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Quantitative X-ray Rietveld analysis of metallic aluminum content in nano-aluminum powders

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ABSTRACT

Accurate analysis of the content of metal aluminum (Al) in nano-Al powders is a difficult task due to the high reactivity of nano-Al powders. Here, the X-ray Rietveld quantitative phase analysis (QPA) method was applied to analyze the content of metal aluminum in nano-Al powders produced by three methods. A good agreement between the observed and calculated diffraction pattern was obtained and the conventional Rietveld factors (R_p, R_{wp} and GOF) converged to satisfactory values, which suggested that Al content was evaluated accurately. At the same time, the mixture sample of 89.77 wt.% micro-Al + 10.23 wt.% α-Al_2O_3 was study and the fitting pattern and R factors were satisfactory, which further verified the reliability of the X-ray Rietveld QPA method.

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1. Introduction

Nano-Al powders have been of much interest in recent years as metallic fuel for various applications due to their high chemical activity that cannot be obtained in the conventional micro-Al powders [1,2]. However, during the period after production and before application, the powders often are oxidized and the aluminum oxide layer forms when coming into contact with oxidizing media in air such as oxygen and steam [3–5]. Then a problem that arises in the use of nano-Al powders is to determine the content of metal Al. Despite some analysis methods have been devoted to this problem, for example chemical methods (the gas volumetric method, the permanganatometric method and the cerimetric method) [6–8] and thermogravimetry (TG) [3, 8], the accurate metal aluminum content still cannot be obtained because of the sensitivity of nano-Al powders to ambient conditions and the limits of chemical methods and TG. Therefore, it is necessary to develop a method to determine the content of metal Al accurately.

The Rietveld method using a whole pattern-fitting algorithm, which was originally developed for crystal structure refinement using neutron diffraction data [9], and after some time it was applied to quantitative X-ray powder phase analysis [10], has been successfully applied to the QPA of nano-materials containing several crystallographic phases nowadays [11–13]. In QPA using the Rietveld method, weight fractions of all phases in a multiphase sample can be calculated directly by their scale factors, which can be obtained by Rietveld fitting. The relationship between the weight fraction (W_i) for each phase i and its scale factor (S_i) determined is obtained from the following relation [14]:

$$W_i = \frac{S_i(ZMV)_i}{\sum_{i=1}^{n} S_i(ZMV)_i} \quad (1)$$

where Z, M, V are the numbers of formula units per unit cell, unit molecular weight of the formula and unit cell volume of phase i in a mixture of n phases, respectively.

Since the Rietveld method would presumably give an accurate and available QPA result. The purpose of this paper is to use the quantitative X-ray Rietveld method to estimate the content of the metallic Al in nano-Al powders and lay the foundation for the Rietveld users of other high chemical activity materials.

2. Experimental methods

Three kinds of commercially available nano-Al powders were used: Al-P, which was synthesized by plasma synthesized method, was supplied by Shanghai st-nano science and technology Co., Ltd, China. Al-E, synthesized by wire electrical explosion, was supplied by Jiaozuo Banlv Nanomaterial Engineering Co. Ltd., China. Al-L, produced by laser-induction complex heating method, was purchased from Shenzhen Junye Nano Material Co., Ltd, China. The mixture sample (89.77 wt.% micro-Al + 10.23 wt.% α-Al_2O_3) was homogenized by hand-grinding in an agate mortar and ready for XRD analysis.

The X-ray diffraction (XRD) data of all powder samples were obtained by Bragg - Brentano geometry X'Pert Diffractometer with

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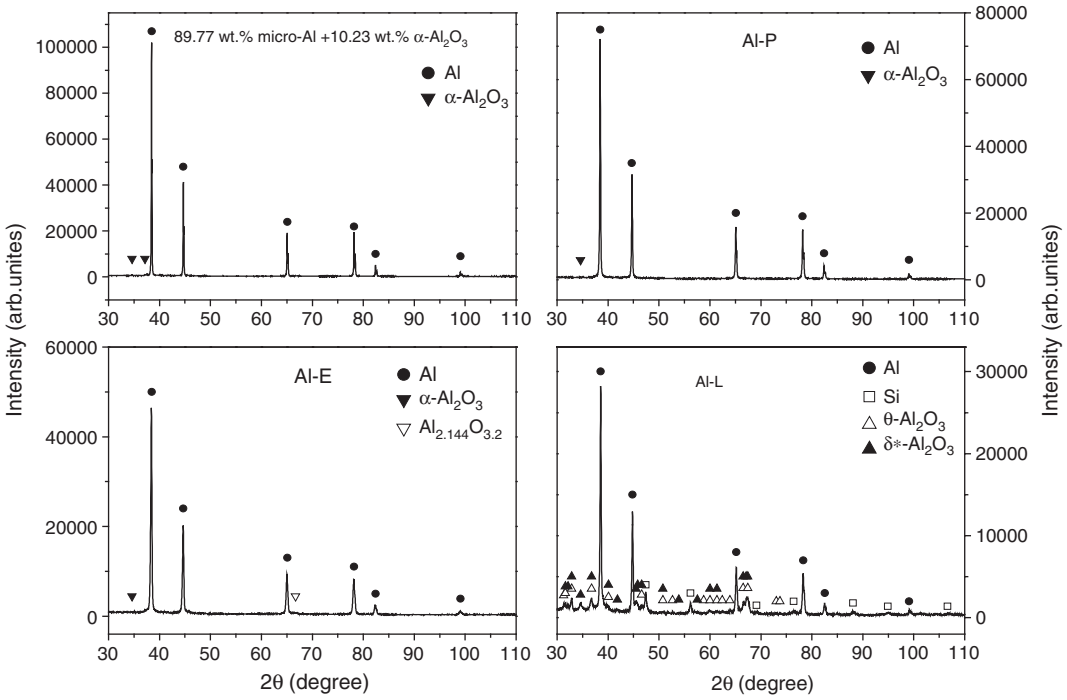

Fig. 1. X-ray diffraction patterns of Al-P, Al-E, Al-L and the mixture sample.

Cu *Kα* radiation at 40 kV and 40 mA. Data collections were carried out over the 30–110° 2θ range, with the counting time of 40 s and the step width of 0.02°. The QPA by the X-ray Rietveld method was carried out by the FULLPROF 2000 program [15] and the Pseudo-Voigt peak shape function. The reliability of the refinement result was judge by the pattern R factor (R_p), the weighted pattern R factor (R_{wp}), and the 'goodness of fit' ($GOF = R_{wp}/R_{exp}$) [16].

3. Results and discussion

Fig. 1 shows the XRD patterns of Al-P, Al-E and Al-L. As the main phase, Al phase is observed in all diffractograms. In the Al-P diffractogram the presence of the α-Al_2O_3 could be established from the extremely weak peak at $2\theta = 34.60°$. In the diffraction pattern of the Al-E, the weak peaks of α-Al_2O_3 ($2\theta = 34.55°$) and $Al_{2.144}O_{3.2}$ ($2\theta = 66.74°$)

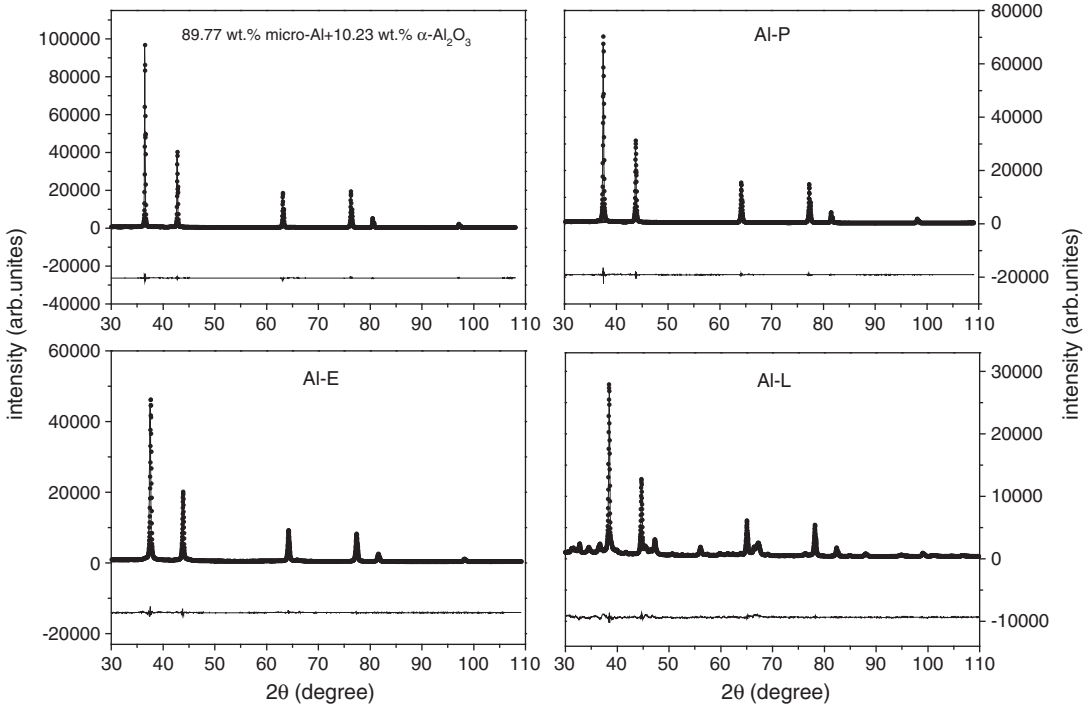

Fig. 2. Observed profile (Points), calculated profile (the solid line) and the profile difference at the bottom for the Rietveld patterns of Al-P, Al-E, Al-L and the mixture sample.

Table 1
Results of quantitative phase analyses and Rietveld factors.

Sample	Phase	Weight content (wt.%)	Agreement factors		
			R_p	R_{wp}	GOF
Al-P	Al	95.79	8.7%	9.44%	1.96
	α-Al_2O_3	4.21			
Al-E	Al	91.88	9.81%	9.50%	1.82
	$Al_{2.144}O_{3.2}$	5.16			
	α-Al_2O_3	2.96			
Al-L	Al	43.31	12.5%	14.8%	2.70
	θ-Al_2O_3	13.99			
	δ^*-Al_2O_3	36.48			
	Si	6.22			
89.77 wt.% micro-Al + 10.23 wt.% α-Al_2O_3	Al	92.03	9.5%	10.7%	2.26
	α-Al_2O_3	7.97			

could also be observed. In the Al-L diffractogram, there exists the peaks of Si and overlapped small peaks from the θ-Al_2O_3 and the δ^*-Al_2O_3. Compared with Al-P and Al-E, the oxidation of Al-L is severer. The reasons may be that oxidation and hydration phenomena were happened during material storage [4], making the Al-L further oxidized.

Initial structure parameters of all phases used for Rietveld method in this study were from the ICSD (Inorganic Crystal Structure Database) cards and the literature [17]. The parameters that had been refined simultaneously include: scale factors, zero point shift, background coefficients, lattice parameters, atomic coordinates, atomic site occupancies, isotropic or anisotropic temperature factors, profile shape parameter and FWHM (Full Width at Half Maximum) parameters, asymmetry and preferred orientation parameters. The corrected preferred orientation planes for the Al-P, Al-E and Al-L samples were (111), (111) and (220) respectively. The total parameters to be refined of Al-P, Al-E and Al-L were 26, 30 and 52 respectively.

Fig. 2 shows the observed, calculated diffraction patterns and difference curves of the Al-P, Al-E and Al-L samples. The R factors and the phase weight percent obtained from the Rietveld method are summarized in Table 1. From these figures and R factors, we can see that the difference curves are flat and the values of R factors are typical and satisfactory, which means successful agreement is obtained between the observed and calculated diffraction pattern. Liang Chen et al. [8] in our research group used Rietveld method to estimate the Al content of the nano-Al powders produced by electro-exploded wire, and the result was more accurate than the gas volumetric method, TG and the permanganatometric method which were underestimated owing to the reaction uncompleted and the interact between Al and hydrogen ions in the solution, in addition, his Rietveld result was similar with the result of Al-E in this paper. In order to further verify the reliability of the quantitative X-ray Rietveld method, we study the mixture sample of 89.77 wt.% micro-Al + 10.23 wt.% α-Al_2O_3, whose XRD pattern, fitting pattern and R factors are shown in Fig. 1, Fig. 2 and Table 1. The refinement result is 92.03 wt.% micro-Al + 7.97 wt.% α-Al_2O_3 and the differences between the calculated value and the real value is 2.26 wt.%.

4. Conclusions

The X-ray Rietveld QPA method is applied to the study of the metal Al in Al-P, Al-E and Al-L, and the mixture sample (89.77 wt.% micro-Al + 10.23 wt.% α-Al_2O_3) of known weight fraction is tested by this method. The Rietveld method which does not change the state of samples like chemical methods and TG avoids the side-reactions with ambient conditions. Besides, this method considers overlapped peaks and the effect of preferred orientation. Therefore, the Rietveld method could be a powerful technique to the QPA of the metal Al content in nano-Al powders. And there is good reason to believe that it also can be used to the QPA of other materials of high chemical activity.

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