POSSIBILITIES OF THE WEAR CONTAMINATION DECREASING OF THE MILLED SILICON POWDER

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MOŽNOSTI ZNÍŽENIA ZNEČISTENIA MLETÉHO KREMÍKA OTEROM

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Abstrakt

Pri energetických a materiálových interakciách medzi mlecími nástrojmi a časticami mletej látky dochádza na jednej strane k opotrebeniu mlecích telies a na druhej strane k znečisteniu mletej látky. Pri príprave špičkových materiálov vysokej čistoty stojíme často pred rozhodnutím, či zabrániť, resp. minimalizovať znečistenie prášku primletými nečistotami vhodnými podmienkami, či postupom mletia alebo kontaminované prášky rafinovať.

V práci sú prezentované dva spôsoby zníženia obsahu nečistôt u kremíka:

Krátkodobé dezagregačné premletie vzorky dlhodobo mletej za sucha v adsorpčne aktívnom prostredí, ktoré je výhodnejšie z hľadiska kvality prášku ako aj životnosti mlecích nástrojov.

Rafinácia produktov mletia vhodnými chemickými činidlami. Ich výber závisí od kvality použitých mlecích telies. Kým odstránenie znečistenia oceľovými telesami je jednoduché a umožňuje prípravu prášku vysokej čistoty, odstránenie znečistenia volfrámkarbidovými telesami je prakticky nemožné.

Pri zvážení týchto argumentov je možné v každom prípade vzhľadom k znečisteniu a jeho možnej eliminácii odporučiť len mlyny s mlecími komorami a telesami na báze nízkolegovaných ocelí.

Abstract

In this work are presented the possibilities of minimisation of contamination contents by convenient milling procedure and chemical purification of milled powders. A combined procedure of long-term dry milling with consequent short-term disaggregative re-milling in adsorption active solvating environment is more advantageous from the view of the powder purity and wear of milling balls in comparison with the long-term milling in liquid environment. There is recommended to use steel milling balls for the preparation of ultrafine powders because of easy purification of iron wear by chemical methods.

Key words: silicon, milling, wear, contamination, powder purification

1. Introduction

The preparation of ultra-fine powders with high purity and controlled composition is connected with the choice of appropriate milling conditions and the selection of mill type. The preparation of silicon-based alloys, composites and ceramics by mechanochemical procedures stimulates the investigation in surface reactivity of finely milled silicon and the protection and cleaning of Si surfaces against contamination by wear. The conditions of intensive milling of silicon in various environments and its contamination by wear were studied in our previous works [1, 2]. The specific surface area increasing and mean particle diameter decreasing were used as a measure of milling intensity. Prevailingly there isn't the way to avoid contamination of milled powder but there exist several processes to its minimisation [3, 4].

In this work are presented two procedures of minimisation of contamination silicon powder milled in vibration and planetary mills, the combined procedure of long-term dry grinding with consequential short-term disagreggative milling in adsorption active environment or milling in liquid environment and subsequent purification by chemical methods.

2. Experimental

The experimental studies were carried out on silicon (99,95 % purity) taken from the monocrystalline ingot production (Tesla Sezam, Czech republic). Milling was performed in a four-chamber laboratory mill made in Institute of Geotechnics SAS, Košice with steel balls like the milling media and planetary mill PULVERISETTE 4 (Fritsch, Germany) with tungsten carbide balls (content of 7 % Co) . Milling conditions were described in work [1]. Experiments were performed by dry and wet milling in various liquids for 4 hours. Dry milled samples were than short-term milled in liquid environments. The changes of specific surface area and particle size distribution were determined before and after short-term milling.

The specific surface area of silicon powders was determined by the standard BET method using the instrument Gemini 2360 (Sy-lab Austria).

The particle size distribution of silicon powders was measured by the method of laser scattering on the granulometer Helos and Rodos (Sympatec GmBH, Germany). Iron, wolfram and cobalt contents of milled samples were determined by method AAS (SpectrAA-30, Varian, Australia).

Chemical treatment of silicon powder was carried out by hydrochloric acid (0,33 $mol.dm^{-3}$). 1 gram of sample was leaching in 250 ml HCl at 69°C for 1 hour.

3. Results and discussion

Preparation of ultra-fine silicon powders by dry milling is better in term of iron impurity concentration like the milling in liquid environment. But production of agglomerates by long-term dry milling has a negative influence on high temperature processes of the solid-state synthesis or sintering. There are some possibilities of milled powder disaggregation. For example the additive short-term milling in solvating active environment effects the disaggregation of the agglomerates prepared by dry milling [5,6,7]. Experiments of the disaggregation milling were realised on the silicon samples prepared by dry milling in vibration and planetary mills for 4 hours. Short-term disaggregative milling

in organic liquids of various quality leads to the increasing of the specific surface area for about 10-30 % and reduces mean particle diameter dm in comparison with the original dry milled sample (Table 1).

The content of the impurities and the wear rate of the milling tools during short-term wet re-milling of four hours dry milled samples in organic liquids were less than the values for the long-term milled samples in organic liquids (Table 2). Contamination of wet milled powder depends on the physical properties of milling environment.

Chemical purification procedures of milled powders are based on the possibilities to remove contamination from wear of milling balls. This is connected with the existence of selective agents to that is silicon resistant but absolutely eliminate impurities and remain the required quality of ultra fine silicon powder. Based on the results of paper [3,8] where the purification of metallurgical silicon powders by inorganic acids and their mixtures was studied, as a purification agent for iron (vibration milling) and cobalt (planetary milling) of contaminated silicon samples hydrochloric acid was selected.

Optimal conditions of dissolution Fe in HCl were determined from simplex experiment planning, where sample of silicon with the highest content of Fe (milled in methanol for 4 h.) was used. In table 3 contents of Fe and Co in the silicon samples milled in vibration and planetary mills in air and various liquids before and after acid treatment are compared. Fe was absolutely removed by purification of the vibration milling products and product purity of 99.99% was received. The tungsten impurities from wear of WC balls at planetary milling weren't removed by HCl purification. The contents of Co were slightly decreased. Purification of silicon powder contaminated by tungsten carbide wear in hydrochloric acid is more difficult like the iron impurity removing [9]. The removing of wolfram from silicon samples requires its thermal treatment at temperature higher than 700°C and its transformation from difficult soluble WC to the better soluble WO_3. However this is impossible because silicon is oxidised to SiO_2 at about 600°C.

The changes of specific surface area of silicon samples removed from iron contamination are compared with silicon samples milled in vibration mill in Table 4. These results are in agreement with the conclusions of works [4,10], where the influence of the iron removing from the milled quartz samples by organic acids on the specific surface area was studied.

4. Conclusions

The aim this work was the preparing of silicon powder with the maximum specific surface area, its corresponding mean particle diameter and with the minimum content of impurities.

In this work are presented two procedures of minimisation of contamination silicon powder at vibration and planetary milling:

the combined procedure of long-term dry milling with subsequent short-term disagreggative milling in adsorption active environment

milling in liquid environment and purification of milled powder by chemical methods.

From the comparison of the impurity contents results that the combined procedure is more advantageous that long-term milling in organic liquids.

The removing of iron from milled silicon samples is more easily by inorganic acid and product purity of 99.99 % Si was received. Purification of planetary milled silicon was failure because of resistant tungsten carbide to inorganic acid. Only the slight decrease of cobalt contents was observed. If these arguments are regarded, it is better to use the mills with steel tools.

The removing of the thin iron layer from the surface of milled particles is connected with the decrease of specific surface area of powders.

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Literature

[1] Tkáčová, K., Števulová, N., Bastl, Z., Stopka, P. and Bálintová, M.: Changes in surface area and composition during grinding of silicon in environments of various quality. J.Mater. Res. vol. 10, No.11, 1995, pp. 2728-2735

[2] Bálintová, M. and Števulová, N.: Contamination of silicon powder during vibration grinding in organic liquid. In: Proc. of International Conference "New Trends in Mineral Processing III.", VŠB TU Ostrava, 1999, pp.111-116

[3] Santos, I.C., Goncalves, A.P., et al.: Purification of metallurgical grade silicon by acid leaching. Hydrometallurgy. vol.23, 1990, pp. 237-246

[4] Tkáčová, K., Števulová, N. and Lipka, J.: Deferritisierung der mechanisch aktivierten Quarzpulvern mit verdüntner Zitronen- und Oxalsäure. Keramische Zeitschrift, vol.44, 1992, pp.609-611

[5] Tkáčová, K. and Števulová, N.: Change in structure and enthalpy of carbonates and quartz accompanying grinding in air and aqueous environments. Powder Technol. vol.52, 1987, pp. 161-166

[6] Tkáčová, K., Števulová, N., Lipka, J. and Šepelák, V.: Contamination of quartz by iron in energy-intensive grinding in air and liquids of various polarity. Powder Technol., vol.83, 1995, pp. 163-171

[7] Tkáčová, K., Heegn, H. and Števulová, N.: Energy transfer and conversion during comminution and mechanical activation. Internat. J. of Mineral Processing. vol.40, 1993, pp 17-31

[8] Števulová, N., Suzuki, M., Senna, M., Bálintová, M., Šepelák, V. and Tkáčová, K.: Mechanochemical oxidation of silicon and selectivity of oxide superficial layer dissolution in aqueous solutions of HF and KOH. Solid State Ionics vol. 101-103, 1997, pp.681-686

[9] Wolf, R., Klinger, S.: Untersuchungen zur Feinstzerkleinerung, Klasierung und chemischen Reinigung von SiC-Pulvern für Konstruktionskeramikbauteile. Silikattechnik, vol. 41, 1990, No.5, pp. 166-168

[10] Števulová, N. and Tkáčová, K.: Einfluss der Entfernung des Eisens auf die Eigenschaften von mechanisch aktivierten Quarzpulvern. Keramische Zeitschrift, vol.45, 1993, pp.400-404