

Functionalization of the Fine Al₂O₃ Abrasive by the Polyacrylamide Deposition

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In order to enhance the dispersion stability of ultra-fine Al₂O₃ powder in aqueous media, the alumina particles were modified with silane coupling agent KH570 at first, and then 2,2'-Azobis(2-amidinopropane) dihydrochloride (AIBA) was anchored onto the modified Al₂O₃ to initiate the graft polymerization of acrylamide monomer (AM), and PAM/Al₂O₃ composite particles were obtained finally. The structure and dispersion property of Al₂O₃ composite particles were characterized by XPS, FTIR, laser particle size analyzer, micro electrophoresis apparatus, SEM and spectrophotometer. The results indicated that the attained composite abrasive when water-soluble azo initiator was added at 40 °C showed good dispersion stability in aqueous media with PAM as shell and Al₂O₃ as core. Compared with unmodified Al₂O₃, the reunion phenomenon of grafting polymerization modified Al₂O₃ powder was improved by AM, the D50 of the modified particles reduced. The isoelectric point (IEP) of the grafting modified particles migrated, and the zeta potential of the modified particles reached to the maximum value when the pH was 9. After PAM/Al₂O₃ abrasive polished, the surface roughness of NiP/Al hard disk surface was obviously reduced.

Keywords: Al₂O₃ ultrafine powder, azo initiator, dispersion, surface modification, composite abrasive.

1. INTRODUCTION

With the rapid development of social progress and sophisticated technology, the surface quality requirements of electronic products continue to increase, and surface flattening technology is also constantly developing. Chemical mechanical polishing (CMP) is widely applied in high-precision planarization of surface parts of advanced electronic products such as integrated circuits and computer hard disks [1–2]. One of the keys to CMP technology is the preparation of abrasives and the dispersion stability of polishing fluids, which directly affect the polishing rate, selectivity and damage to the surface of the substrate [3–4].

As an abrasive used widely, Al₂O₃ has the disadvantages of poor dispersion stability and easy agglomeration in the process of formulating slurry. The surface of Al₂O₃ was modified by chemical method, in general [5]. The modification methods include surface chemical coating modification method, physical modification method, mechanical modification method, etc. [6]. At present, the surface chemical coating modification method is used [7]. Since the organic matter is difficult to coat directly on the surface of the Al₂O₃ powder, even if it is coated, most of it is physically adsorbed, and the bonding is unstable. However, the hydroxyl group on the surface of Al₂O₃ powder is easy to react with the alkoxy group, and the silane coupling agent (CH₂=C(CH₃)COOC₃H₆Si(OCH₃)₃, abbreviated as KH570) is selected as the intermediate transition layer [8], which can set up a “molecular bridge” between the interfaces of the inorganic materials and organic materials, connecting two materials with different properties together.

Therefore, the outer layer selects acrylamide (CH₂=CHCONH₂, AM) to form water-soluble molecular polyacrylamide ([–CH₂–CH(CONH₂)_n–], referred to as PAM) through the polymerization reaction, which can improve the hydrophilicity of Al₂O₃ particles [9].

The surface of the Al₂O₃ particles is anchored with an azo initiator to reduce the polymerization temperature and increase the conversion rate of the polymerization reaction [10]. In recent years, water-soluble azo-initiated systems have been greatly developed and highly applied [11], since peroxides such as potassium persulfate and ammonium persulfate must initiate polymerization at higher temperatures [12]. However, AIBA is a water-soluble azo initiator with lower activation energy, which can initiate polymerization at a low temperature and low concentration. And its polymerization has the advantage of reaction fast, high degree of completion and constant pH. In addition, AIBA can produce polymers with ultra-high molecular mass and high water solubility [13], which can effectively increase the decomposition rate of free radicals on the surface of Al₂O₃ particles and produce more surface-active sites [14].

In this paper, the polyacrylamide PAM/Al₂O₃ composite particles were synthesised by anchoring the azo initiator on the surface of Al₂O₃ particles to initiate the polymerization of acrylamide. The dispersion stability of Al₂O₃ particles in aqueous medium was improved, and the dispersion of particles and dispersion stability in aqueous medium was analysed.

2. EXPERIMENTAL

Al₂O₃ ultrafine powder: D50 = 1.930 μm, Al₂O₃ content is 99.99 % (mass fraction, the same below), Zhejiang Superfine Chemical Co., Ltd.; silane coupling agent (KH570, analytical grade, Nanjing Xinhuai

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Technology Co., Ltd.); acrylamide (analytically pure, 99.0 %, produced by Chengdu Kelong Chemical Reagent Factory); Azobisisobutylphosphonium hydrochloride (analytical grade, 98.0 %, produced by Nanjing Dulai Biotechnology Co., Ltd.); Anhydrous ethanol (analytically pure, 99.7 %, Chengdu Changzheng Chemical Reagent Factory); Nitrogen (99.99%, produced by Chengdu Xuri Chemical Co., Ltd.).

10 g of Al_2O_3 was dispersed in 200 ml of absolute ethanol, and ultrasonicated in an ultrasonic machine for 30 min; 5.0 g of a silane coupling agent was added to a 500 ml three-necked flask and uniformly mixed with an anhydrous ethanol solution of Al_2O_3 . The mixture, firstly, was heated to 80 °C in a magnetic stirring water bath, then refluxed for 5 h and centrifuged to remove ethanol from the Al_2O_3 powder. The mixture, finally, was washed 6 times with absolute ethanol and dried under vacuum at 80 °C for 12 h. 5 g of Al_2O_3 modified with KH570 was dispersed in 100 ml of distilled water, stir for 30 min, vacuum and fill with nitrogen for 5 times, 0.025 g of azo initiator was added in a three-necked flask, heated up to 40 °C, and reacted for 25 min. The three-necked flask was opened and 5 g of acrylamide monomer was added in one time. After magnetic stirring for 4 h, it was naturally cooled to room temperature under a nitrogen atmosphere.

In polishing the experiment, a self-made polishing solution was used, and the computer NiP/Al hard disk substrate was polished with a M480 flat polishing machine. The polished workpiece was a $\Phi 95$ mm NiP/Al hard disk substrate. The polished disc substrate was washed in a cleaning solution containing a surfactant, and measured after drying. Surface roughness (R_a) and morphology were characterized with a SPA400 atomic force microscope (AFM) from Seiko Corporation.

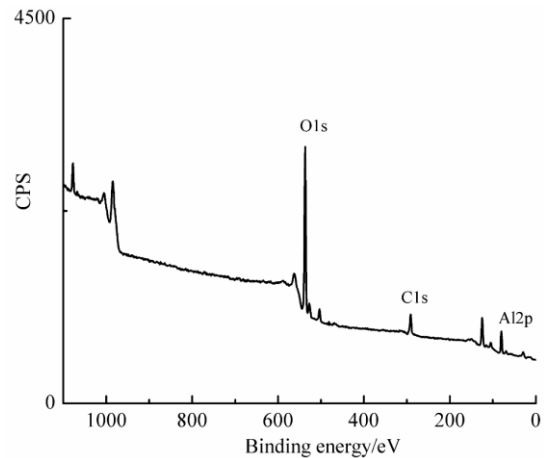
The phase composition and morphology of samples was analyzed by scanning electron microscopy (SEM, HITACHI TM-1000). The content and binding energy were investigated by X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi). The zeta potentials of the samples with variation of pH were measured by zetasizer nano (Malvern Instrument). The chemical structure of the samples was characterized by a Fourier infrared spectrometer (FT-IR, Nicolet 6700). The particle size distribution of samples in ultrapure water was analyzed by a laser particle size meter (Rise-2008, China). The light transmittance of suspension was investigated by spectrophotometer (752N, China).

3. RESULTS AND DISCUSSION

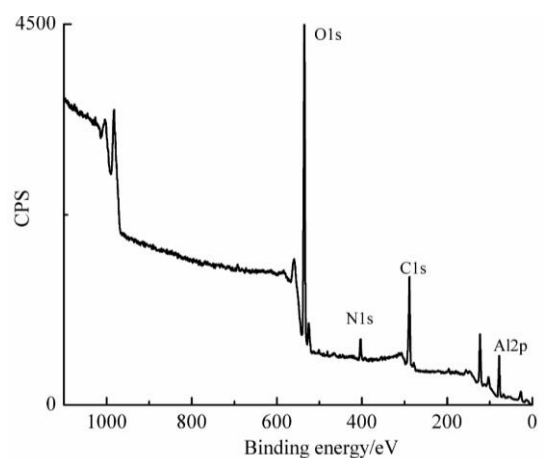
3.1. XPS analysis

Fig. 1 shows the XPS spectra of pure Al_2O_3 and modified Al_2O_3 powders, respectively. It can be seen from the comparison of Fig. 1 a and Fig. 1 b that the intensity of Cls is obviously enhanced. Since XPS measurement range is surface atomic layer with thickness ≤ 10 nm, this is mainly the contribution of acrylamide to carbon. Moreover, the XPS spectrum before and after the modification can also be found that the peak of N appears on the surface after modification, and the binding energy of N1s is 404.1 eV, which corresponds to N in acrylamide.

This indicates that acrylamide has been successfully grafted onto the surface of Al_2O_3 .



a



b

Fig. 1. XPS survey spectra of Al_2O_3 powders: a–before modification; b–after modification

3.2. FT-IR analysis

It can be seen from Fig. 2 and Fig. 3 that before and after the modification, there is a $-\text{OH}$ stretching vibration peak near 3437.21 cm^{-1} ; $\text{Al}-\text{O}$ is between 1000 cm^{-1} and 500 cm^{-1} .

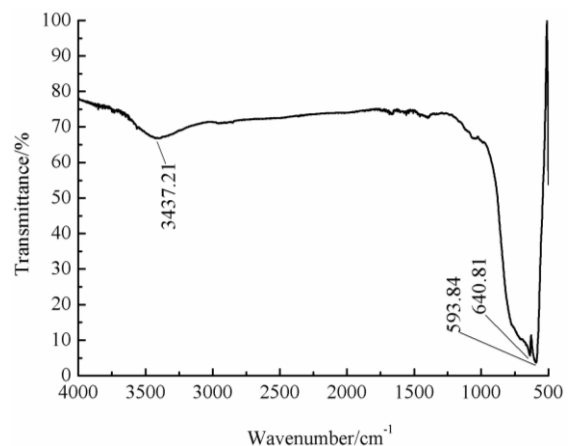


Fig. 2. FT-IR spectra of raw Al_2O_3 powders.

The KH570 ester-modified Al_2O_3 showed a C=O absorption peak in the KH570 ester group at 1643.85 cm^{-1} , and a methyl stretching vibration peak appeared at 2921.63 cm^{-1} and 2857.99 cm^{-1} . At the same time, a new absorption peak appeared at 1400.09 cm^{-1} . Fig. 3 a shows that the newly emerging absorption peak in the infrared spectrum is formed by the characteristic peak of the functional group corresponding to KH570, indicating that KH570 has been coupled to the surface of Al_2O_3 by chemical bonding.

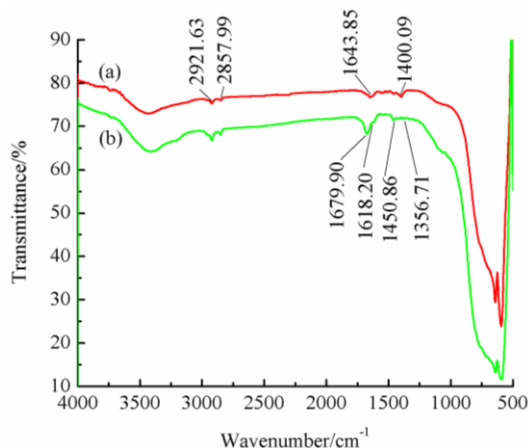


Fig. 3. a–FT-IR spectra of Al_2O_3 powders modified with KH570; b–FT-IR spectra of Al_2O_3 powders with grafting AM

According to the literature [15], in the characteristic absorption band of amide, the NH_2 absorption band is located near 1620 cm^{-1} , and the NH_2 absorption band appears at 1618.20 cm^{-1} of Fig. 3 b. And the hydroxyl absorption peak of the amide appeared at 1679.90 cm^{-1} , the C=C stretching vibration peak in the acrylamide monomer was around 1640 cm^{-1} , and there was no such peak in the polyacrylamide, only the carbonyl group of about 1680 cm^{-1} . The absorption peak indicates that the acrylamide monomer forms a polyacrylamide by reaction. At the same time, there are several new absorption peaks between 1500 cm^{-1} and 1000 cm^{-1} , and the C–N or C–C bond stretching vibration peaks connected to C=O appear at 1450.86 cm^{-1} and 1356.71 cm^{-1} , respectively. The analysis indicated that the acrylamide monomer-initiated polymerization on the surface of the inorganic particles by the "molecular bridge" action of KH570, which had been graft polymerized onto the surface of the modified Al_2O_3 .

3.3. SEM analysis

The dispersion of pure Al_2O_3 and modified Al_2O_3 powder in water was observed by US FEI environmental scanning electron microscope, as shown in Fig. 4. It can be seen that the dispersibility of the modified Al_2O_3 is greatly improved compared with the pure Al_2O_3 . The pure Al_2O_3 particles adsorbed to each other, and the agglomeration was serious. The large particles and fine particles formed a large agglomerate; while the modified Al_2O_3 fine particles increased significantly, and the surface agglomeration of the particles was significantly decreased. This is due to the grafting of KH570-modified polyacrylamide on the surface of Al_2O_3 . On the one hand, the surface energy of Al_2O_3 particles is reduced after grafting the acrylamide monomer,

and the polyacrylamide chain grafted on the surface of Al_2O_3 is in the water.

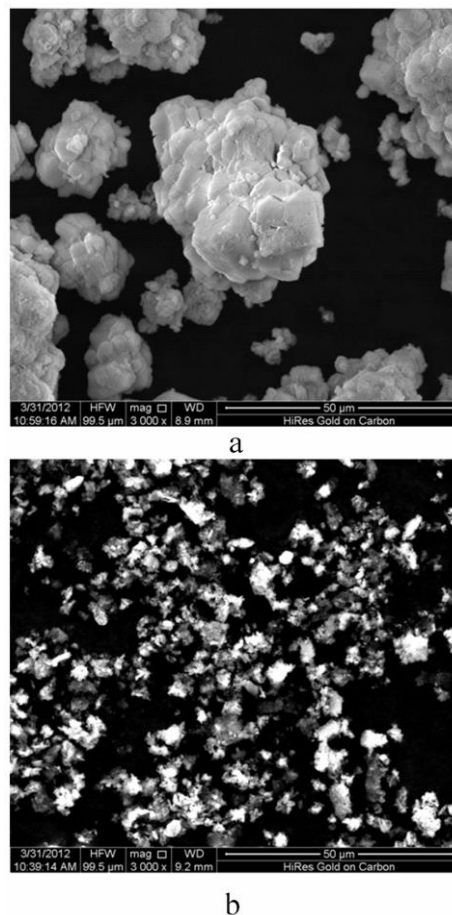


Fig. 4. SEM images of Al_2O_3 powders: a–before modification; b–after modification

Stretching out, a certain thickness of the steric layer can be formed on the surface of Al_2O_3 to achieve the effect of the steric barrier (position resistance), and the surface agglomeration of the Al_2O_3 particles is prevented by the resistance of the position repulsive force.

3.4. Particle size analysis

The pure Al_2O_3 powder and the modified Al_2O_3 powder were prepared into a dilute solution, respectively, and after ultrasonic dispersion, the particle size and distribution of the Al_2O_3 powder before and after the modification were measured by a laser particle size analyzer. The results are shown in Fig. 5. It can be seen from Fig. 5 and Table. 1 that after the surface modification of the pure Al_2O_3 powder, the median particle size D50 is significantly reduced, which is due to the improvement of the surface agglomeration phenomenon of the powder and the improvement of the dispersibility in the aqueous medium.

3.5. Zeta potential analysis

The type of charge carried on the surface of the particle and the charge density on the surface of the particle can be reflected from the zeta potential value, which can usually be used to judge the dispersion stability of the ultrafine powder in an aqueous medium. The zeta

potential curves of pure Al₂O₃ and graft modified Al₂O₃ are shown in Fig. 6.

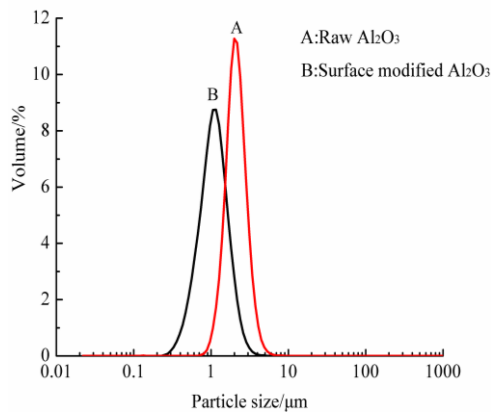


Fig. 5. Particle size distribution of Al₂O₃ powders before and after modification

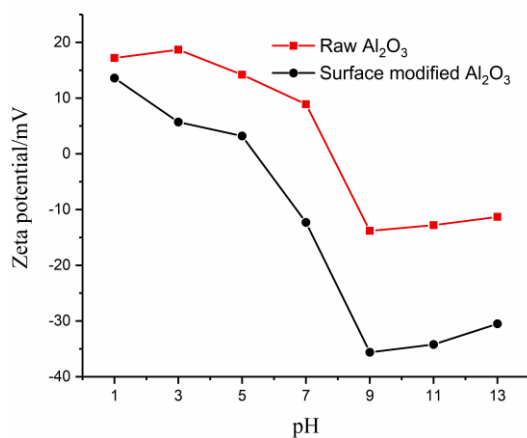


Fig. 6. Zeta potential curves of Al₂O₃ powders before and after modification

It can be seen that the electrical properties of the coated Al₂O₃ particles after grafting with polyacrylamide have changed. The isoelectric point (IEP) of pure Al₂O₃ is near pH = 8.0, and the absolute value of the maximum potential is about 18.7 mV (pH = 3). The IEP of modified Al₂O₃ moves from alkaline to acidic, and the IEP is located near pH = 5.7, and the absolute value of the maximum potential is 35.6 mV (pH = 9). The charge properties of the surface of Al₂O₃ particles are related to the properties of polyacrylamide, and the negative charge increases, and the IEP moves toward alkalinity. And under alkaline conditions, the modified Al₂O₃ exhibits a higher absolute value of the zeta potential than pure Al₂O₃.

Studies have shown that under the action of the initiator, the C=C double bond of the acrylamide monomer is opened and grafted with the tail end of the coupling agent on the surface of the powder to form a certain spatial structure. The polyacrylamide organic coating has a certain spatial structure and hydrolysis activity, and can be converted into a carboxyl group-containing polymer by hydrolysis of its amide group. The hydrolysis reaction mechanism is as shown in Fig. 7.

The hydrolysate with a carboxylic acid group structure is an important anionic polyelectrolyte, so the relationship between the zeta potential and the pH of the double-coated Al₂O₃ suspension solution is the same as

that of the ceramic powder adsorbing the anionic polyelectrolyte [16].

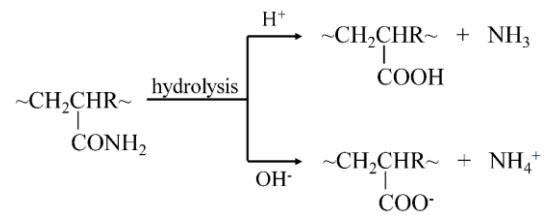


Fig. 7. The schematic diagram of hydrolysis reaction mechanism

The carboxylic acid group of the hydrolyzed polyacrylamide is either present as -COOH or dissociated to -COO⁻, and the fraction of the dissociated -COOH group is closely related to the pH of the solution. When the solution is strongly acidic, -COOH hardly dissociates; when the solution is alkaline, -COOH is completely dissociated. As the degree of -COOH dissociation increases, the surface charge properties of the polymer change from neutral to very high electronegativity. This fully confirms that the polyacrylamide has been successfully grafted onto the surface of the Al₂O₃ powder.

3.6. Dispersion stability analysis

According to the change of light transmittance, the dispersion stability of Al₂O₃ in aqueous medium can be reflected. The light transmittance of the Al₂O₃ powder suspension before and after the modification was measured, as shown in Fig. 8. The transmittance of pure Al₂O₃ suspension increased rapidly as time goes by. Light transmittance reached 78 % or more only 3 days and reached over 90 % after 7 days, indicating that the dispersion stability of pure Al₂O₃ suspension was poor, 7 days almost complete settling.

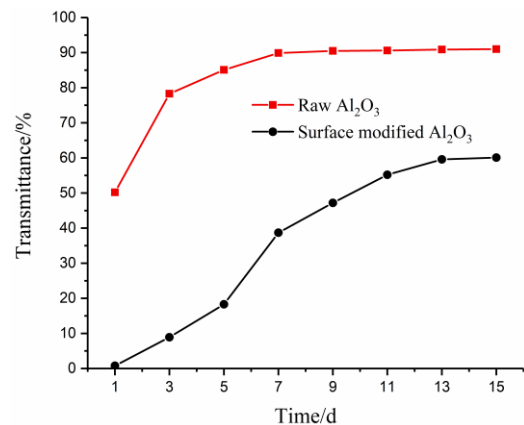


Fig. 8. Stability of Al₂O₃ powders before and after modification in the natural sedimentation

The light transmittance of the dispersion is greatly reduced after grafting polyacrylamide, and the light transmittance of the suspension is less than 10 % after storage for 1 to 3 days; the light transmittance is less than 40 % after 7 days. The light rate is less than 65 % after storage for 15 days. The results show that the dispersion stability of Al₂O₃ is obviously improved after modification. The reasons are as follows:

First, carboxylate functional groups were produced due to hydrolysis of polyacrylamide, which increased the

surface charge of the particles and the charge repulsion between the particles, and the particles are thermodynamically more unstable, so that a stable dispersion system can be formed in water. Second, the branched polyacrylamide is a long-chain polymer, which forms an outer shell on the surface of the particle through the interaction force of the polymer chain, and its steric hindrance prevents agglomeration between the particles; third, the branched polyacrylamide is a water-soluble polymer, which can improve the hydrophilicity and wettability of the particles, and the solvation effect makes the surface energy of the Al_2O_3 particles greatly reduced, and can stably exist in an aqueous medium. The mutual adsorption of Al_2O_3 particles can be prevented through the combination of static electricity and steric hindrance, and the dispersion stability of Al_2O_3 particles in aqueous medium can be improved.

3.7. Hard disk polishing experiment

From Fig. 9 a, the surface of unpolished NiP/Al hard disk was rough, and R_a was very large ($R_a = 154 \text{ nm}$). The surface of unpolished NiP/Al hard disk was uneven, had obvious grooves and pits, and had great undulations. From Fig. 9 b, the R_a of NiP/Al hard disk is significantly reduced ($R_a = 4.67 \text{ nm}$). The defect pits on the NiP/Al hard disk surface basically disappear, and the depth of the scratches becomes significantly shallower. The viscoelastic polymer coated on the surface of PAM/ Al_2O_3 abrasive reduced particle hardness. The polymer acted as a buffer when the abrasive particles hit the hard disk surface, reducing the impact strength of PAM/ Al_2O_3 particles on NiP/Al hard disk. Therefore, the micro-morphology of NiP/Al hard disk surface was improved, and the R_a was obviously reduced.

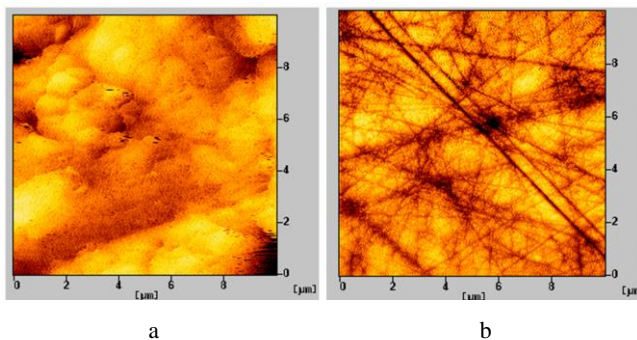


Fig. 9. a—AFM images of hard disk surface before polishing; b—after PAM/ Al_2O_3 polishing

4. CONCLUSIONS

The polyacrylamide PAM/ Al_2O_3 composite particles have been successfully synthesised by anchoring the azo initiator on the surface of Al_2O_3 particles to initiate the polymerization of acrylamide. The characterization and experimental results indicated that the attained composite abrasive when water-soluble azo initiator was added at $40 \text{ }^\circ\text{C}$ showed good dispersion stability in aqueous media with PAM as shell and Al_2O_3 as core. This paper can be summarized as follows:

1. XPS and FT-IR spectral analysis showed that polyacrylamide had been grafted onto the surface of Al_2O_3 powder by chemical bond;
2. The D50 of the modified Al_2O_3 was reduced, the particle size distribution range is narrowed, and the content of fine particles were obviously increased; the light transmittance was less than 70 % after 15 days of storage; the IEP position of the modified Al_2O_3 migrates. After PAM/ Al_2O_3 abrasive polished, the surface roughness of NiP/Al hard disk surface was obviously reduced;
3. The reason for PAM/ Al_2O_3 stably existing in an aqueous medium was that carboxylate functional groups from polyacrylamide hydrolysis increased the surface charge of particles and the charge repulsion between the particles.

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