe2)
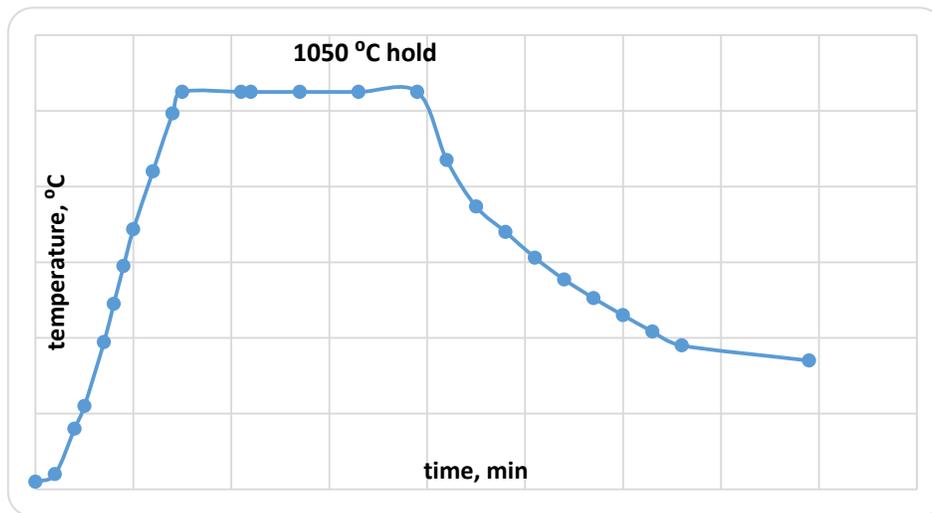Temperature mode - heating rate - 20°C/min, hold at 1050°C – 1.3 hours, free cooling.

Fig. 5. Graphic dependence of temperature-time of the reduction process of scale at 1050°C and hold 1.3 h.
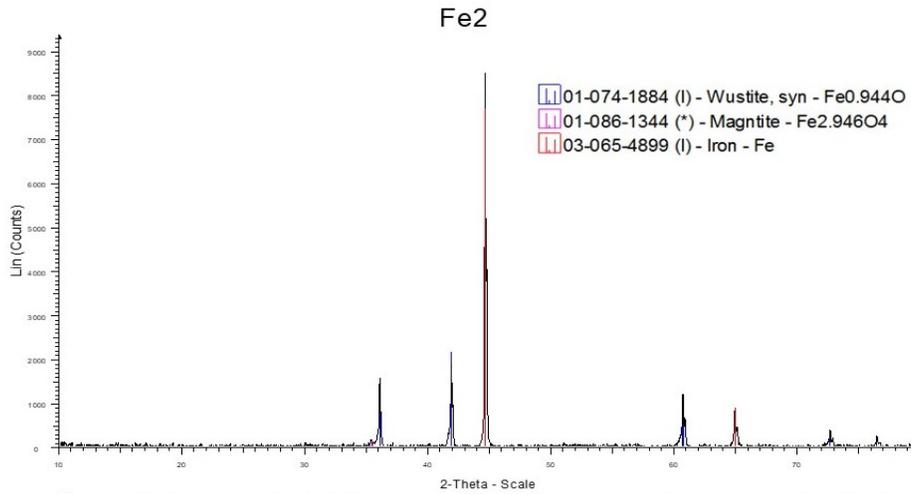
Fig. 6. Diffractogram of the phases obtained after reduction of scale at 1050ºC and hold 1.3 h

Semi-quantitative analysis (wt.%) with an error of up to 5%:
Regime Fe2 (Fig. 5, 6):

$Fe = 60\%$,
$Fe_{0.94}O = 38\%$,
$Fe_{2.94}O_4 = 2\%$.

3.3. Thermochemical treatment at temperature regime No 3 (Fe3)

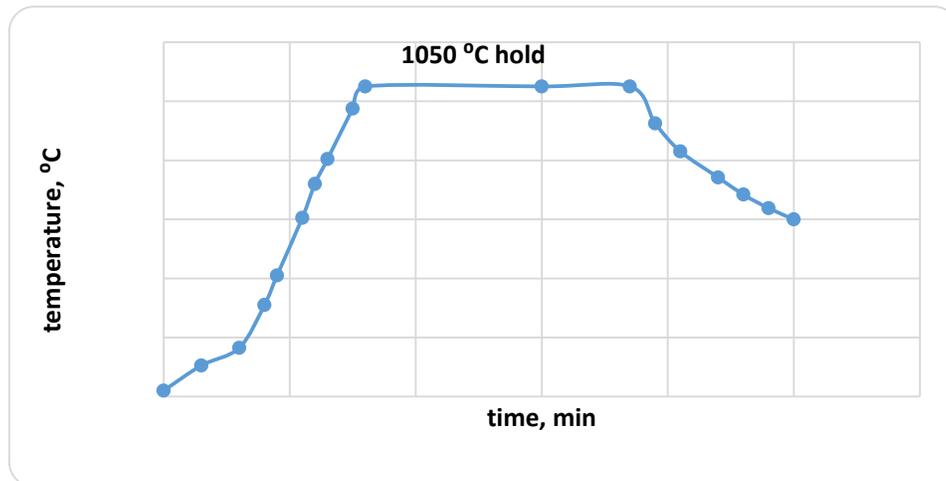Temperature mode - heating rate - 20ºC / min, hold at 1050ºC - 2 hours, free cooling.

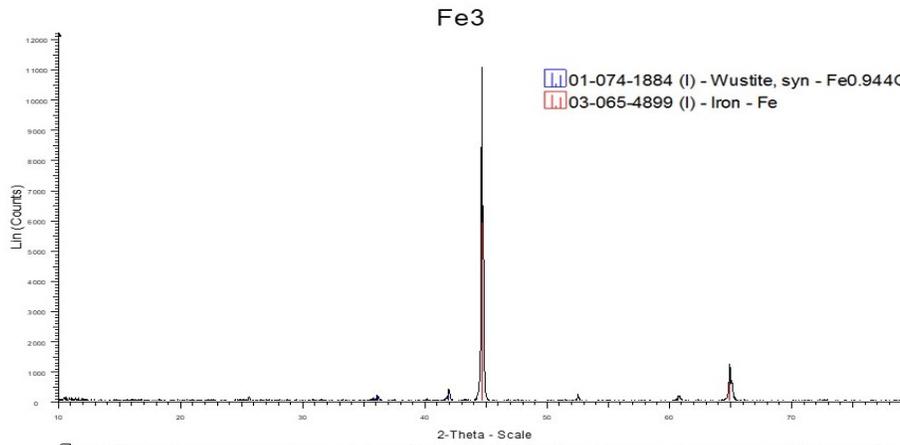Fig. 7. Graphic dependence of temperature-time of the reduction process Fe3 at 1050ºC and 2h hold

Fig. 8. Diffractogram of the phases obtained after reduction of scale at 1050ºC and hold 2 h

The process is carried out in a ceramic ladle, a thin layer about 12 mm thick. The colour of the powder after reduction is gray.

Semi-quantitative analysis (wt.%) with an error of up to 5%:

Regime Fe3 (Fig. 5, 6):

Fe = 95%,

$Fe_{0.94}O$ = 5%.

The difference between regime F2 (Fig. 6) and F3 (Fig. 8) is that the hold in regime F2 is 40 minutes smaller (instead of 2 hours it is 1.3 hours), i.e. the reduction is not completed. Forced stop of the process leads to smaller hold at 1050°C. Subsequent cooling was performed without protective gas, which further led to partial oxidation of the powder.

3.4. Thermochemical treatment at temperature regime No 4 (Fe4)

Temperature mode - heating rate - 20ºC / min, hold at 1150ºC - 1 hour, free cooling.
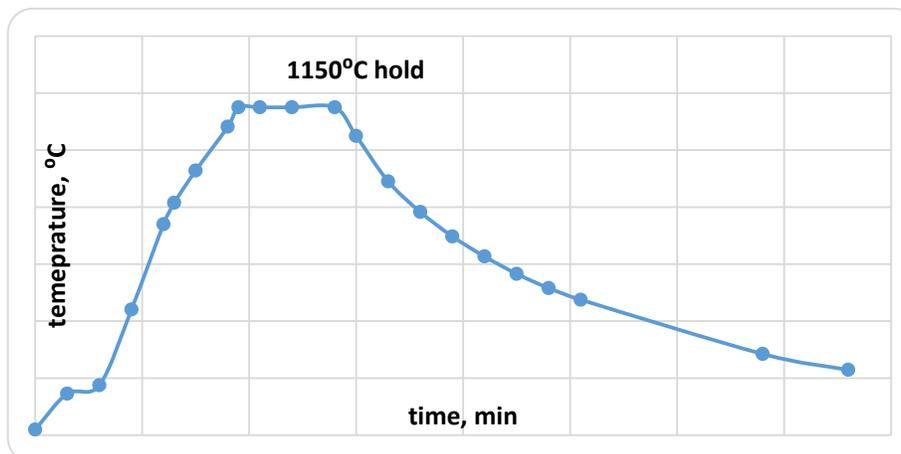

Fig.9. Graphic dependence of temperature-time of the reduction at temperature regime at 1150ºC and hold 1h (Fe4)

The process was carried out in a ceramic ladle, with a layer thickness of about 12 mm. The colour of the Fe powder after reduction was light gray (fig. 12). The powder was very hot. A hard crust was formed on the surface layer.
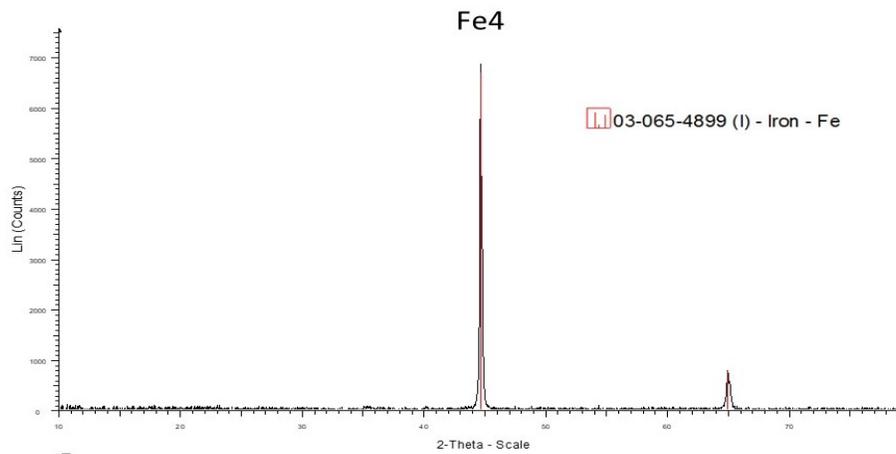

Fig. 10. Diffractogram of the phases obtained after reduction of scale at 1150ºC and hold 1h

Semi-quantitative analysis (wt.%) with an error of up to 5%:
Regime Fe4 (Fig. 9, 10):
  Fe = 100 %,
  $Fe_{0.94}O$ = 0 %.

Figure 11 presents the phases of the pure iron before the mechanical treatment delivered by the assigner. The XRD test was made for comparison. The diffractogram is identical with that of Fe4.
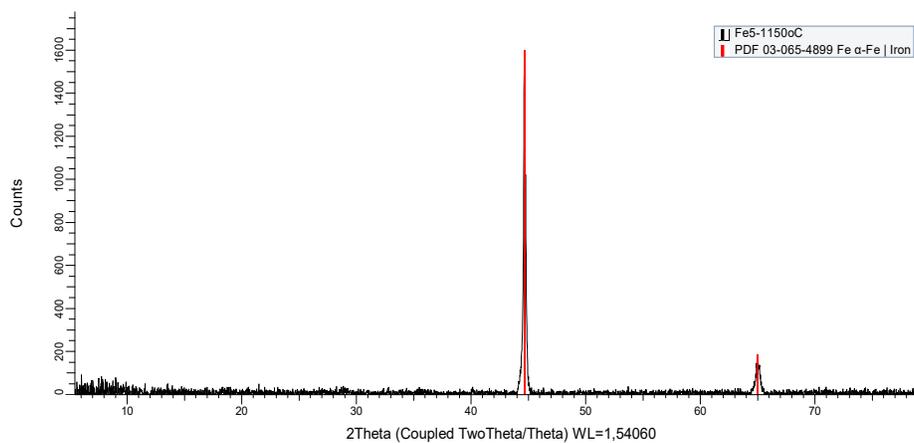

Fig.11. Diffractogram of the phases of pure iron for comparative analysis

Semi-quantitative analysis (wt. %) with an error of up to 5%:
Comparative sample (standard) Fig. 11:
  Fe = 100 %.

The results at different temperature regimes are summarized in Table 3.

Table 3. The obtained results at different temperature regimes

Temperature regime, No	Maximal temperature, °C	Heating rate, °C/min.	Hold at max. temp., h	Composition, wt.%		
				Fe	$Fe_{0.94}O$	$Fe_{2.94}O_4$
No 1 (Fe1)	1050	20	1	79.7	16.8	3.5
No 2 (Fe2)	1050	20	1.2	60	38	2
No 3 (Fe3)	1050	20	2	95	5	0
No 4 (Fe4)	1150	20	1	100	0	0
Standard	-	-	-	100	0	0

Fig. 12. Image of initial scale powder before (dark colour) and after reduction – pure iron (light gray colour)

4. Conclusions

- The possibility for reduction of scale consisting of different iron oxides with a gas mixture of argon + 35% hydrogen in the temperature range 1000°C - 1150°C has been proven. The degree of reduction increases with increasing temperature at a constant hold.
- The reduction of scale is totally completed with the production of pure iron at 1150°C (Fig. 10) and the diffractogram is identical compared to that of the iron provided by the assigner (Fig. 11).
- The process hold is directly dependent on the contact surface of the scale with the reducing gas.
- Samples obtained at 1050°C are looser and darker in colour compared to samples reduced at 1150°C, which are more sintered and lighter in colour.
- Probably the most economically advantageous will be the implementation of a complete reduction of scale at 1100°C.

References

1. Martin M. I., Lopez F.A., Torrabla J. M., "Ironmaking and Steelmaking", vol. 39, No3, (2012), p. 155-162
2. Lakov L., B. Jivov, M. Aleksandrova, Y. Ivanova, K. Toncheva, "An innovative composite material based on sintered glass foam granules", Journal of Chemical Technology and Metallurgy, vol. 53, No 6, (2018), p. 1081-1086.
3. Lakov L., B. Jivov, S. Yordanov, M. Aleksandrova, S. Rafailov, K. Toncheva, "Application of waste silicate raw materials for obtaining of composite materials", International Journal "NDT Days", vol. 1, No 3, (2018), p. 282-289.
4. Gidikova N., V. Manolov, V. Petkov, R. Valov, S. "Stanev, Mill Scale Reduction", Journal of Materials Science and Technology, vol. 25, No 1, (2017), p. 12-19, ISSN 0861-9786.