

REDUCTION OF ULTRA-FINE TUNGSTEN POWDER WITH TUNGSTEN (VI)-OXIDE IN A VERTICAL TUBE REACTOR

REDUKCIJA ULTRAFINIPIH PRAHOV VOLFRAMOVEGA(VI) OKSIDA V REAKTORJU Z VERTIKALNO CEVJO

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The reduction of WO_3 with hydrogen in a vertical tube reactor is a new approach to the reduction of tungsten oxide compared to conventional procedures in a stationary layer. The advantage of this method is the intensive contact between the reductant and the oxide particles, a higher degree and a shorter time of reduction of only a few seconds, compared to the several hours processing time in a horizontal tube reactor.

The characterization of the WO_3 powder and of the tungsten powder included a SEM microstructural examination and DT/TG analyses. The SEM examination of the tungsten powder indicates the presence of small particles with a size of about $1 \mu m$, also within an agglomerated porous foam structure. Tungsten powder with a particle size of less than $1 \mu m$ is obtained at an optimal temperature with a suitable flow of hydrogen, as a result of stretching and the cracking of large particles, first in the reaction zone, and then, due to appropriate shock of the temperature, outside of this zone.

Using an appropriate mathematical model, the degree of reduction and the time required for the formation of tungsten particles during the hydrogen reduction of WO_3 in a vertical tube reactor were determined. Experimental studies have shown that the degree of reduction of WO_3 with hydrogen in a vertical tube reactor increases with the temperature and the flow of hydrogen.

Keywords: tungsten (VI)-oxide, reduction, vertical tube reactor, tungsten powder

Redukcija WO_3 z vodikom v reaktorju z vertikalno cevjo je nov postopek v primerjavi s konvencionalnimi postopki v stacionarni plasti. Prednost postopka je intenziven kontakt med reducentom in oksidnimi zrnji, kar izboljša in skrajša čas redukcije na nekaj sekund, medtem ko traja procesiranje v reaktorju z vodoravno celo nekaj ur.

Karakterizacija prahov WO_3 je obsegala SEM-opazovanje in DT/TG-analize.

SEM-opazovanje volframovega prahu odkrije prisotnost majhnih delov z velikostjo $1 \mu m$ s strukturo iz penastih aglomeratov. Volframov prah z velikostjo manjšo od $1 \mu m$ dobimo pri optimalni temperaturi in ustreznem toku vodika kot rezultat obremenitve in razpokanja večjih delcev, najprej v reakcijski zoni nato pa zaradi temperaturnega šoka zunaj te zone.

Razvit je bil računalniški model za nastanek zrn volframa z redukcijo WO_3 z vodikom v reaktorju z vertikalno cevjo. Rezultati raziskave kažejo, da stopnja redukcije WO_3 raste s temperaturo in s tokom vodika.

Ključne besede: volframov(VI) oksid, redukcija, reaktor z vertikalno cevjo, volframov prah

1 INTRODUCTION

The more intensive development of science and industry requires the application of new materials with specific properties. The basis for most of these materials is rare metals and their alloys. Due to their good mechanical, electrical, electro-erosive, tribological and magnetic properties, tungsten and its alloys are frequently used materials in industry ¹. Besides, tungsten has a high melting temperature, a high boiling point, a low evaporation rate at high temperatures and a low thermal expansion coefficient.

In industrial conditions, these materials, are often submitted to a reduction process with a gas as the most commonly used reductant, which easily penetrates into the oxide pores and ensures a good contact with the surface and in the interior of the reduced material ². Recently, a number of authors investigated the synthesis

of tungsten-based powders using different methods, such as: the sol-gel method, chemical method co-precipitation, processes of mechanical activation, and plasma reduction ³⁻⁷. With the aim to obtain a pure tungsten powder, the latest world research is oriented toward the application of new reducing agents and the development of new or a modification of existing technological processes. The process of the reduction of tungsten oxide, due to the low reaction temperature and the high degree of purity of the obtained products, was the subject of extensive research ^{3,6,7}. The results indicated that the properties of the synthesized tungsten powder depend, above all, on the properties of the starting powders and of the parameters of the technological process, mostly its simplification. At the same time, the variation of the parameters of the technological process, such as the temperature and the flow of hydrogen, as well as the processing in isothermal and non-isothermal conditions,

led to the conclusion that with the process it is possible to obtain ultra fine, homogenous and loose tungsten powders. With the aim to shorten the time of the process, Lackner⁸ performed the reduction of tungsten oxide in a vertical tube for four temperatures at (800, 900, 1000 and 1100) °C. The starting powder tungsten(VI)-oxide had an average particles size of 28 μm and tungsten powder particles with a size of 17.3 μm were obtained by a reduction at 1100 °C in 1.7 s.

A study of the mechanism and kinetics of hydrogen reduction of tungsten oxide pointed out that the main problem of this process is the formation of several sub-oxides as intermediate products⁹⁻¹². The reduction of WO₃, occurs through the following stages of oxidation^{8,13}: WO₃ (α-oxide) → WO_{2,9} (β-oxide) → WO_{2,72} (γ-oxide) → WO₂ (δ-oxide) → metal, α- or β-tungsten.

According to Fouad¹⁰, the reduction of WO₃ with hydrogen occurs through three stages: WO₃ → WO_{2,72} → WO₂ → W, where the activation energy is in the range from 100.48 kJ/mol to 133.98 kJ/mol. In accordance with^{10,13,14}, the reduction of WO₃ with hydrogen under isothermal conditions occurs in two stages: WO₃ → WO₂ → W, with the activation energy, according to Bustnes¹⁵, of the reduction of WO₂ to W of 83kJ/mol. A kinetic analysis of the reduction of tungsten oxide in a vertical tube⁸ indicates that the process occurs with an activation energy of 126 kJ/mol.

Although the most common method of producing tungsten powder is tungsten oxide reduction with hydrogen, the reaction conditions and the kinetics of other reducing agents, such as the reduction of WO₂ with carbon in the form of graphite or soot^{16,17}, resulting in pure tungsten, and the reduction of oxide tungsten with CO, when the WC is the final products were also investigated¹⁸.

As a part of this study the process of hydrogen reduction of WO₃ powder in a vertical tube reactor was examined. It is a completely new approach to the reduction of oxides of tungsten, compared to conventional procedures in a horizontal tube reactor. The advantage of the procedure is the intensive contact between the reducing agents and the oxide particles, which results in a higher degree of reduction and a shortening of the reduction time to only a few seconds, while the process in a horizontal tube lasts for several hours.

2 EXPERIMENTAL

For the synthesis of ultra-fine tungsten powder with the reduction of tungsten oxide a vertical tube reactor was used. In **Figure 1**, the scheme of the apparatus for the reduction of WO₃ by hydrogen in a vertical tube reactor is shown. The apparatus consists of:

- a system of supply,
- gas-purifier system,
- units for heating,
- system to add a starting powder (vibration feeder),

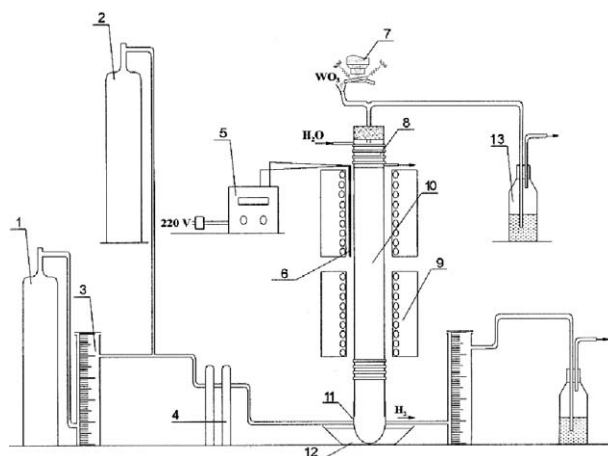


Figure 1: Schematic review of the apparatus for tungsten trioxide reduction in a vertical tube reactor. 1. Hydrogen bottle, 2. Nitrogen bottle, 3. Rotameter, 4. Purification columns, 5. Thermoregulator, 6. Thermopar, 7. Vibration supplier, 8. Radiator, 9. Electroresistant furnace, 10. Quartz tube, 11. Glass supplement, 12. Ice bowl, 13. Cleanser

Slika 1: 1. Jeklenka z vodikom, 2. Jeklenka z dušikom, 3. Rotameter, 4. Čistilne kolone, 5. Termoregulator, 6. Termopar, 7. Vibrator, 8. Radiator, 9. Elektroporovna peč, 10. Kremenova cev, 11. Stakleni dodatak, 12. Posoda z ledom, 13. Čistilnik

- instruments for measurement and controlling the process,
- quartz tubes, diameter of 22 mm and height $h = 540$ mm,
- cooling system.

The system for gas supply consists of two bottles, one with compressed hydrogen and one with nitrogen. The bottle with hydrogen is connected through the rubber hose to the column containing CaCl₂, which is further connected through the rubber hose to a rinser with sulphuric acid, both used to remove moisture from the hydrogen. The flow of gas at the exit from the bottle with hydrogen is measured with a flowmeter. The quartz heating tube is used in an electric furnace. The process parameters are the temperature and the flow of hydrogen. The holding time of the WO₃ powder particles in the furnace reaction zone is calculated using an equation based on values of the relevant parameters: tube length, particle diameter, particle density, gas speed, gas density, viscosity and gravity. The temperature is measured and controlled with a thermoregulator, connected to the furnace with a PtRh-Pt thermocouple. The quartz tube (inner diameter, $\phi = 22$ mm and height, $h = 540$ mm) is placed vertically through the furnace and it is attached to the metal frame. The tube is closed from both sides with rubber seals. The part of the quartz tube in the furnace is cooled using a copper heat sink, of spiral form, through which water circulates. The oxygen supply and the drain occur from the bottom of the quartz tube. At the end the hydrogen hose outlet has a rinser with water that serves as a powder collector. During the process of reduction, the bottom of the quartz tube is placed in a glass cup filled with cold water and ice, and the Pyrex powder

collector is completely submerged to prevent the re-oxidation of the reduced particles. This will achieve additional stresses in the particles due to cracking thermoshocks, which leads to their fracture. On the quartz tube top a rubber seal is placed and it is drawn into the glass tube with a rubber hose. A glass funnel is placed to the rubber hose in which a certain amount of powder is inserted. The inner diameter of the glass funnel is 4.75 mm and outside is 7.75 mm. The powder dosing is accomplished with a vibratory feeder. At the end of this hose there is a rinser with water.

Synthetic powder of tungsten (VI)-oxide (Merck, Darmstadt) with a particle size of less than 30 μm was used as a base material. This material is hygroscopic and prone to agglomeration. Before the reduction process, WO_3 powder is dried at a temperature of 100 $^\circ\text{C}$. Occasionally, the powder was taken out from the dryer and mechanically ground. To remove the remaining agglomerates, after the completion of the drying process, the powder is sifted through a sieve with 63 μm holes.

The WO_3 powder's hydrogen reduction was carried out at six temperatures (700, 725, 750, 800, 850 and 900) $^\circ\text{C}$ and four hydrogen flow rates (10, 20, 30 and 50) dm^3/h .

The characterization of the used WO_3 powder and of the obtained tungsten consisted of a SEM microstructural examination and a DT/TG analysis. The SEM analysis was carried out using a JEOL T20 JSM 5300 microscope. For the DT/TG analysis, a NETZCH STA model 409EP with a maximum temperature of 1100 $^\circ\text{C}$ was used. A thermocouple Pt-Pt-Rh S type (10 % Rh) and a reference material $\alpha\text{-Al}_2\text{O}_3$ were used.

The degree of reduction was determined and, using the appropriate mathematical model, the time required for the formation of tungsten particles during the hydrogen reduction of tungsten in a vertical tube reactor was deduced. Based on the obtained results the influence of the temperature, the time and the hydrogen flow on the reduction degree of tungsten trioxide were determined.

3 RESULTS AND DISCUSSION

In **Figure 2**, the initial powder of synthetic WO_3 , and in **Figure 3**, the initial powder of synthetic WO_3 after drying, grinding and sifting are shown. The examination of the initial powder of synthetic WO_3 (**Figure 2**) indicates large agglomerates with a size of 80 μm and particles smaller than 30 μm . After drying, grinding and sifting, an irregular shape of particles with a size below 15 μm and large agglomerates of size below 40 μm consisting of a great number of small particles connected to one another are observed. In addition, small particles cover the large as a patch and cause a spongy morphology. Since the initial powder is very fine and hygroscopic, the primary 'condition' for agglomerate formation is fulfilled. Namely, the agglomeration of the small particles is due to their large surface, i.e., a high surface energy

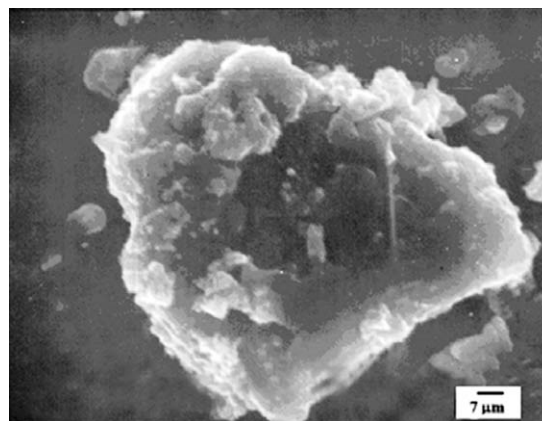


Figure 2: SEM of the initial WO_3 powder
Slika 2: Posnetek začetnega prahu WO_3

and the interaction through Van der Waals forces that exist between them.

Figure 4 shows the resulting tungsten powder in the form of a porous agglomerate of size less than 30 μm . Also, particles of tungsten of size about 1 μm and smaller, particles are present suggesting that the reduction process contributed to the fragmentation of the powder particles.

Figure 5 indicates clearly the presence of a large, porous foam structure agglomerate with a size of about 50 μm with smaller agglomerates in the background. All the agglomerates consist of single particles smaller than 1 μm . The occurrence of the porous tungsten powder is explained by the fact that the reduction reaction was heterogeneous and chemically controlled.

The reduction speed was determined from the speed of the chemical reaction at the interface of the oxide/product, which causes the porosity of tungsten powder. Tungsten powder particles with a size of less than 1 μm are produced with stretching and cracking of the large particles in the reduction zone. The hydrogen molecules diffuse through the surface of the WO_3 particles and metal tungsten nucleation may occur at the begin-

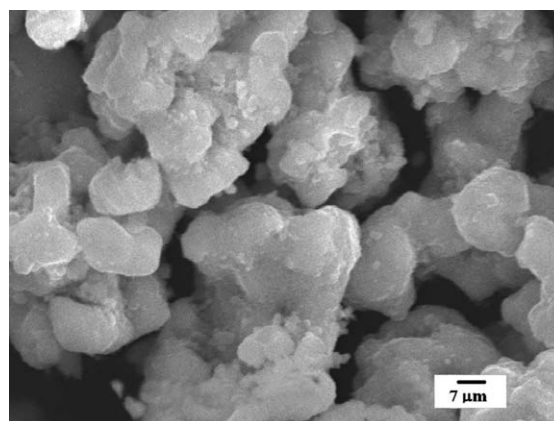


Figure 3: SEM of the initial WO_3 powder after drying, grinding and sifting
Slika 3: Začetni prah WO_3 po sušenju, drobljenju in sejanju

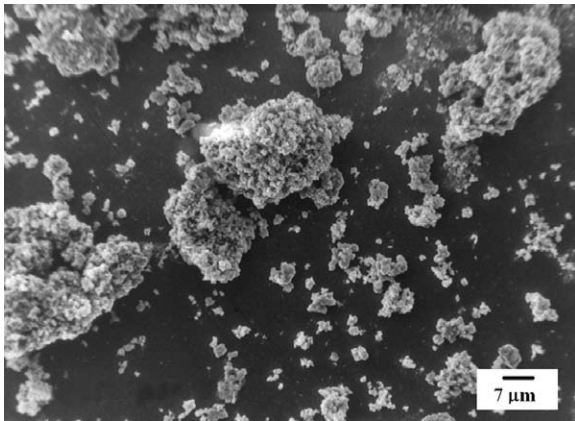


Figure 4: SEM of the obtained tungsten powder
Slika 4: SEM-posnetek pridobljenega volframovega prahu

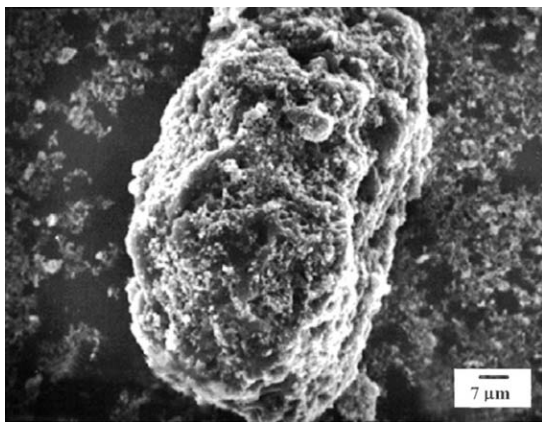


Figure 5: SEM of the obtained tungsten powder
Slika 5: SEM-posnetek pridobljenega volframovega prahu

ning of the process of reduction; however, tungsten nuclei begin to grow when most of the WO_3 is changed into WO_2 . The released oxygen surplus created during the transformation of WO_3 into WO_2 diffuses through the surface and reacting with hydrogen, creates steam, which as reduction product becomes trapped in the WO_3 lattice. The steam and the growth of tungsten nuclei cause stresses and later the cracking of larger oxide particles

into smaller fragments. Additional stresses occur during the transition of reduced particles from the furnace reaction zone, heated to a temperature of 900 °C in the unheated to the quartz tube zone and during cooling in the collector iced water. The temperature shock causes the rupture and further fragmentation of particles. The described reduction mechanism suggests that the process advances in two stages.

The degree of reduction was determined stoichiometrically from the weight difference of the starting WO_3 powder and the reduced tungsten powder, i.e., the differences in the amounts of oxygen. Table I shows the obtained experimental values of the degree of reduction.

The time when the WO_3 particles fall through the quartz tube of the vertical reactor during the reduction process could not be precisely determined with a simple measurement using a stopwatch. For this reason, it was determined using the appropriate mathematical model based on the physical laws of the movement of particles through a fluid, i.e., on the application of Stock's law to the moving of one particle through the fluid. One of the conditions of the application Stock's law is that the particles diameter is not greater than 50 μm ^{19,20}, a condition that was fulfilled as the starting WO_3 powder mean particles size was about 30 μm .

According to Stock's law, the speed limit of small spherical particles which fall out of the fluid is:

$$V_t = \frac{2R^2(\rho_s - \rho)g}{9\eta} \quad (1)$$

where:

- ρ_s – particle density,
- ρ – fluid density,
- η – dynamic viscosity,
- g – acceleration due to gravity,
- R – diameter of a spherical particle,
- V_t – speed of depositing particles.

In this case, the time for a small spherical particle to fall through the fluid which streams in the opposite direction is:

Table 1: Experimental values of the degree of reduction and the mathematically calculated values of the reduction time of the tungsten trioxide particles

Temperature, T/°C	700	725	750	800	850	900
q/dm ³ /h	10	10	10	10	10	10
α /%	24	29	34	44	53	59
t/s	3.04	3.1	3.16	3.29	3.42	3.53
q/dm ³ /h	20	20	20	20	20	20
α /%	35	42	49	60	67	74
t/s	3.28	3.36	3.44	3.62	3.78	3.95
q/dm ³ /h	30	30	30	30	30	30
α /%	45	53	60	70	78	84
t/s	3.55	3.65	3.76	3.99	4.21	4.44
q/dm ³ /h	50	50	50	50	50	50
α /%	65	72	78	88	95	99
t/s	4.32	4.51	4.69	5.12	5.58	6.09

$$t = \frac{1}{v_t - v_{\text{gas}}} \quad (2)$$

where:

l – length of the tube reaction zone,

v_t – speed of a spherical particle,

v_{gas} – fluid rate.

Since the particle does not flow through an unlimited fluid, but through a fluid in a dish, the influence of the walls on the dish during the particles' falling must be taken into account. If a particle falls on the axis cylinder dish, the actual fall time is shorter and it is ²⁰:

$$t^* = \frac{t}{1 + \left(\frac{9r}{4R}\right) + \left(\frac{9r}{4R}\right)^2} \quad (3)$$

where:

R – dish diameter,

r – distance from the dish's central axis.

In **Table I** the obtained experimental values for the degree of reduction and the mathematically calculated values of the reduction time for the tungsten trioxide particles are shown.

The described mathematical model to determine the time refers to a single particle. However, during the reduction of tungsten trioxide powder in a vertical tube reactor the particles fall in the form of small agglomerates. The particle agglomerates mass is significantly greater than the mass of one particle and for this reason, the falling speed of the agglomerated particles is higher than the falling speed of single particles. For this reason, the actual reaction time with hydrogen is less than 1 s.

Based on the obtained results, shown in **Table I**, the analysis of the influence of temperature, time and hydrogen flow on the degree of reduction of tungsten trioxide was carried out. The influence of the temperature and time on the degree of reduction of WO_3 is shown in **Figure 6**. The reduction degree of tungsten trioxide increases with the temperature and the highest values (re-

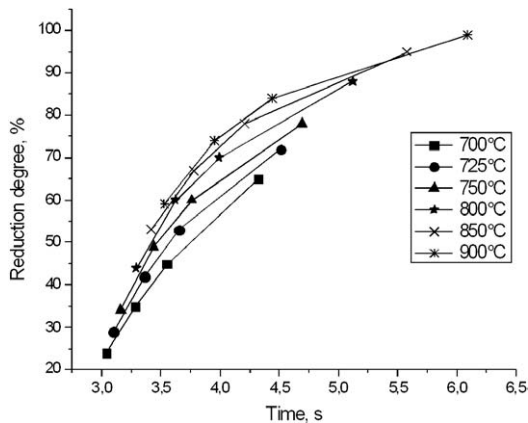


Figure 6: Influence of temperature and time on the degree of reduction for the WO_3

Slika 6: Vpliv temperature in časa na stopnjo redukcije WO_3

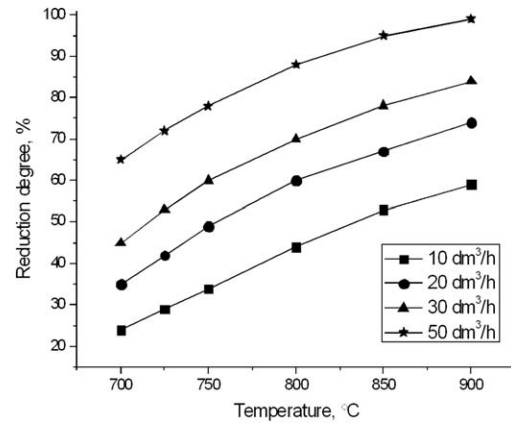


Figure 7: Influence of the flow of hydrogen on the degree of reduction for the WO_3

Slika 7: Vpliv toka vodika na stopnjo redukcije WO_3

duction degree 99 %) were achieved at a temperature of 900 °C. In **Figure 7** the dependence of the degree of reduction of tungsten trioxide on hydrogen flow is shown.

With an increasing of the gas flow, the reduction degree increases and the greatest degree of reduction is achieved with a hydrogen flow of 50 dm^3/h . This phenomenon is explained as a result of the increasing gas-adsorption properties with its quantity increase per unit of time and the increase of the diffusion coefficient, which is greater with a smaller molecular weight of gas. Bearing in mind that hydrogen has the smallest molecular mass of all known gas reducers, i.e., a high coefficient of diffusion, it is clear that the speed of penetration of hydrogen into small, spherical particles of tungsten trioxide is high, and therefore the degree of reduction of the oxide is greater.

During the experiment the analyses of the DT and DG (**Figure 8**) of obtained tungsten powder were also carried out. The described mechanism of reduction indicates that the process goes through two stages and it is completely in accord with the results of the DT analysis, where two exothermic peaks, at 365 °C and 469

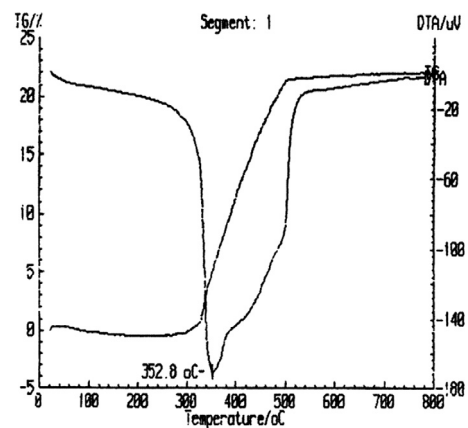


Figure 8: DT/TG analysis of tungsten powder

Slika 8: DT/TG-analiza volframovega prahu

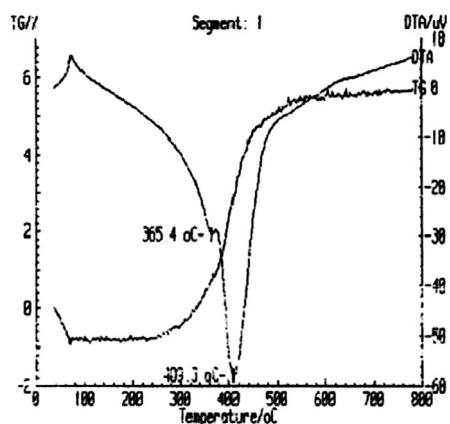


Figure 9: DT/TG analysis of sample W + W_xO_y
Slika 9: DT/TG-analiza vzorca W + WO_3

°C, respectively (Figure 9) were observed for the sample W + W_xO_y .

The TG analysis shows a mass increase in the oxidation of tungsten (250–500 °C) to a value of 22.61 %. The increase in mass in this temperature zone for pure tungsten is 26.14 %, and this indicates that the examined tungsten sample was not totally pure, i.e., that it contained a significant content of oxides of tungsten. Based on these results, the calculated degree of reduction is 86.49 %, and in agreement with the experimental results obtained (88 %) with the appropriate stoichiometric analysis.

4 CONCLUSION

With the reduction procedure in a vertical tube reactor, tungsten powder with particles of size less than 1 μm were obtained. Compared to conventional procedures performed in a stationary layer the procedure is a new approach to the reduction of oxides of tungsten. The advantage of this method is intensive contact between the reductant and the oxide particles, which results in a higher degree of reduction and a shortening of the reduction time to only a few seconds, when compared to the process in a horizontal tube reactor of several hours that results in a less-reduced powder.

Tungsten powder particles with a size of less than 1 μm were obtained for the optimum temperature conditions and flow of hydrogen as result of the stretching and cracking of large particles, first in the reaction zone and then, due to an appropriate temperature shock, outside of this zone. The obtained tungsten powder shows a similar tendency to agglomerate as the basic tungsten trioxide powder and the agglomerate formed is due to its large area and the high surface energy and the effect of the attractive forces.

The described mechanism of reduction indicates that the process occurs in two stages and in accordance with the results of the DT analysis, where two exothermic peaks can be observed, at 365 °C and 469 °C, respec-

tively, for the sample W + W_xO_y . Based on the results of the TG analysis a degree of reduction of 86.49 % is calculated, which is in good agreement with the experimental results obtained (88 %) with the stoichiometric analysis.

The results showed that the degree of hydrogen reduction of WO_3 in a vertical tube reactor increases with temperature and the highest values (99 %), achieved at 900 °C, of less than 1 s indicate that the process is very fast and intensive. With an increasing of the gas flow, the degree of reduction increases and the highest values were achieved with a hydrogen flow of 50 dm^3/h .

Further research will be aimed towards optimizing the process of reduction in a vertical tube reactor with intensification of the reactions and cost-reduction. Also, it would be useful to achieve a separation of the large fractions of powder at the exit of the quartz tube and their re-direction in the process of reduction and obtain a circular system and therefore a higher efficiency of the process.

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