DEVELOPMENT OF SPION-BASED NANOABRASIVES FOR SUPERFINISH OPTICAL POLISHING

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by

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Submitted

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Dedicated to

My teachers, parents, and my family

Certificate

This is to certify that the thesis entitled "**DEVELOPMENT OF SPION-BASED NANOABRASIVES FOR SUPERFINISH OPTICAL POLISHING**" submitted by **MD AMIR** to the Centre for Sensors, Instrumentation and Cyber-physical System Engineering, Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This thesis is a bonafide record of the research carried out by him under our guidance and supervision. In our opinion, the thesis has reached the standards fulfilling the requirements for the submission relating to the degree.

The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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"Indeed, we belong to him, and indeed to him, we will return". Quran 2:156

Thank you all...!!!

Md Amir

Abstract

The aim of this research is to develop nanomaterial-based abrasives that can improve the efficiency and effectiveness of the chemical-mechanical optical polishing process for superfinish surfaces. The focus is on overcoming the limitations of the conventional abrasive particle by producing nano-sized abrasive particles with required features such as fine particles, narrow particle size distribution, high surface area, and high zeta potential. This allows more efficient cutting and polishing of the glass surface, resulting in a smoother and more uniform surface finish. The research involves the development and characterization of the nanoabrasives and investigating their polishing efficiency using different polishing parameters such as pH, concentration, and polishing time. The research also investigated the impact of the chemical and mechanical action of the CMP by the nanoabrasive particles on the polishing performance.

Magnetic field-based polishing techniques, such as MRF, BEMRF, and their variations, rely on two essential factors: the finishing abrasive and the magnetic particles. However, the presence of magnetic particles can impede the direct contact of non-magnetic abrasive particles with the surface to be polished, leading to a decrease in the overall polishing efficiency. Therefore, the effectiveness of magnetic-assisted finishing depends on the ability of the active abrasive particles to interact with the surface being polished. Additionally, the optical and semiconductor industries use a significant amount of commercial abrasives for polishing, which cannot be recycled or reused, resulting in significant waste. This research addresses this issue by introducing an abrasive system that can provide Angstrom-level surface roughness in a sustainable and reusable manner for both magnetic and non-magnetic optical fabrication processes.

The following four major investigations have been carried out to achieve the goal of the research work in the thesis.

- A magnetic nanoparticle-based abrasive was developed to fabricate superfinish surfaces via a conventional chemical mechanical polishing process.
- To further resolve the limitation of the bared nanoparticle-based abrasive, a functionalization process was utilized to alter the bared-nanoparticle's physical and chemical features, such as particle size and its distribution, high surface area, and high zeta potential. This allowed to lower the surface roughness of the polished surface to one Angstrom.

- To eliminate the need for two types of particles, such as magnetic particles and abrasive particles (non-magnetic), for the MR-based finishing process, a dual nature magnetic nanoparticle was developed and utilized in BEMRF polishing.
- To further enhanced the finishing efficiency of dual-nature magnetic nanoparticle-based MR fluid, a hybrid core-shell-based nanoabrasive was developed for both magnetic and non-magnetic polishing processes.

It is expected that the results of this study will substantially increase the efficiency of traditional polishing abrasives of both magnetic and non-magnetic processes for the development of superfinish optical surfaces.

The first chapter of this thesis presents the needs and applications of superfinish optical components and fabrication technologies available for such optical component along with its metrology techniques, challenges involved with the commercially available abrasive for superfine optical components. The second chapter introduces the nanomaterial-based nanoabrasive and its applications in optical fabrication. Importance of the magnetic nanoparticles and a list of possible synthesis methods are also described along with their characterization techniques.

The third chapter of the thesis focuses on the development of a SPION nanoparticle-based nanoabrasive for superfine optical polishing. Detailed characterizations of the developed nanoabrasive are presented along with its precision polishing performance for the development of superfinish substrate. Moreover, the polishing performance of the SPION nanoabrasives is also compared with a cerium nanoabrasive. In fourth chapter, the effect of different surface modifiers on the structural, surface morphology, particle size, dispersion property and chemical mechanical polishing performance of the bared SPION nanoparticle are investigated in detailed for the development of superfinish optical surface.

The fifth chapter presents the development of a dual nature magnetic nanoparticle-based abrasives for magnetic field assisted polishing process. Ball end magnetorheological finishing is chosen for finishing in this study using developed dual-nature magnetic nanoparticle. The superparamagnetic characteristics of the magnetic nanoparticle aid in surface finishing without the usage of another magnetic particle like carbonyl iron particles. The sixth chapter focuses on the development of the recyclable and reusable core-shell-based hybrid nanoabrasive for both magnetic and non-magnetic polishing process for the development of superfinish optical substrates. In the seventh chapter, the advantages, limitations, and the scope for future studies

of the of the research works on developed SPION-based nanoabrasives for the development of superfinish optical surface are discussed as conclusions.

सारांश

इस शोध का उद्देश्य नैनोमटेरियल-आधारित अपघर्षक को विकसित करना है जो कि सुपरफिनिश सतहों के लिए रासायनिक-यांत्रिक ऑप्टिकल पॉलिशिंग प्रक्रिया की दक्षता और प्रभावशीलता में सुधार कर सकता है। महीन कण, संकीर्ण कण आकार वितरण, उच्च सतह क्षेत्र और उच्च ज़ेटा क्षमता जैसी आवश्यक विशेषताओं के साथ नैनो-आकार के अपघर्षक कणों का उत्पादन करके पारंपरिक अपघर्षक कणों की सीमाओं पर काबू पाने पर ध्यान केंद्रित किया गया है। इससे कांच की सतह को अधिक कुशल तरीके से काटने और पॉलिश करने की सहायता मिलती है, जिसके परिणामस्वरूप एक चिकनी और अधिक समान सतह पर फिनिश प्राप्त होती है। अनुसंधान में नैनोएब्रेसिव्स का विकास और लक्षण वर्णन शामिल है और पीएच, एकाग्रता और पॉलिशिंग का समय जैसे विभिन्न पॉलिशिंग मापदंडों का उपयोग करके उनकी पॉलिशिंग दक्षता की जांच की जाती है। शोध में पॉलिशिंग प्रदर्शन पर नैनो-अपघर्षक कणों द्वारा सीएमपी की रासायनिक और यांत्रिक क्रिया के प्रभाव की भी जांच की गई।

चुंबकीय क्षेत्र-आधारित पॉलिशिंग तकनीक, जैसे एमआरएफ, बीईएमआरएफ, और उनकी विविधताएं, दो आवश्यक कारकों पर निर्भर करती हैं: परिष्करण, अपघर्षक और चुंबकीय कण। हालाँकि, चुंबकीय कणों की उपस्थिति पॉलिश की जाने वाली सतह के साथ गैर-चुंबकीय अपघर्षक कणों के सीधे संपर्क में बाधा डाल सकती है, जिससे समग्र पॉलिशिंग दक्षता में कमी आ सकती है। इसलिए, चुंबकीय-सहायता वाली फिनिशिंग की प्रभावशीलता पॉलिश की जा रही सतह के साथ बातचीत करने के लिए सक्रिय अपघर्षक कणों की क्षमता पर निर्भर करती है। इसके अतिरिक्त, ऑप्टिकल और सेमीकंडक्टर उद्योग पॉलिशिंग के लिए बड़ी मात्रा में वाणिज्यिक अपघर्षक का उपयोग करते हैं, जिन्हें पुनर्नवीनीकरण या पुन: उपयोग नहीं किया जा सकता है, जिसके परिणामस्वरूप अधिक मात्रा में अपशिष्ट बनता है। यह शोध एक अपघर्षक प्रणाली की शुरुआत करके इस मुद्दे को संबोधित करती है जो चुंबकीय और गैर-चुंबकीय ऑप्टिकल निर्माण प्रक्रियाओं दोनों के लिए टिकाऊ और पुन: प्रयोज्य तरीके से एंगस्ट्रॉम-स्तरीय सतह खुरदरापन प्रदान कर सकता है। थीसिस में शोध कार्य के लक्ष्य को प्राप्त करने के लिए निम्नलिखित चार प्रमुख जाँचे की गई हैं।

• एक पारंपरिक रासायनिक यांत्रिक पॉलिशिंग प्रक्रिया के माध्यम से सुपरफिनिश सतहों को बनाने के लिए एक चुंबकीय नैनोकण-आधारित अपघर्षक विकसित किया गया था।

• नग्न नैनोकण-आधारित अपघर्षक की सीमा को और अधिक हल करने के लिए, नग्न नैनोकणों की भौतिक और रासायनिक विशेषताओं, जैसे कण आकार और उसके वितरण, उच्च सतह क्षेत्र और उच्च ज़ेटा क्षमता

को बदलने के लिए एक कार्यात्मकता प्रक्रिया का उपयोग किया गया था। इससे पॉलिश की गई सतह की खुरदरापन को एक एंगस्ट्रॉम तक कम करना संभव हो गया।

• एमआर-आधारित परिष्करण प्रक्रिया के लिए दो प्रकार के कणों, जैसे चुंबकीय कण और अपघर्षक कण (गैर-चुंबकीय) की आवश्यकता को खत्म करने के लिए, एक दोहरी प्रकृति चुंबकीय नैनोकण विकसित किया गया था और बीईएमआरएफ पॉलिशिंग में उपयोग किया गया था।

• दोहरे प्रकृति वाले चुंबकीय नैनोकण-आधारित एमआर द्रव की परिष्करण दक्षता को और बढ़ाने के लिए, चुंबकीय और गैर-चुंबकीय पॉलिशिंग प्रक्रियाओं दोनों के लिए एक हाइब्रिड कोर-शेल-आधारित नैनोअपघर्षक विकसित किया गया था।

यह उम्मीद की जाती है कि इस अध्ययन के नतीजे सुपरफिनिश ऑप्टिकल सतहों के विकास के लिए चुंबकीय और गैर-चुंबकीय दोनों प्रक्रियाओं के पारंपरिक पॉलिशिंग अपघर्षक की दक्षता में काफी वृद्धि करेंगे।

इस थीसिस का पहला अध्याय ऐसे ऑप्टिकल घटक के लिए उपलब्ध सुपरफिनिश ऑप्टिकल घटकों और निर्माण प्रौद्योगिकियों की जरूरतों और अनुप्रयोगों को प्रस्तुत करता है, साथ ही इसकी मेट्रोलॉजी तकनीकों, सुपरफाइन ऑप्टिकल घटकों के लिए व्यावसायिक रूप से उपलब्ध अपघर्षक से जुड़ी चुनौतियों को भी प्रस्तुत करता है। दूसरा अध्याय नैनोमटेरियल-आधारित नैनोअपघर्षक और ऑप्टिकल निर्माण में इसके अनुप्रयोगों का परिचय देता है। चुंबकीय नैनोकणों का महत्व और उनके लक्षण वर्णन तकनीकों के साथ संभावित संश्लेषण विधियों की एक सूची भी वर्णित है।

थीसिस का तीसरा अध्याय सुपरफाइन ऑप्टिकल पॉलिशिंग के लिए SPION नैनोकण-आधारित नैनोअपघर्षक के विकास पर केंद्रित है। सुपरफिनिश सब्सट्रेट के विकास के लिए इसके सटीक पॉलिशिंग प्रदर्शन के साथ विकसित नैनोएब्रेसिव के विस्तृत लक्षण प्रस्तुत किए गए हैं। इसके अलावा, SPION नैनोएब्रेसिव्स के पॉलिशिंग प्रदर्शन की तुलना सीरियम नैनोएब्रेसिव से भी की जाती है। चौथे अध्याय में, सुपरफिनिश ऑप्टिकल सतह के विकास के लिए नग्न SPION नैनोकण की संरचनात्मक, सतह आकृति विज्ञान, कण आकार, फैलाव विशेषता और रासायनिक यांत्रिक पॉलिशिंग प्रदर्शन पर विभिन्न सतह संशोधक के प्रभाव की विस्तृत जांच की गई है।

पाँचवाँ अध्याय चुंबकीय क्षेत्र सहायता प्राप्त पॉलिशिंग प्रक्रिया के लिए दोहरी प्रकृति वाले चुंबकीय नैनोकण-आधारित अपघर्षक के विकास को प्रस्तुत करता है। विकसित दोहरे प्रकृति वाले चुंबकीय

नैनोकण का उपयोग करके इस अध्ययन में परिष्करण के लिए बॉल एवं मैग्नेटोरियोलॉजिकल फिनिशिंग को चुना गया है। चुंबकीय नैनोकण की सुपरपराचुंबकीय विशेषताएं कार्बोनिल लौह कणों जैसे किसी अन्य चुंबकीय कण के उपयोग के बिना सतह परिष्करण में सहायता करती हैं। छठा अध्याय दोनों मैग्नीज़ के लिए पुन: प्रयोज्य और पुन: प्रयोज्य कोर-शेल-आधारित हाइब्रिड नैनोअपघर्षक के विकास पर केंद्रित है।

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AFM	Atomic Force Microscope
AGM	Alternate Gradient Magnetometry
BEMRF	Ball-end magnetorheological finishing
BET	Brunauer–Emmett–Teller
BJH	Barret-Joyner-Halenda
CAD	Computer-Aided Design
CCI	Coherence Correlation Interferometry
CMP	Chemical mechanical polishing
CNC	Computer Numerical Control
DLS	Dynamic light scattering
EDX	Energy Dispersive X-ray
FESEM	Field Emission Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full-Width Half Maximum
JCPDS	Joint Committee on Powder Diffraction Standards
MFAP	Magnetic Field-Assisted Polishing
MRF	Magnetorheological Finishing
MRR	Material Removal Rate
PPMS	physical properties measurement system
RMS	Root Mean Square

SPION	Superparamagnetic Iron Oxide Nanoparticle
TEM	Transmission electron microscopy
VSM	Vibrating Sample Magnetometry
W-H	Williamson-Hall
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction