

Mechanical alloying of platinum with 5% ZrO₂ nanoparticles for glass making tools

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Abstract: Synthesis and characterization of mechanically alloyed Pt–5%ZrO₂ (volume fraction) for structural components in the glass industry were described. Zirconia (ZrO₂) nanoparticles (<100 nm) were produced by the electrical explosion of zirconium (Zr) wires, and blended with platinum (Pt) powders (<44 μm) for 2–72 h in ambient atmosphere. The Pt particle size followed the typical decreasing trend of the normal ball milling process up to 48 h, but particle agglomeration was observed at 72 h. The grain size evolution was similar to that of the particle size, dropping down to around 50 nm at 48 h. The root mean square strain of the Pt crystallites showed the opposite behavior, maximizing at 48 h with a subsequent relaxation process. For the 48 h ball milled powders, spark plasma sintering was carried out to form a bulk disk. The measured mass loss of the sintered bulk sample shows a decent thermal stability despite its relatively low density.

Key words: platinum; zirconia; nanoparticle; electrical wire explosion; mechanical alloying

1 Introduction

Platinum (Pt) and platinum group metals are highly valuable because only a few hundred tons are produced annually. In spite of their high price, platinum metals have been widely used in the glass industry because of their physical properties and excellent corrosion resistance against aggressive glass melts in the high temperature range [1]. Typical applications of platinum and its alloys are feeder systems, bubble tubes, drain bushings, tank linings, melting crucibles and glass fiber bushings. Depending on the specific application, these components usually operate at temperatures of about 1223 K in atmospheres composed of a mixture of ammonia and air, 1523 K in the liquid glass environments, and up to 1873 K in atmospheres of air or industrial gases [2].

However, the use of pure platinum in the glass industry is not suitable for glass making tools owing to its low strength and coarsening at high temperature. A significant increase in strength can be achieved by

alloying through a solid solution hardening mechanism. Rhodium (Rh) and iridium (Ir) have been considered promising elements in Pt–X solid solution hardened alloy because they are not detrimental to the chemical stability of the platinum. Nevertheless, the use of these elements is limited considering that the dissolution of the smallest traces of the alloying elements in the glass melts, resulting in an undesirable change in the optical properties of glass products [3]. Furthermore, at high temperature around 1873 K, Pt–Rh and Pt–Ir solid solution hardened alloys provide a limited increase in mechanical strength, and could not prevent extreme grain growth [4].

For this reason, oxide dispersion strengthened (ODS) Pt has been developed for both pure Pt and Pt alloys [5]. The provided finely dispersed oxide particles of zirconia (ZrO₂) or yttria (Y₂O₃) in the Pt matrix are very small (<1 μm) and their inter-particle spacing is also small (<10 μm), the particles will hinder the movement of dislocations in the matrix and thus give an increase in strength [6]. Furthermore, the dispersed particles hinder the movement of grain boundaries at high temperature

and therefore restrict grain coarsening, leading to an increase of stress–rupture strength. ODS Pt alloys can be manufactured by two different approaches. One is the typical powder metallurgy route [5], and the other is the internal oxidation path, commercially named as DPH (dispersion hardened) platinum materials [6]. Both methods have their own advantages and disadvantages in terms of material properties or processing conditions. And also, a precipitation hardened Pt-based alloy, analogous to the Ni-based super alloy, was introduced as an another alternative solution [7]. As known from the existing literature, many properties, such as stress–rupture strength, creep resistance, ductility, formability, weldability and corrosion/oxidation resistance, have been satisfied for industrial applications. However, strengthening of Pt alloys has remained as a primary condition for the structural component at high temperature, with an increasing demand for better mechanical stability.

One possible way to improve mechanical stability is decreasing the size of the reinforcing particles. Recently, we have produced metallic nanoparticles less than 100 nm by the electrical explosion of metal wire [8]. Electrical explosion is a physical method which is effective in producing high purity nanoparticles, compared to those prepared by chemical methods [9]. In this method, a high current pulse is passed through a thin metal wire, which leads to explosion, evaporation and ionization. The vaporized and ionized metal expands outward, and it is cooled by interacting with the surrounding gas or liquid media. Finally, the condensed vapor forms into nanoparticles.

Another way of strengthening Pt alloys is minimizing the crystallite size without the addition of solute atoms, which are potential contamination sources to the glass melts. Mechanical alloying (MA), which was originally developed to produce ODS super alloys for the aerospace industry, would also be an effective way to produce ODS Pt alloys. MA is a solid-state powder processing technique involving repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill [10]. Several reports on mechanical alloying of platinum powder with micro-scale zirconia and/or yttria powders have been made [5, 11–13]. However, the mechanical alloying behavior of ODS Pt alloy with nano-scale oxides has not been well addressed yet.

In this work, we have produced nano-scale zirconia powders using an electrical wire explosion technique, investigated the microstructural properties of the ball milled Pt–5%ZrO₂ (volume fraction) powders, and prototyped a bulk sample via spark-plasma sintering process.

2 Experimental

2.1 Raw materials

High purity (3N5) Pt powders with a particle size smaller than 44 μm were purchased from Colonial Metals, Inc (Elkton, Maryland, USA). ZrO₂ nanopowders were synthesized by the electrical explosion of Zr wires (2N2) with a diameter of 0.25 mm. The wires were exploded in an argon/oxygen atmosphere (70%Ar+30%O₂, volume fraction) with a 80 mm in feeding length, 24 kV in charging voltage, and 6 μF in capacitance. X-ray diffraction confirmed that the produced powders were Baddeleyite ZrO₂ phase. Figure 1 shows scanning electron micrographs of the Pt powders and the ZrO₂ nanoparticles. SEM images reveal that the size of produced ZrO₂ powders is less than 100 nm, while Pt powders are less than 50 μm .

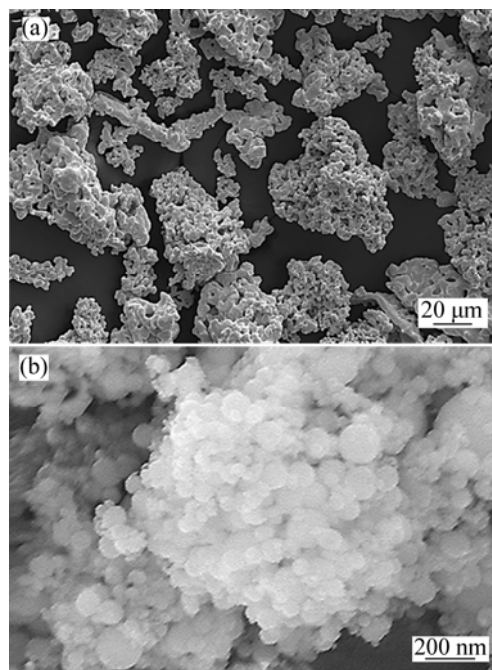


Fig. 1 SEM images: (a) Pt powders; (b) Produced ZrO₂ nanopowders.

2.2 Mechanical alloying

Pt powders (95%, volume fraction) were blended together with ZrO₂ (5% (volume fraction), or 1.37% (mass fraction)) nanoparticles, then ball milled at 100 r/min for 2, 8, 24, 48, and 72 h. ZrO₂ ceramic balls (1 mm in diameter) and a ZrO₂ container (500 mL) were used to suppress contamination during mechanical milling. The volume ratio of ball to powder was maintained at 100:1.

2.3 Synchrotron radiation experiment

Lab source X-ray can provide a general idea about the phase and lattice information. However, synchrotron

radiation experiments with high flux and high resolution were proposed in order to investigate the precise microstructural behavior according to the milling time. Experiments were performed at the National Synchrotron Light Source (NSLS), beam line X10A in Brookhaven National Laboratory, USA. For high resolution, a single-bounce Ge monochromator (analyzer) was placed in front of the scintillator detector to produce 0.003° full width half maximum (FWHM) in 2θ , indicating that measurable grain size from the Scherrer equation goes up to $2\text{ }\mu\text{m}$ under a given beam conditions (beam size: $1\text{ mm}\times 1\text{ mm}$, energy: 11.31 keV ; $\lambda=1.0964\text{ \AA}$).

2.4 Consolidation to bulk sample

The 48 h mechanically alloyed Pt–5%ZrO₂ (volume fraction) powders were finally spark plasma sintered at 1673 K for 30 min under a 45 MPa load. The density of sintered sample was determined by Archimedes' principle. Mass change in the sintered sample was measured from the initial and final masses after heat treatment at 1573 K for 96 h in ambient atmosphere.

3 Results and discussion

3.1 Microstructure from SEM

Figures 2(a)–(e) show the SEM micrographs of Pt–5%ZrO₂ (volume fraction) composite powders ball milled for different time. In the early stages of milling (2 h), the powder shape became flattened due to cold welding effects. With increasing milling time (up to 48 h), powders became more rounded in shape and finer in particle size. This result indicates that predominant processes at this stage are cold welding and fracturing. Indeed, the powder size is estimated to be less than $5\text{ }\mu\text{m}$ after a milling for 48 h. However, after a milling time of 72 h, there is a rise in the particle size due to agglomeration.

Based on the SEM images, it is speculated that onset of particle agglomeration is driven by the accumulated strain and thermal energy during the ball milling process. It has been generally known that particle size becomes stable through a dynamic balance between

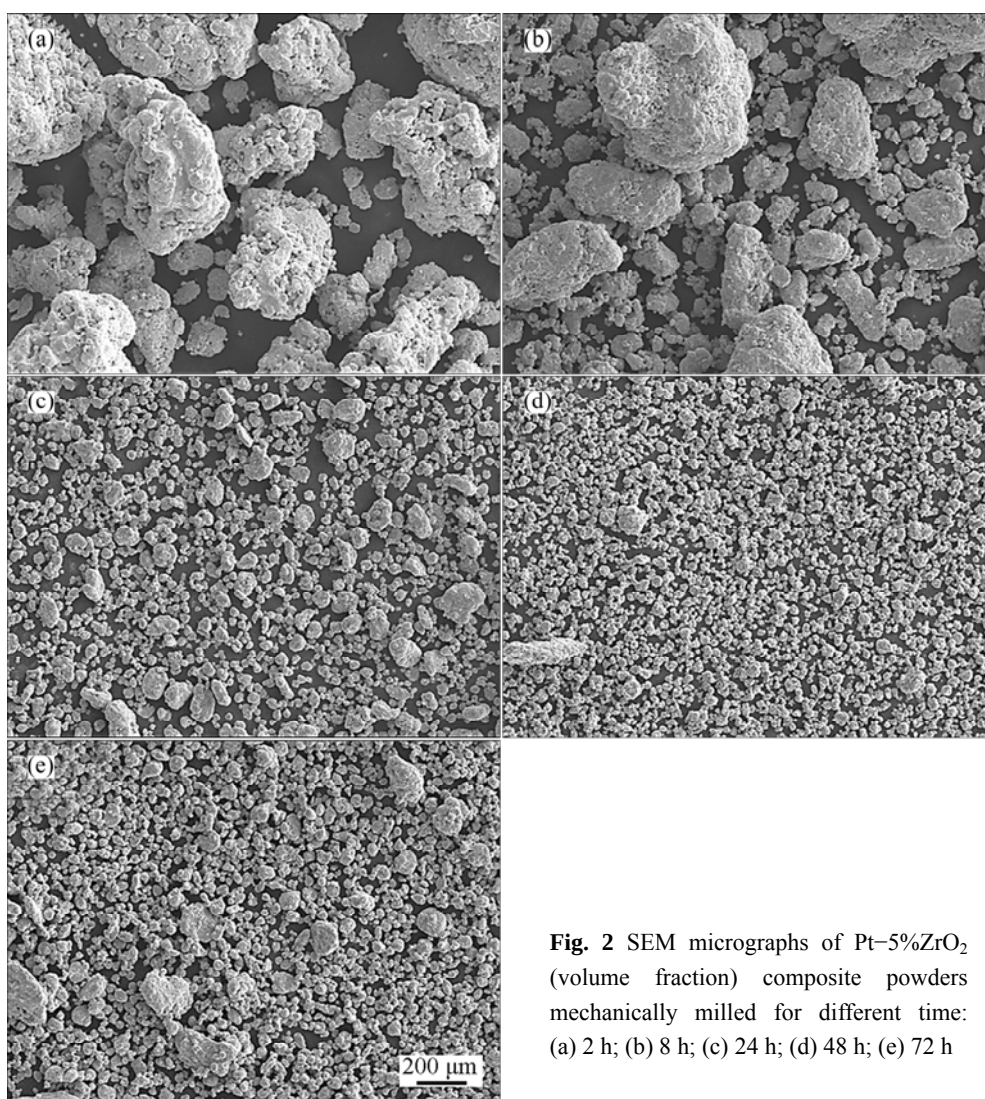


Fig. 2 SEM micrographs of Pt–5%ZrO₂ (volume fraction) composite powders mechanically milled for different time: (a) 2 h; (b) 8 h; (c) 24 h; (d) 48 h; (e) 72 h

welding and fracturing [10]. However, RAMAR et al [14] reported particle agglomeration at the later stage of ball milling. They observed constant hardness values and crystallite sizes by FWHM of diffraction peaks even at the point of particle growth. This means that particles are in touch with each other without microstructural change, but our SEM image, Fig. 2(e), seems to suggest internal change in microstructure.

3.2 Grain size and RMS strain from diffraction analysis

In order to quantify recrystallization and growth kinetics, time resolved ex-situ synchrotron diffraction measurements and peak shape analysis have been performed. The reference Pt and ZrO_2 powders are displayed in Figs. 3(a) and (b), respectively. Pt was

identified as a pure FCC (JCPDS 4-802) phase, but ZrO_2 turned out to be a mixture of major monoclinic (JCPDS 37-1484) and minor tetragonal (JCPDS 79-1763) phases. Figures (c)–(e) illustrate the phase evolution of ZrO_2 according to the milling time. Monitoring ZrO_2 peaks is important because the oxides dispersion strengthening would require ZrO_2 to be intact for the subsequent consolidation process. Otherwise, it is likely to cause solid solution hardening via decomposition of ZrO_2 into zirconium and oxygen within Pt matrix.

The synchrotron data show that ZrO_2 peaks lose their intensity with peak broadening up to 8 h, as shown in Fig. 3(e), but it was difficult to observe after 24 h milling. Peak broadening is due to the grain size minimization or local strain among crystallites, while the intensity drop corresponds to phase extinction or

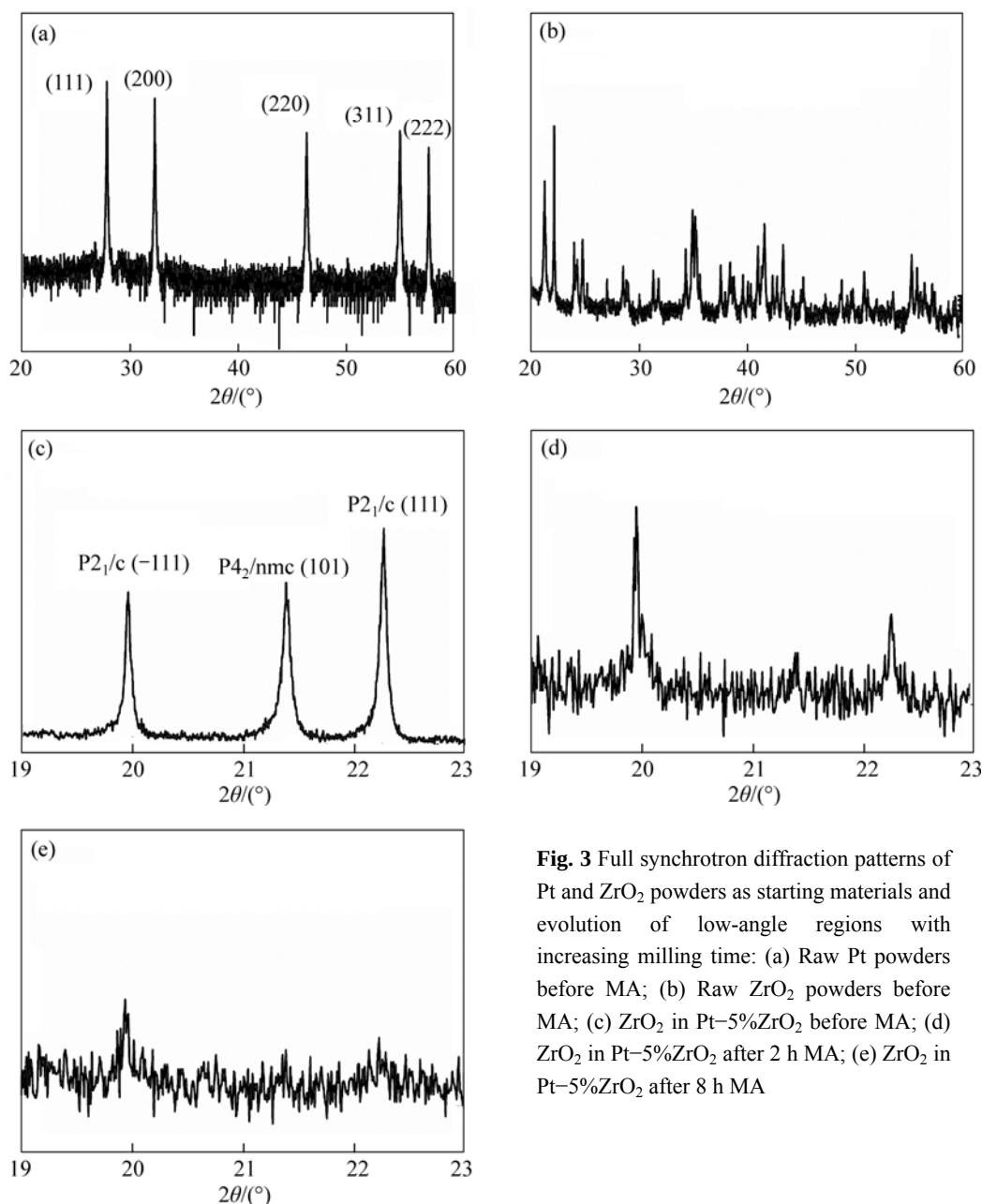


Fig. 3 Full synchrotron diffraction patterns of Pt and ZrO_2 powders as starting materials and evolution of low-angle regions with increasing milling time: (a) Raw Pt powders before MA; (b) Raw ZrO_2 powders before MA; (c) ZrO_2 in Pt-5% ZrO_2 before MA; (d) ZrO_2 in Pt-5% ZrO_2 after 2 h MA; (e) ZrO_2 in Pt-5% ZrO_2 after 8 h MA

amorphization of the crystals. OKUDA and FUJIWARA [15] reported that carbide, nitride or intermetallic compounds can dissolve in metal during mechanical alloying by force, and oxides such as Y_2O_3 , which do not have any solubility limit, can dissolve in metal during a mechanical alloying process [15]. ALINGER et al [16] also showed from small angle scattering data that Y_2O_3 dissolved into ferric alloys during MA process. However, RAMAR et al [14] commented that oxides can still be maintained as particles, and the disappearance of the ZrO_2 peaks can be due to the very small ZrO_2 particles size, which is reduced by the milling. Authors share the same idea as RAMAR because it is possible to lose coherent scattering power of the crystallites, considering the nano-scale small volume fraction of ZrO_2 . Secondary ion mass spectroscopy (SIMS) would reveal more details, but at this point, there is no direct evidence indicating that zirconium and oxygen are decomposed into Pt matrix (solid solution hardening), or maintained as amorphous or very fine nano-clusters outside Pt particles (oxide dispersion strengthening).

Whether or not ZrO_2 powders are dissolved in Pt matrix, Pt powders experience peak broadening with decreasing intensity at all five reflections. Figure 4(a) shows time-resolved Pt (111) diffraction profiles;

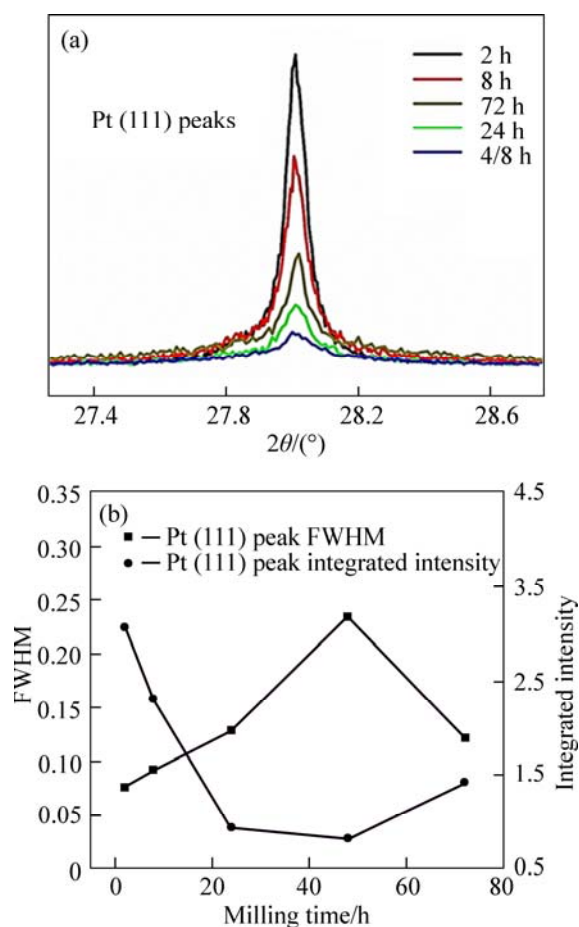


Fig. 4 Time-resolved Pt (111) diffraction profile (a) and FWHM and integrated intensity vs ball milling time (b)

FWHM and integrated intensity (fitted to Lorentzian profiles) for each milling step are plotted in Fig. 4(b). It is clearly seen that (111) peak loses its intensity up to 48 h, but increases again at 72 h. FWHM shows the opposite behavior, indicating strain relaxation via recrystallization and/or grain growth.

Both instrument and sample contribute to the FWHM of the diffracted intensity. Since the incident beam is very sharp (0.003° in 2θ), it was assumed that diffracted peak profiles are mostly from samples. However, it is still necessary to separate size and strain broadening in the sample; hence, Williamson–Hall (W–H) method [17,18] (Eq. (1)) was employed based on the fact that grain size is not dependent on hkl , but strain is. Equation (1) contains size (Scherrer equation) and strain components as follows.

$$\beta = \frac{C\lambda}{t \cos \theta} + 4\varepsilon \tan \theta \quad (1)$$

where t is the averaged dimension of crystallites; C is Scherrer constant (here $C \approx 1$); λ is the wavelength of X-ray; β is the FWHM of the peak.

If one plots $\beta \cos \theta$ against $\sin \theta$ as shown in Fig. 5(a), the y-intercept will be λ/t , and the strain broadening can be calculated from the slope. By applying W–H plots in all cases, grain size and root mean square (RMS) strain

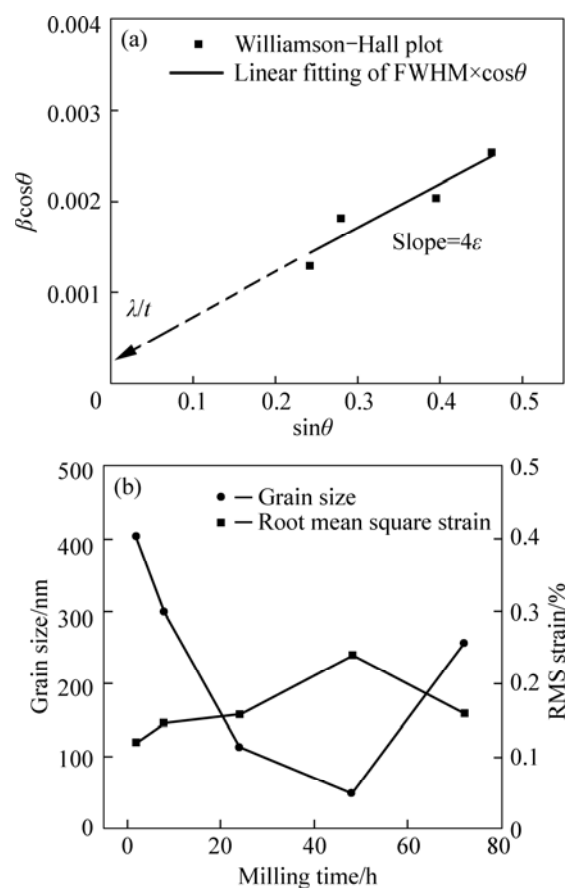


Fig. 5 Williamson–Hall plot (a) and calculated grain size and RMS strain information (b)

values are extracted and plotted in Fig. 5(b). The results show that grain size starts decreasing from 400 nm at 2 h ball milling conditions, down to 50 nm at 48 h. Then, it increases again back to 250 nm. RMS strain values also increase up to 0.25% with relaxation at 72 h. Therefore, it can be concluded that the ball milling process causes both particle and grain size to decrease while increasing RMS strain within particles. At 72 h, the relaxation phenomenon was more obvious in grain size and strain profile (obtained from synchrotron data) than particle size/shape information (from SEM micrographs). This suggests that agglomeration of the particles is the secondary process after recrystallization & grain growth unlike the observation from Ref. [14], or at least a concurrent event with microstructural relaxation. It should be noted that W–H method reliably predicts size and strain evolution within an order of magnitude, but the absolute value should not be taken seriously due to the several assumptions made in W–H analysis.

3.3 Mass loss measurement from bulk sample

For the 48 h ball milled Pt–5%ZrO₂ (volume fraction) powders, a spark plasma sintering was carried out at 1673 K for 30 min under a load of 45 MPa. No visible defects such as crack or macro-pore are seen in the 50 mm diameter, 1 mm thick disk. The density of sintered sample was estimated to be 89.5 % of the nominal value of Pt–5%ZrO₂ (volume fraction). Mass loss of platinum-group metals at high temperature is an important estimate for the life of the Pt products and it has been known to occur by the formation of volatile oxides [19]. Table 1 shows the mass loss after heat treatment at 1573 K for 96 h. For comparison, Pt and Pt–20%Rh (mass fraction) alloy were prepared by the casting process and compared with sintered Pt–5%ZrO₂ (volume fraction). Note that the sintered Pt–5%ZrO₂ (volume fraction) is not fully dense, while the cast Pt and Pt–20%Rh (mass fraction) alloy are fully compact.

Table 1 Comparative result of mass loss for sintered sample after heat treatment at 1573 K

Material	Temperature/ K	Time/ h	Linear rate of mass loss (mg·mm ⁻² ·h ⁻¹)
Platinum (fully dense)	1573	96	2.98×10^{-4}
Pt–20%Rh (fully dense)			1.73×10^{-4}
Pt–5%ZrO ₂ (volume fraction; density 89.5%)			2.84×10^{-4}

Our measurements show that mass loss of the Pt–20%Rh (mass fraction) alloy is smaller than any other samples, and the sintered Pt–5%ZrO₂ (volume fraction) shows a bit less mass loss than pure Pt. It has been

known that a linear rate of mass loss of rhodium is lower than that of platinum [20], which is consistent with our measurement. For the sintered Pt–5%ZrO₂ (volume fraction) to be a promising alternative to pure Pt, its mass loss value should be comparable to that of Pt–20%Rh (mass fraction), but it is only slightly better than Pt. Considering the fact that the sintered powder is not fully dense compared to others, this result is not so disappointing. Since loose grain boundary or free volume can act as an efficient diffusion path for oxygen, it is expected to have more mass loss with less dense materials. As the density can be controlled to some extent by rolling conditions, mass loss can be improved, but it may affect other mechanical or chemical properties. Therefore, more comprehensive study in terms of processing conditions and materials selection (for example, amount of ZrO₂ nanoparticles) must be performed, and a variety of measurements, such as tensile strength, rupture strength, creep rate, corrosion resistance, need to be understood for the actual applications.

4 Conclusions

In an attempt to develop a strengthened Pt-based alloy (or composites) system for the glass industry, 95% Pt (volume fraction; less than 44 μm) and 5% ZrO₂ (volume fraction; less than 100 nm) powders are ball milled for 2, 8, 24, 48, and 72 h. ZrO₂ powders are synthesized from the electrical explosion of zirconium wire to ensure high quality nanoparticles. SEM images illustrate that the average size of Pt particles decreases during the first 48 h of ball milling, but between 48 and 72 h the particle size grows again due to agglomeration. Williamson–Hall analysis of the synchrotron diffraction data shows the same trend in grain size evolution, and the opposite behavior for the root mean square strain of the Pt crystallites, suggesting that optimum ball milling time would be between 48 and 72 h to obtain powder of the minimum grain size and with a maximum internal strain.

Having determined that a 48 h milling time was optimal, spark plasma sintering was employed to form a 50 mm diameter disk from the mechanically alloyed Pt–5%ZrO₂ (volume fraction) powders. Mass loss measurement seems to indicate decent thermal stability from the bulk sample although it is not completely dense. Since numerous materials properties and processing conditions have to be satisfied for the actual glass making tool in industry, more systematic mechanical alloying designs, such as materials selection and processing optimization, should be investigated. Such experiments are in progress.

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玻璃制作工具用 5% ZrO₂ 纳米铂材的机械合金化制备

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摘要: 对机械合金化制备的玻璃工业中用作结构零件的 Pt–5%ZrO₂(体积分数)的进行表征。通过铂丝电爆炸法制备氧化锆(ZrO₂)纳米颗粒(粒径<100 nm), 并在室温下与铂粉(粒径< 44 μm)球磨 2~72 h。普通球磨至 48 h 时, 铂粒径遵循经典的递减趋势, 至 72 h 时观测到颗粒团聚现象。晶粒尺寸演变规律与颗粒尺寸规律相似, 48 h 后减至 50 nm 左右。但是, 铂晶粒的均方根应变规律相反, 一直在增长, 直至 48 h 时得到最大值, 然后出现弛豫。粉末球磨 48 h 后, 采用放电等离子体烧结制成块体。根据测量得到烧结体的质量损失表明: 合金虽然相对密度较低, 但有较好的热稳定性。

关键词: 铂; 氧化锆; 纳米粒子; 电爆炸法; 机械合金化

(Edited by Lü-xiang DENG)