

**IN SITU MICROSCOPIC TRIBOLOGY OF
NEAR EUTECTIC Al-Si ALLOY UNDER
BOUNDARY LUBRICATED CONDITIONS**

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**DEPARTMENT OF MATERIALS SCIENCE AND
ENGINEERING**

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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled “**IN SITU MICROSCOPIC TRIBOLOGY OF NEAR EUTECTIC Al-Si ALLOY UNDER BOUNDARY LUBRICATED CONDITIONS**” being submitted by **Mr. PRASHANT MITAL** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by him under my supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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Abstract

Aluminium (Al)-based lightweight alloys are extensively used in various engineering applications such as automotive engine components due to their high specific strength. This allows a significant weight reduction of components, resulting in improved engine fuel efficiency and lower exhaust emissions. The Aluminium-Silicon (Al-Si) alloys are one of the most frequently used materials in automotive-based applications, especially for the engine block and cylinder bore. Tribological properties of these alloys are critical as sliding contacts are involved in automobile engine components. Therefore, there is a need for suitable additives that can improve the tribological properties by minimizing friction and wear efficiently. One of the most commonly used antiwear additive is zinc dialkyl dithiophosphate (ZDDP) which is used to prevent wear by formation of tribofilm over the substrate. In addition to ZDDP, molybdenum dialkyl-dithiocarbamate (MoDTC) is another important additive, which works as friction modifier for reducing friction. Apart from conventional lubricant additives such as ZDDP and MoDTC, it is critically important to explore emerging new lubricant additives which can provide superior tribological properties as well as either replace ZDDP and MoDTC or reduce their concentration, which is detrimental for the automotive catalytic converters. Hexagonal boron nitride (h-BN), commonly referred to as white graphene, is a promising lubricant additive that reduces friction and wear efficiently. However, there is insufficient information on growth mechanisms, specifically growth modes, chemical and mechanical properties of the tribochemical films formed on the localised regions of aluminium die casting (ADC12) alloy. None of the previous studies quantified how the tribofilm formation takes place on the individual phases of ADC12 which are chemically and mechanically distinct. The interaction of ZDDP, MoDTC and h-BN on Al-Si alloy is not yet understood at the microscopic lengthscale. Therefore, it is necessary to understand the contribution of the individual phases

of Al-Si alloy on tribofilm growth as well as friction and wear in presence of conventional lubricant additives such as ZDDP, MoDTC and h-BN and their combinations. For this, Atomic Force Microscopy (AFM) is used to investigate the in situ growth of tribofilms and the evolution of tribological properties on various chemically and mechanically distinct regions of Al-Si alloys at the microscopic length scale.

Sliding tests using an alumina counter surface were performed simultaneously over Al and Si phase in ZDDP containing lubricant reveal ZDDP tribofilms grow with sliding time at high temperature (110 °C) and an optimum contact pressure over different regions including the Al matrix and Si phase of the ADC12 substrate. The thickness of the tribofilms and coefficient of friction (COF) is higher on harder Si phases where relatively larger contact stresses occur. Thinner tribofilm on the Al matrix also shows higher roughness due to larger spacing between the patches. This suggests that the growth of the tribofilm is activated by temperature and contact stress. Significant wear and increase in the COF was observed when sliding occurs within the Al matrix region alone in ZDDP containing lubricant. The addition of MoDTC in ZDDP results in relatively thinner tribofilm over Si phase in comparison to ZDDP alone when sliding is performed over the Al matrix and Si phase. The antiwear properties are found to be significantly improved when sliding only on the Al matrix. However, friction reduction was observed in both cases. The addition of h-BN in ZDDP containing lubricant shows better antiwear and anti-frictional properties as compared to ZDDP and ZDDP + MoDTC on Si as well as Al matrix regions which makes it a potentially superior additive in comparison to MoDTC.

In summary, this work examines the microscopic tribological properties of ADC12 by measuring the individual response of different phases, including friction, wear and tribofilm growth, under lubricant with different additives using in situ AFM.

सार

एल्युमीनियम (Al) आधारित हल्के मिश्र धातु का उपयोग विभिन्न इंजीनियरिंग अनुप्रयोगों जैसे ऑटोमोटिव इंजन पुर्जों में उनकी उच्च विशिष्ट शक्ति के कारण बड़े पैमाने पर किया जाता है। यह पुर्जों के महत्वपूर्ण वजन में कमी करता है, जिसके परिणामस्वरूप बेहतर इंजन ईंधन दक्षता और कम निकास उत्सर्जन होता है। एल्युमीनियम-सिलिकॉन (Al-Si) मिश्र धातु ऑटोमोटिव-आधारित अनुप्रयोगों में सबसे अधिक उपयोग की जाने वाली सामग्रियों में से एक है, विशेष रूप से इंजन ब्लॉक और सिलेंडर बोर के लिए। इन मिश्र धातुओं के ट्राइबोलॉजिकल गुण महत्वपूर्ण हैं, क्योंकि स्लाइडिंग संपर्क ऑटोमोबाइल इंजन पुर्जों में शामिल हैं। इसलिए, उपयुक्त एडिटिव्स की आवश्यकता है जो घर्षण और घिसाव को कम करके ट्राइबोलॉजिकल गुणों में सुधार कर सके। सबसे अधिक इस्तेमाल किए जाने वाले एंटीवियर एडिटिव में से एक जिंक डायलकाइलडाइथियोफॉस्फेट (ZDDP) है, जिसका उपयोग सबस्ट्रेट पर ट्राइबोफिल्म के गठन से घिसाव को रोकने के लिए किया जाता है। ZDDP के अलावा, मोलिब्डेनम डायलकाइलडाइथियोकार्बमेट (MoDTC) एक अन्य महत्वपूर्ण एडिटिव है, जो घर्षण को कम करने के लिए घर्षण संशोधक के रूप में काम करता है। ZDDP और MoDTC जैसे पारंपरिक लुब्रिकेंट एडिटिव्स के अलावा, उभरते हुए नए लुब्रिकेंट एडिटिव्स का पता लगाना महत्वपूर्ण है, जो बेहतर ट्राइबोलॉजिकल गुण प्रदान कर सकते हैं और साथ ही ZDDP और MoDTC को बदल सकते हैं या उनकी मात्रा को कम कर सकते हैं, जो ऑटोमोटिव कैटेलिटिक कन्वर्टर्स के लिए हानिकारक है। हेक्सागोनल बोरोन नाइट्राइड (h-BN), जिसे आमतौर पर “सफेद ग्राफीन” कहा जाता है, एक आशाजनक लुब्रिकेंट एडिटिव है, जो घर्षण और घिसाव को कुशलता से कम करता है। हालांकि, एल्युमिनियम डार्क कास्टिंग (ADC12) मिश्र धातु के वैयक्तिक फेजेस पर गठित ट्राइबोकेमिकल फिल्मों के विकास तंत्र, विशेष रूप से विकास मोड, रासायनिक और यांत्रिक गुणों के बारे में अपर्याप्त जानकारी है। पिछले अध्ययनों में से कोई भी यह निर्धारित नहीं करता है कि ADC12 के विभिन्न फेजेस में ट्राइबोफिल्म का गठन कैसे होता है जो

रासायनिक और यंत्रवत् रूप से भिन्न होते हैं। Al-Si मिश्र धातु पर ZDDP, MoDTC और h-BN की परस्पर क्रिया अभी तक सूक्ष्म लंबाई के पैमाने पर समझ में नहीं आई है। इसलिए, पारंपरिक लुब्रीकेंट एडिटिव्स जैसे ZDDP, MoDTC और h-BN और उनके संयोजनों की उपस्थिति में ट्राइबोफिल्म विकास के साथ-साथ घर्षण और घिसाव पर Al-Si मिश्र धातु के व्यक्तिगत फेज के योगदान को समझना आवश्यक है। इसके लिए, एटॉमिक फार्स माइक्रोस्कोपी (AFM) का उपयोग, इन-सीटू ट्राइबोफिल्म के विकास और सूक्ष्म पैमाने पर Al-Si मिश्र धातु के विभिन्न रासायनिक और यांत्रिक रूप से अलग-अलग फेजेस पर ट्राइबोलॉजिकल गुणों के विकास की जांच के लिए किया जाता है।

एल्यूमिना काउंटर सतह का उपयोग करते हुए स्लाइडिंग परीक्षण, लुब्रीकेंट युक्त ZDDP में Al और Si फेज में एक साथ किए गए, जिसमें पता चलता है कि ZDDP ट्राइबोफिल्म उच्च तापमान (110 डिग्री सेल्सियस) पर स्लाइडिंग समय के साथ बढ़ती हैं और एक अनुकूलतम संपर्क दबाव ADC12 सबस्ट्रेट के Al मैट्रिक्स और Si फेज सहित विभिन्न क्षेत्रों पर होता है। ट्राइबोफिल्म की मोटाई और घर्षण का गुणांक (COF) कठोर Si फेज पर अधिक होता है जहां अपेक्षाकृत ज्यादा संपर्क तनाव होता है। Al मैट्रिक्स पर पतली ट्राइबोफिल्म भी पैच के बीच बड़े जगह के कारण उच्च खुरदरापन होता है। इससे पता चलता है कि ट्राइबोफिल्म की वृद्धि तापमान और संपर्क तनाव से सक्रिय होती है। COF में महत्वपूर्ण वृद्धि और सार्थक घिसाव तब देखा गया जब ZDDP युक्त लुब्रीकेंट में स्लाइडिंग केवल Al मैट्रिक्स क्षेत्र में हुई। ZDDP में MoDTC को डालने से अकेले ZDDP की तुलना में Si फेज पर अपेक्षाकृत पतली ट्राइबोफिल्म बनती है, जब Al मैट्रिक्स और Si फेज पर साथ स्लाइडिंग की जाती है। केवल Al मैट्रिक्स पर स्लाइडिंग करने पर एंटीवियर गुणों में काफी सुधार पाया गया है। हालांकि, दोनों ही मामलों में घर्षण में कमी देखी गई। ZDDP युक्त लुब्रीकेंट में h-BN को डालने से Si के साथ-साथ Al मैट्रिक्स क्षेत्रों पर ZDDP और ZDDP + MoDTC की तुलना में बेहतर एंटीवियर और एंटी-फ्रिक्शनल गुण दिखाई देते हैं जो इसे MoDTC की तुलना में संभावित रूप से बेहतर एडिटिव बनाता है।

संक्षेप में, यह कार्य विभिन्न फेजेस की व्यक्तिगत प्रतिक्रिया को मापकर ADC12 के सूक्ष्म ट्राइबोलॉजिकल गुणों की जांच करता है, जिसमें इन-सीटू AFM का उपयोग करके विभिन्न एडिटिक्स युक्त लुब्रीकेंट में घर्षण, घिसाव और ट्राइबोफिल्म वृद्धि शामिल है।

Table of Contents

CERTIFICATE.....	i
Acknowledgements	iii
Abstract.....	v
Table of Contents	xi
List of Figures.....	xv
List of Tables	xxvii
Chapter 1: Introduction	1
Chapter 2: Literature Survey	7
2.1 Tribology.....	7
2.1.1 Tribology at macro, micro and nanoscale.....	11
2.2 Friction	12
2.2.1 Kinetic friction	13
2.2.2 Adhesion	13
2.2.3 Ploughing	14
2.2.4 Rolling friction.....	15
2.2.5 Liquid mediated contact friction.....	16
2.2.6 Friction at small scales	16
2.3 Wear	18
2.3.1 Abrasive wear	18
2.3.2 Adhesive wear.....	19
2.3.3 Corrosive wear	20
2.3.4 Fatigue/Delamination wear	20
2.3.5 Oxidative wear	21
2.3.6 Fretting wear	22
2.3.7 Deformation and ploughing	22
2.3.8 Wear at small scale	23
2.4 Lubrication regimes.....	23
2.5 Lubricants and additives.....	29
2.6 ZDDP antiwear additive.....	34
2.6.1 Introduction.....	34

2.6.2	Structure of ZDDP	36
2.6.3	Proposed mechanism of ZDDP antiwear tribofilm growth on ferrous surfaces	37
2.6.4	Properties of ZDDP tribofilms	42
2.6.5	Studies of ZDDP on non-ferrous alloys	49
2.7	Organomolybdenum friction modifiers (OFMs)	57
2.7.1	Introduction	57
2.7.2	History of organo molybdenum compounds	58
2.7.3	Types of organo molybdenum compounds	59
2.7.4	Tribological behaviour of organo molybdenum compounds on ferrous substrates	59
2.7.5	Tribological behaviour of organo molybdenum compounds on Al-Si alloy	67
2.8	h-BN as a lubricant additive	71
2.8.1	Structure of h-BN	71
2.8.2	Tribological behaviour of h-BN	73
2.9	Summary of the literature review	83
Chapter 3: Motivation and Objectives		85
Chapter 4: Materials and Methodologies		87
4.1	Introduction	87
4.2	Material	88
4.2.1	Al-Si Alloy (ADC12)	88
4.2.2	Lubricants	88
4.3	Sample preparation and microstructural analysis of ADC12	89
4.4	Microstructural characterization tools	91
4.4.1	Optical microscopy	91
4.4.2	Scanning electron microscopy (SEM)	91
4.4.3	Atomic force microscopy (AFM)	92
4.5	Nanoindentation	104
Chapter 5: Friction, wear and tribofilm formation on ADC12 in presence of lubricant containing ZDDP		107
5.1	Introduction	107
5.2	Results and discussion	107
5.2.1	In situ imaging of antiwear tribofilm growth	107
5.2.2	In situ friction measurement during sliding test	114
5.2.3	Chemical characterization of the tribofilm	117

5.2.4	Characterization of the counter surface (AFM probe) after experiment.....	118
5.3	Summary	119
Chapter 6: Friction, wear and tribofilm formation on ADC12 in presence of lubricant containing ZDDP and MoDTC		121
6.1	Introduction	121
6.2	Results and discussion.....	121
6.2.1	In situ imaging during sliding experiments	121
6.2.2	In situ friction measurement during sliding test	129
6.2.3	Tribofilm characterization	133
6.2.4	Effect of MoDTC concentration on tribofilm growth.....	136
6.2.5	Characterization of the counter surface (AFM probe) after experiment.....	142
6.3	Summary	144
Chapter 7: Effect of adding h-BN in ZDDP containing lubricant on tribological response of ADC12.....		147
7.1	Introduction	147
7.2	Results and discussion.....	147
7.2.1	In situ sliding experiments under lubricant containing only h-BN additive....	147
7.2.2	In situ sliding experiments under lubricant with combination of ZDDP and h BN.....	154
7.2.3	Characterization of the counter surface (AFM probe) after experiment.....	167
7.3	Summary	168
Chapter 8: Conclusions and Future Work		171
8.1	Conclusions	171
8.2	Future work	174
References.....		177
Appendix: A1.....		205
Appendix: A2.....		211

List of Figures

Figure 1.1: Al-Si binary phase diagram showing the eutectic composition at 12.3 wt.% of Si (sectional) [3].	2
Figure 1.2: Microstructure of Al-Si alloys for (a) eutectic or hypo-eutectic, (b) hyper-eutectic (c) Al-Si alloy hypo- or hyper-eutectic showing the dendritic structure, (d) Cu rich phases in Al-Si alloy [3].	3
Figure 2.1: Interaction of tribology with other branches of science [19]	8
Figure 2.2: Schematic diagram showing the tribological system [17].	9
Figure 2.3: Factors affecting the tribological systems [17].	9
Figure 2.4: Fuel energy consumption breakdown in passenger cars [16].	11
Figure 2.5: Schematic diagram showing tribological contacts at different length scales [23].	12
Figure 2.6: Schematic diagram of two body abrasion [25].	19
Figure 2.7: Schematic diagram showing three-body abrasion [25]	19
Figure 2.8: Schematic diagram showing adhesive wear [25]	20
Figure 2.9: Mechanism of fatigue wear [31]	21
Figure 2.10: Schematic diagram showing fretting wear [33]	22
Figure 2.11: Possible wear mechanism at the nanoscale [44]	23
Figure 2.12: Evolution of the field of boundary lubrication [48]	26
Figure 2.13: Stribeck curve showing the dependence of Hersey number on friction coefficient [47].	27
Figure 2.14: Pie chart showing relative friction loss in the valve train, bearings and piston assembly [49].	28
Figure 2.15: Development of lubricant additives [5].	30
Figure 2.16: Dimeric Structure of ZDDP [5].	36
Figure 2.17: Example of two primary alkyl group and one secondary alkyl group in ZDDP [80].	37
Figure 2.18: Stages of ZDDP behaviour [5]	37
Figure 2.19: Thermal Decomposition of ZDDP suggested by Dicker et al. [84]	39
Figure 2.20: Schematic diagram of in-situ AFM based approach for simultaneous monitoring of the growth kinetics of tribofilms, friction and wear [104]	40
Figure 2.21: Tribofilm growth dependence on (a) sliding cycles, (b) contact pressure and (c) temperature [104].	41

Figure 2.22: Log plot of ZDDP film formation rate vs. maximum shear stress proposed by Zhang and Spikes [105].	42
Figure 2.23: Structure of ZDDP antiwear tribofilm [121].	44
Figure 2.24: Layered structure of ZDDP proposed by Martin et al. [115].	44
Figure 2.25: Schematic diagram showing pad-like structures of the ZDDP tribofilm and their composition [5].	44
Figure 2.26: Layered ZDDP structure proposed by Bell et al. [98].	45
Figure 2.27: EDS and AES analysis of ZDDP tribofilm and outside the ZDDP tribofilms, i.e. steel substrate [104].	45
Figure 2.28: APT maps of ZDDP tribofilm on steel substrate constructed by Zhou et al. [122].	46
Figure 2.29: Schematic diagram of MTM-SLIM [125].	47
Figure 2.30: Schematic diagram illustrates the principle of SLIM[126].	47
Figure 2.31: AFM image and section analysis of 52100 steel with ZDDP at time (a) t=0 (b) t=12 hrs and (c) t=24 hrs [129].	48
Figure 2.32: Controlled growth of tribofilms of ZDDP and Zirconia nanoparticles on steel substrate using a novel AFM based approach [132].	49
Figure 2.33: Topographic AFM image of Si phase showing antiwear pads form over it [145].	50
Figure 2.34: Schematic model of ZDDP tribofilm formation on Al-Si alloy surface proposed by Nicholls et al. [145].	50
Figure 2.35: Schematic model proposed by Dienwiebel et al. [150].	51
Figure 2.36: Wear mechanism model proposed by Dey et al. [155].	53
Figure 2.37: Proposed model by Burkinshaw et al. [156] for Si surfaces lubricated with ZDDP.	54
Figure 2.38: Hypothetical model proposed by Shimizu et al. [6] at low and high load conditions.	55
Figure 2.39: Main types of organo molybdenum compounds [171].	59
Figure 2.40: Variation of COF with sliding time with (a) three different MoDDP [172] and (b) two different MoDTC against steel/steel tribopair [173].	60
Figure 2.41: HRTEM showing MoS ₂ nanosheet like structure in wear debris [177].	61
Figure 2.42: AFM lateral force map showing the presence of MoS ₂ nanosheets (dark spots) [180].	62

Figure 2.43: (i) AFM height and phase image of ZDDP/MoDTC tribofilm revealing nanostrips on increasing normal load from 660mV to 900mV and then decrease to 850 mV. 1-1' to 5-5' showing topographic line profile as shown in Figure 2.43(ii) [189].	63
Figure 2.44: Proposed reaction mechanism for the formation of MoS ₂ and MoO ₃ from MoDTC [177].	64
Figure 2.45: Proposed reaction mechanism pathway for the formation of MoS ₂ from MoDTC [193].	65
Figure 2.46: COF under different lubricants [8].	66
Figure 2.47: COF and the wear scar after the experiments in PAO, and PAO + MoDTC and PAO + MoDTC + ZDDP [12].	67
Figure 2.48: COF and the wear scar after the experiments with the difference in ZDDP concentration in PAO, PAO + MoDTC and PAO + MoDTC + ZDDP [11].	67
Figure 2.49: COF under different material and lubricant additives [9].	69
Figure 2.50: Three wear schemes at different MoDTC concentration proposed by Xia et al.[9].	69
Figure 2.51: COF measured with four different tribocouples and different oil additives [13].	70
Figure 2.52: Schematic diagram of h-BN structure [196].	72
Figure 2.53: Average COF after the experiments with the difference in h-BN concentration in water against steel carbide/silicon wafer tribopair [216].	74
Figure 2.54: Average wear width after the experiments with the difference in h-BN concentration in water against steel carbide/silicon wafer tribopair [216].	74
Figure 2.55: Specific wear rate and COF of different samples (increasing order of h-BN concentration) [217].	75
Figure 2.56: Average wear rate and COF under conventional diesel engine oil and optimized nano-oil [218].	77
Figure 2.57: SEM micrograph shows the sliding area after experiments under conventional engine oil and optimized nano oil. EDS spectrum shows the tribolfilm containing elements such as B and O within the experimental area [218].	77
Figure 2.58: A schematic diagram of interaction of h-BN nanosheets in blended oil at the sliding surface under tribo stress conditions [220].	79
Figure 2.59: (a) Wear scar width and average COF of aluminium disc lubricated with SN 500 lube oil without and with 0.02 mg/ml of h-BNNPs-TOA. (b) Change in average COF as a function of h-BNNPs-TOA concentration [15].	80

Figure 2.60: (a) COF and (b) wear depth of Polyol engine lube oil of without and 0.04 mg/ml h-BNNPs-ODTES under tribo contact conditions [14].	81
Figure 2.61: Variation in average COF as a function of h-BNNPs-ODTES concentration [14].	81
Figure 2.62: FESEM and EDS elemental mapping shows the presence of boron (B) and nitrogen (N) on the worn track [14].	82
Figure 4.1: Schematic representation of the experimental techniques used in this work.	87
Figure 4.2: (a) Optical microscope of a polished ADC12 sample. (b) SEM micrograph and (c-e) EDS elemental maps showing Al, Si and Fe rich phases of a polished ADC12 sample.	90
Figure 4.3: (a) AFM topographic image of ADC12 alloy showing Al matrix and Si phase. (b) topographic line profile across Al matrix and Si phase.	91
Figure 4.4: Schematic diagram of various components and the basic principle of an AFM	94
Figure 4.5: Schematic of a force vs distance (FD) curve obtained using an AFM cantilever	94
Figure 4.6: Schematic diagram showing forward and backward scanning of AFM tip	95
Figure 4.7: (a) AFM experimental setup showing various components (b) schematic diagram illustrating the in-situ AFM experimental setup.	96
Figure 4.8: (a) Two separate silicon wafer containing glue and alumina microsphere. (b) cantilever holder with cantilever in which alumina microsphere was to be attached (c) shows the cantilever approach towards the wafer containing glue. (d) shows the cantilever approach towards the silicon wafer containing alumina microsphere.	98
Figure 4.9: SEM images of alumina microsphere attached to an AFM cantilever	99
Figure 4.10: Elastic contact between a sphere and elastic-half space	100
Figure 4.11: (a) Alumina microsphere imaging through AFM (b) 3D AFM topographic image of the alumina microsphere.	102
Figure 4.12: Schematic diagram showing (a) AFM-based sliding experiments in different regions where either simultaneous sliding over the Al matrix and Si phase is performed or sliding only on the Al matrix is performed. (b) Schematic showing line by line scanning path of the AFM probe in a region containing Si phase and Al matrix.	104
Figure 5.1: (a)-(h) 12 μm x 5 μm AFM deflection images of the sliding zone where tribofilm growth is monitored with increasing sliding time at 110 $^{\circ}\text{C}$ using an alumina probe as countersurface. The nucleation and growth of the tribofilm can be seen over the Al matrix as well as over the Si phase.	108

Figure 5.2:(a) AFM topographic image acquired after sliding the alumina probe simultaneously over Al matrix and Si phase for 500 cycles in the dotted rectangular region (experimental scan area) where tribofilm growth has occurred. (b) Topographic height profile along Al matrix and Si phase revealing thickness of the tribofilm on Al matrix and Si phase. 110

Figure 5.3: (a) AFM topographic image of a zoomed-out region, showing significant wear of the matrix region (scan area) where the alumina probe was slid for 500 cycles. (b) AFM topographic height profile revealing the wear depth and material pile-up near the periphery of the sliding zone. 111

Figure 5.4: (a) Optical image of the region of interest, acquired before performing indentation. An array of 20 x 5 indentations performed across the Al-Si interface with separation between each indent of ~1.0 μm (b) P-h curve of Al matrix (red) and Si phase (black) in ADC12 alloy. (c) Plot showing the variation of elastic modulus (GPa) and hardness (GPa) across Al matrix and Si phase 112

Figure 5.5:(a) AFM topographic image acquired after scanning the alumina probe simultaneously over Al matrix and Si phase for 500 cycles in the dotted rectangular region (experimental scan area) at RT. (b) Topographic height profile along Al matrix and Si phase shows no tribofilm formation..... 113

Figure 5.6: (a) AFM topographic image acquired after scanning the alumina probe over Al matrix for 500 cycles in the dotted rectangular region (experimental scan area) at RT. (b) Topographic height profile along Al matrix within the experimental region..... 113

Figure 5.7: Variation of the COF (μ) with sliding time (min) when sliding tests were performed on both Al matrix (circle symbols) and Si phase (square symbols) simultaneously, combined with sliding only on the Al matrix (triangle symbols). The break in the Y-axis is to magnify the friction data measured simultaneously for Al and Si phase (circle and square data points respectively) where COF is gradually increasing with tribofilm growth as a function of sliding time. 115

Figure 5.8: COF vs. sliding time (min), measured simultaneously on Si and Al regions in base oil (without ZDDP) at RT. 116

Figure 5.9: Variation of the COF with sliding time (min) when sliding tests were performed on both Al matrix (circle symbols) and Si phase (square symbols) simultaneously, combined with sliding only on the Al matrix (triangle symbols) at RT. 117

Figure 5.10: (a) SEM image and (b)-(d) EDS maps of S, P and Zn distribution within the tribofilm formed on ADC12 alloy where the higher intensity of these signals can be seen on the Si phase. 118

Figure 5.11: (a) 15 μm x 15 μm 3D AFM topographic image of the alumina probe surface obtained using a sharp AFM contact mode probe. (b) Topographic image of alumina probe in 2D and (c) corresponding topographic height profile confirming the material build-up on the probe surface after sliding experiments. 119

Figure 6.1: (a) AFM topographic image of the ADC12, with experimental scan area shown in dashed rectangular region, acquired after simultaneous sliding over Al matrix and Si phase regions for 500 cycles with the alumina microsphere under lubricant containing ZDDP and 1 wt.% MoDTC additives at 110 °C. (b) The line profiles are showing the topographic heights of the Al matrix and the Si phase regions, revealing the wear of the Al matrix and tribofilm formation over the Si phase. 124

Figure 6.2: (a) AFM topographic image of the experimental area, shown in dashed rectangular region, acquired after sliding over the Al matrix for 500 cycles against an alumina microsphere under lubricant containing 1 wt.% ZDDP and 1 wt.% MoDTC additives at 110 °C. (b) The line profile is showing the topographic height of the Al matrix, revealing slight wear and material pile-up at the edges of the experimental region along with small patchy regions within the sliding zone. 124

Figure 6.3: Schematic diagram of the experimental region showing results of a simultaneous sliding test over the Al matrix and Si phase and a sliding test only on the Al matrix under lubricant containing 1 wt.% ZDDP and 1 wt.% MoDTC additives..... 125

Figure 6.4: (a) AFM topographic image of the ADC12, with experimental scan area shown in dashed rectangular region, acquired after simultaneous sliding over Al matrix and Si phase regions for 500 cycles with the alumina microsphere under lubricant containing 1 wt.% ZDDP and 1 wt.% MoDTC additives at RT. (b) The line profiles are showing the topographic heights of the Al matrix and the Si phase regions do not show any tribofilm formation..... 126

Figure 6.5: (a) AFM topographic image of the experimental area, shown in dashed rectangular region, acquired after sliding over the Al matrix for 500 cycles against an alumina microsphere under lubricant containing 1 wt.% ZDDP and 1 wt.% MoDTC additives at RT. (b) The line profile is showing the topographic height of the Al matrix. 127

Figure 6.6: AFM topographic image of the ADC12, with experimental scan area shown in dashed rectangular region, acquired after simultaneous sliding over Al matrix and Si phase regions for 500 cycles with the alumina microsphere under lubricant containing 1 wt.% MoDTC additive at 110 °C. (b) The line profiles are showing the topographic heights of the Al matrix and the Si phase regions do not show tribofilm formation and wear. 128

Figure 6.7: AFM topographic image of the experimental area, shown in dashed rectangular region, acquired after sliding over the Al matrix for 500 cycles against an alumina microsphere under lubricant containing 1 wt.% MoDTC additives at 110 °C. (b) The line profile is showing the topographic height of the Al matrix. 128

Figure 6.8: COF vs. sliding time measured simultaneously on Si (black square) phase and Al matrix (red circle) and is compared with sliding performed only on the Al matrix (blue triangle) under lubricant containing ZDDP and 1 wt.% MoDTC additives. Variation of COF in the presence of ZDDP is shown in the inset. Experiments were carried out at 110 °C..... 130

Figure 6.9: COF vs. sliding time measured simultaneously on Si (black square) phase and Al matrix (red circle) and is compared with sliding performed only on the Al matrix (blue triangle) under lubricant containing 1 wt.% MoDTC additives at 110 °C..... 132

Figure 6.10: COF vs. sliding time measured simultaneously on Si (black square) phase and Al matrix (red circle) and is compared with sliding performed only on the Al matrix (blue triangle) under lubricant containing ZDDP + 1 wt.% MoDTC additives at RT. 133

Figure 6.11: (a) SEM image of the sliding area and points considered for elemental spectroscopy on the Al matrix and Si phase. The point spectrum (b) and (c) shows peaks of Mo, S, P, and Zn on the Si phase. The point spectrum (d) and (e) shows the absence of P and S peaks on the Al matrix when sliding simultaneously over the Al matrix and Si phase of ADC12. 134

Figure 6.12: AFM topographic image of the region corresponding to the SEM image shown in Figure 6.5(a)..... 135

Figure 6.13: (a) SEM image of the sliding area on the Al matrix, (b) point spectrum indicating the presence of Mo, P, S, and Zn while sliding only on the Al matrix. 135

Figure 6.14: AFM topographic image of the ADC12, with experimental scan area shown in dashed rectangular region, acquired after simultaneous sliding over Al matrix and Si phase regions for 500 cycles with the alumina microsphere under lubricant containing ZDDP and (a) 300 ppm Mo (b) 600 ppm Mo and (c) 900 ppm Mo. The corresponding line profiles (d), (e) and (f) are showing the topographic heights of the Al matrix and the Si phase regions along (a), (b) and (c)..... 137

Figure 6.15: AFM topographic image of the experimental area, shown in dashed rectangular region, acquired after sliding over the Al matrix for 500 cycles against an alumina microsphere under lubricant containing ZDDP and (a) 300 ppm Mo (b) 600 ppm Mo and (c) 900 ppm Mo. The corresponding line profiles (d), (e) and (f) are showing the topographic heights of the Al

matrix along (a), (b) and (c), revealing slight wear and material pile-up at the edges of the experimental region.	138
Figure 6.16: COF vs. sliding time measured simultaneously on Si (black square) phase and Al matrix (red circle) and is compared with sliding performed only on the Al matrix (blue triangle) at 110 °C under lubricant containing ZDDP and (a) 300 ppm Mo (b) 600 ppm Mo and (c) 900 ppm Mo.	138
Figure 6.17: (a) SEM image of the sliding area and points considered for elemental spectroscopy on the Al matrix and Si phase at 300 ppm Mo. The point spectrum (b) and (c) shows peaks of Mo, S, P, and Zn on the Si phase. The point spectrum (d) and (e) shows the absence of P and S peaks on the Al matrix when sliding simultaneously over the Al matrix and Si phase of ADC12.	140
Figure 6.18: (a) SEM image of the sliding area and points considered for elemental spectroscopy on the Al matrix and Si phase at 600 ppm Mo. The point spectrum (b) and (c) shows peaks of Mo, S, P, and Zn on the Si phase. The point spectrum (d) and (e) shows the absence of P and S peaks on the Al matrix when sliding simultaneously over the Al matrix and Si phase of ADC12.	141
Figure 6.19: (a) SEM image of the sliding area on the Al matrix at 300 ppm Mo, (b) point spectrum indicating the presence of Mo, P, S, Si and Zn while sliding only on the Al matrix.	141
Figure 6.20: (a) SEM image of the sliding area on the Al matrix at 600 ppm Mo, (b) point spectrum indicating the presence of Mo, P, S, Si and Zn while sliding only on the Al matrix.	142
Figure 6.21: (a) 3D AFM topographic image of the alumina microsphere (counter surface), obtained using a sharp AFM probe. Some material build-up is visible within the contact zone and around the contact zone on alumina microsphere after sliding experiments. (b) 2D topographic image and (c) corresponding topographic height profile, showing flattening due to probe wear.	143
Figure 6.22: (a) SEM image and (b)-(g) are EDS maps of Al, Mo, P, S, Si and Zn on the alumina microsphere (counter surface) after the sliding experiments.	143
Figure 7.1: (a) AFM topographic image of the experimental region (dashed rectangular area) when sliding simultaneously on Al matrix and Si phase in the presence of lubricant containing 0.02 mg/ml h-BN and base oil at 110 °C. (b) Topographic height profile along the Al matrix and Si phase, showing material pile up on the Si phase due to transfer of Al from the surrounding matrix which is undergoing wear.	149

Figure 7.2: (a) AFM topographic image of the experimental region (dashed rectangular area) when sliding only on Al matrix in the presence of lubricant containing 0.02 mg/ml h-BN and base oil at 110 °C. (b) Topographic height profile showing severe wear on the Al matrix. . 150

Figure 7.3: Variation in COF against sliding time when measured simultaneously on Al matrix and Si phase (Si phase (black square) and Al matrix (red circle)) and scanning only on the Al matrix (Al matrix (blue triangle)) in the presence of lubricant containing base oil and 0.02 mg/ml h-BN at 110 °C. 150

Figure 7.4: (a) AFM topographic image of the experimental region (dashed rectangular area) when sliding simultaneously on Al matrix and Si phase in the presence of lubricant containing 0.05 mg/ml h-BN and base oil at 110 °C. (b) Topographic height profile along the Al matrix and Si phase, showing material pile up on the Si phase due to transfer of Al from the surrounding matrix which is undergoing wear. 151

Figure 7.5: (a) AFM topographic image of the experimental region (dashed rectangular area) when sliding only on Al matrix in the presence of lubricant containing 0.05 mg/ml h-BN and base oil at 110 °C. (b) Topographic height profile showing severe wear on the Al matrix. . 151

Figure 7.6: (a) FESEM image of the sliding simultaneously over Al and Si region and (b-h) corresponding EDS over the sliding area in the presence of lubricant containing 0.02 mg/ml h-BN at 110 °C. 152

Figure 7.7: (a) FESEM image of scanning only on the Al matrix and (b-f) corresponding EDS over the sliding area in the presence of lubricant containing 0.02 mg/ml h-BN at 110 °C. ... 152

Figure 7.8: (a) FESEM image of the sliding simultaneously over Al and Si region and (b-h) corresponding EDS over the sliding area in the presence of lubricant containing 0.05 mg/ml h-BN at 110 °C. 153

Figure 7.9: (a) FESEM image of scanning only on the Al matrix and (b-f) corresponding EDS over the sliding area in the presence of lubricant containing 0.05 mg/ml h-BN at 110 °C. ... 153

Figure 7.10: (a) AFM topographic image of the experimental region (dashed rectangular region) showing tribofilm growth when sliding simultaneously on Al matrix and Si phase in the presence of lubricant containing 0.02 mg/ml h-BN and ZDDP at 110 °C. (b) Topographic height profile showing tribofilm thickness on the Al matrix and Si phase. 156

Figure 7.11: (a) AFM topographic image of the experimental region (dashed rectangular region) showing tribofilm growth when sliding only on the Al matrix in the presence of lubricant containing 0.02 mg/ml h-BN and ZDDP at 110 °C. (b) Topographic height profile showing tribofilm thickness over the Al matrix. 157

Figure 7.12: Schematic diagram of sliding experiments results, when sliding test was performed simultaneously over Al matrix and Si phase and when sliding only on the Al matrix (away from the Si phase) in the presence of ZDDP + h-BN compared with ZDDP + MoDTC and ZDDP alone..... 158

Figure 7.13: (a) AFM topographic image of the experimental region (dashed rectangular area) showing tribofilm growth when sliding simultaneously on Al matrix and Si phase in the presence of lubricant containing 0.05 mg/ml h-BN and ZDDP at 110 °C. (b) Topographic height profile along the Al matrix and Si phase, showing material pile up on the Si Phase and wear on the Al matrix. 159

Figure 7.14: (a) Zoomed out AFM topographic image of the experimental region (dashed rectangular area) when sliding only on Al matrix in the presence of lubricant containing 0.05 mg/ml h-BN and ZDDP at 110 °C. (b) Topographic height profile showing severe wear on the Al matrix. 160

Figure 7.15: Variation in COF vs sliding time when measured on Si phase (black square) and Al matrix (red circle) simultaneously, which is compared when sliding experiments were performed only on the Al matrix (blue triangle) in presence of lubricant containing base oil and (a) ZDDP with 0.02 mg/ml h-BN (b) ZDDP with MoDTC additives (c) ZDDP, at 110 °C. 163

Figure 7.16: Variation in COF vs. sliding time when measured on Si phase (black square) and Al matrix (red circle) simultaneously, which is compared when sliding experiments were performed only on the Al matrix (blue triangle) in the presence of lubricant containing ZDDP and 0.05 mg/ml h-BN at 110 °C. 164

Figure 7.17: (a) FESEM image of the sliding simultaneously over Al and Si region and (b-f) corresponding EDS elemental mapping of P, Zn, S, B and N over the sliding area in presence of lubricant containing ZDDP and 0.02 mg/ml h-BN at 110 °C. 165

Figure 7.18: (a) FESEM image of the sliding only over Al matrix and (b-f) corresponding EDS elemental mapping of P, Zn, S, B and N over the sliding area in presence of lubricant containing ZDDP and 0.02 mg/ml h-BN at 110 °C..... 166

Figure 7.19: (a) FESEM image of the sliding simultaneously over Al and Si region and (b-h) corresponding EDS over the sliding area in presence of lubricant containing ZDDP and 0.05 mg/ml h-BN at 110 °C. 166

Figure 7.20: (a) 3D AFM topographic image of the alumina probe (counter surface) of size 10 μm x 10 μm with the help of a sharp AFM probe. (b) topographic image of the alumina microsphere in 2D shows material build-up within and around the periphery of the contact zone

and (c) corresponding height profile reveals the flattening of the probe surface due to wear during sliding experiments.....167

Figure 7.21: (a) SEM image and EDS elemental mapping (b-h) shows the presence of Al, Si, P, S, Zn, B, and N confirms the material build-up (tribofilm) over the alumina microsphere (counter surface).168

List of Tables

Table 2.1: Lubricant additives [58].....	34
Table 2.2: Summary of lubrication of Al-Si alloy [9].	52
Table 2.3: Effect of addition of MoDTC in ZDDP on wear for different tribocouples [13]...	70
Table 4.1: Chemical composition of the ADC12 alloy	88
Table 4.2: Specific test conditions	89
Table 4.3: Lubricant and additives.....	89
Table 4.4: Elastic modulus and Poisson’s ratio for different materials of interest.	101
Table 6.1: Details of load, Hertzian contact radius and contact pressure calculated for experiments under ZDDP and ZDDP with MoDTC (900 ppm Mo) containing lubricants...	122
Table 6.2: Summary of results using 1 wt.% MoDTC with 1 wt.% ZDDP in comparison to only 1 wt.% ZDDP containing lubricant.....	131
Table 7.1: The experimental parameters as used for ZDDP and ZDDP + MODTC and ZDDP + h-BN experiments.....	154
Table 7.2: Summary of the results in presence of various lubricant additives.	163