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环境友好型氨基酸基离子液体作为水润滑 添加剂的摩擦学机制研究

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摘 要: 本文中以美国食品药品监督管理局(Food and Drug Administration, FDA)批准的食品添加剂月桂酰肌氨酸钠和氨基酸为原料, 采用简单的质子交换反应合成了2种氨基酸基离子液体Lys-LS和Arg-LS, 并将其用作水基润滑添加剂. 利用SRV-V微动摩擦磨损试验机 and 全自动真彩共聚焦显微镜考察了2种离子液体添加剂的摩擦学性能, 并采用扫描电镜(SEM)、石英晶体微天平(QCM)和X射线光电子能谱仪(XPS)深入探究了其润滑机理. 研究表明: 2种氨基酸基离子液体添加剂具有良好的热稳定性且可以显著抑制铸铁在水中的腐蚀. 与去离子水相比, 当Lys-LS和Arg-LS的添加质量分数为0.5%时, 水基润滑液的摩擦系数和磨损体积分别降低了约70%和85%, 具有显著的减摩抗磨效果. 机理分析结果表明, 离子液体在界面处形成的摩擦化学反应膜与物理/化学吸附膜协同作用, 有效地阻止了滑动摩擦副之间的直接接触, 进而赋予水基润滑液优异的摩擦学性能. 2种润滑添加剂制备简单, 安全无毒且绿色环保, 有望作为水基金属加工液和难燃液压液的关键润滑添加剂使用.

关键词: 氨基酸基离子液体; 水基润滑添加剂; 摩擦学性能; 润滑机理; 环境友好型添加剂

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Tribological Mechanism of Environment-Friendly Amino Acid-Based Ionic Liquids as Water Lubrication Additives

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Abstract: The utilization of water-based lubricants in certain applied fields, as an alternative to oil-based lubricants that are prone to causing environmental pollution, represents one of the effective strategies for achieving green tribology. To tackle the issues of subpar lubrication properties and susceptibility to corrosion of friction interface for water-based lubrication, two amino acids-based ionic liquids, Lys-LS and Arg-LS, were synthesized in this manuscript by a simple proton exchange reaction using L-lysine or L-arginine and Lauroyl sarcosine, and were utilized as water-based lubricant additives. The thermal decomposition 5% temperatures of Lys-LS and Arg-LS reached 219.8 °C and 217.5 °C, respectively, exhibiting exceptional thermal stability. The corrosion resistance properties of Lys-LS and Arg-LS aqueous solutions against first-grade gray cast iron sheets were assessed in accordance with the methodologies outlined in the national standard GB 6144-2010. Both the corrosion area and the number of corrosion stains were significantly reduced compared to deionized water when the two amino acids-based ionic liquids were incorporated at a mass fraction of $\geq 0.5\%$. The tribological properties of Lys-LS and Arg-LS additives were investigated using an SRV-V fretting friction and wear tester and automatic true-color confocal microscope. Compared with deionized water, the friction coefficient and wear volume of the water-based lubricants were reduced by about 70% and 85%, respectively, when Lys-LS and Arg-LS were supplemented at a concentration of 0.5%, providing a significant friction reduction and anti-wear performance. The micro-morphological analysis results of the wear spot surface revealed that the wear surface was smoother after lubricated by the aqueous solution containing ionic liquids additives, and at the same time, the adhesive wear and corrosive wear were effectively suppressed. The lubrication mechanisms of two ionic liquids additives were investigated in depth using the quartz crystal microbalance (QCM) and the X-ray photoelectron spectroscopy (XPS). The QCM tests indicated that the two amino acid-based ionic liquids could be effectively adsorbed onto the rubbing interface during the friction process to form a stable adsorption films. The XPS analysis results revealed that the tribochemical reaction occurred between the two additives and the surface of the friction pair, and a tribological protective films enriched with C, Fe, O and N elements were generated. The tribochemical reaction films and physical/chemical adsorption films formed by the ionic liquids at the interface worked synergistically to effectively prevent direct contact between the sliding pairs, endowing the water-based lubricant with excellent tribological properties. The two amino acids-based ionic liquids additives were characterized by simple preparation, non-toxicity and greenness, and were promising to be employed as critical additives for metalworking fluids and flame-retardant hydraulic fluids.

Key words: amino acid-based ionic liquids; water-based lubricants; tribological properties; lubrication mechanism; eco-friendly additives

摩擦磨损会导致机械零件的损坏和资源的浪费,在大多数工业化国家,这些损失总计约占国民生产总值的5%~7%^[1-2]. 合理的使用润滑油是减少摩擦磨损最有效的方式之一. 润滑油因其优异的摩擦学性能,在工业各个领域得到了广泛的应用. 但润滑油存在导热系数小和易燃易爆等缺点^[3-4],限制了其在煤矿、金属加工和液压传动等领域的应用. 此外,油基润滑液还存在着生物降解性差、污染环境等弊端^[5]. 因此,寻找资源节约和环境友好型的绿色润滑介质逐渐成为科学家关注的重点^[6].

水基润滑液具有冷却性能优异、难燃、导热系数高、来源广泛和易降解等优点^[7],被广泛用作金属加工液和难燃液压液. 然而,水基润滑液普遍存在着润滑性不足和抗腐蚀性能差等问题,严重制约了水基润滑体系的发展与应用^[8]. 合理的使用添加剂能显著提高水的物理化学性能和润滑性能.

离子液体是1种完全由阴阳离子构成的室温熔融盐^[9],具有低挥发性、不可燃、蒸汽压低、热稳定性高和表面吸附性能强等优点^[10-16]. 自2001年离子液体首次作为润滑剂应用于摩擦学领域以来^[17],得到了广泛的关注. 将离子液体作为润滑添加剂使用既可保留其优异的摩擦学特性^[18],又可以节约成本. 早期对于离子液体添加剂的研究,多数集中于水-甘油溶液^[19]和水-乙二醇^[20]2种体系中,且多数含有杂原子^[21-22]和卤素^[23]等,水解稳定性较差,在摩擦过程中容易对摩擦副产生腐蚀,同时对环境具有一定的污染. 近年来,人们对于离子液体添加剂的研究重点偏向于含氨基酸及其衍生物的绿色离子液体. Zheng等^[24]利用N-油酰肌氨酸与甲基乙醇胺原位合成了离子液体[osar][mea],研究其在水-甘油中的摩擦学性能,证明了[osar][mea]可显著提升水-甘油的抗腐蚀能力,同时具有优异的摩擦学性能. Yang等^[25]合成了7种氨基酸-四丁基磷离子

液体作为水基添加剂,发现离子液体分子中的P和N元素协同作用使得水溶液具有优良的摩擦学性能,同时产物的生物降解性强,对环境的影响较小.张恩惠等^[8]合成了3种不同极性的多肽,将其作为添加剂时能显著提高水-乙二醇溶液的润滑性能.受氨基酸基离子液体在水中的溶解能力所限,当前对于氨基酸型离子液体添加剂的研究主要集中在水-甘油/乙二醇体系,而作为纯水基润滑添加剂的研究较少.此外,目前所发展的氨基酸型离子液体仅阴离子或阳离子为氨基酸或氨基酸衍生物.因此,开发绿色、新型的阴阳离子均为氨基酸及其衍生物的多功能水润滑添加剂具有重要的理论意义和实际价值.

本文中以FDA批准的且可生物降解的食品添加剂月桂酰肌氨酸钠和氨基酸为原料,通过简单的质子交换反应得到了2种氨基酸基离子液体,并将其用作水润滑添加剂^[26].2种离子液体的阴阳离子均为氨基酸及其衍生物,且在水中具有优异溶解性.对2种离子液体作为水基润滑添加剂时的热稳定性、运动黏度、抗腐蚀性能和摩擦学性能进行了评价.采用石英晶体微天平(QCM)和X射线光电子能谱仪(XPS)研究了氨基酸基离子液体作为水基润滑添加剂时的润滑机理.本研究中合成的绿色离子液体有望应用于金属加工液和难燃液压液领域,并为新型绿色水基添加剂的设计和实际应用提供了理论指导.

1 试验部分

1.1 试验材料

N-月桂酰肌氨酸钠(98%)、L-赖氨酸(98%)和L-精氨酸(98.5%)均购于上海阿拉丁生化科技股份有限公司;无水乙醇(AR)、乙酸乙酯(AR)、盐酸(AR)和丙酮(AR)均购于上海沪试化工有限公司.

1.2 离子液体的制备

离子液体制备过程:(1)称取2.933 9 g (10 mmol) N-月桂酰肌氨酸钠加入三口烧瓶中,再加入100 mL去离子水作为溶剂,在40 ℃下搅拌30 min至完全溶解.随后用恒压滴管漏斗向三口烧瓶中逐滴缓慢加入20 mmol HCl持续搅拌反应2 h.反应结束后,使用乙酸乙酯进行萃取3次,合并有机相,旋蒸、干燥后,得到N-月桂酰肌氨酸(N-LS);(2)将等当量的L-赖氨酸或L-精氨酸与N-LS加入圆底烧瓶中,再分别加入去离子水和无水乙醇混合溶液(质量比=1:1)作为溶剂,80 ℃搅拌8 h.反应结束后,将体系冷却至室温,随后旋蒸除去溶剂,在室温真空条件下干燥24 h至恒重,得到的

离子液体Lys-LS和Arg-LS.图1所示为所合成的2种离子液体的分子结构.采用¹H NMR(Bruker, 500 MHz)和傅里叶变换红外光谱仪(FTIR, IR Tracer-100)对所合成的离子液体的分子结构进行了表征.

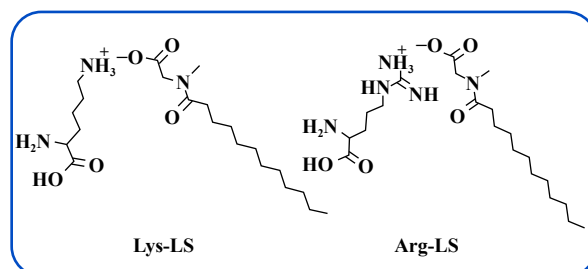


Fig. 1 The molecular structures of Lys-LS and Arg-LS
图1 Lys-LS与Arg-LS的分子结构

1.3 离子液体的物理化学性能表征

采用热失重分析仪(TGA, PT1000)分析Lys-LS和Arg-LS的热稳定性,在N₂气氛下,以10 ℃/min的升温速率由室温升至800 ℃.根据国标GB6144-2010的规定,将抛光后的铸铁片分别浸泡于去离子水和含质量分数为0.10%、0.25%、0.50%、0.75%和1.00%的2种离子液体水溶液中,在55±2 ℃条件下进行24 h的腐蚀测试.结束后铸铁片采用无水乙醇冲洗干净并用N₂吹干,观察铸铁片表面的腐蚀状况,并与腐蚀标准样品比较确定铸铁片的腐蚀等级.采用品氏黏度计测量去离子水、不同浓度的Lys-LS溶液和Arg-LS溶液在25和40 ℃下的运动黏度.

1.4 摩擦磨损试验

2种氨基酸基离子液体添加剂的摩擦学性能通过SRV-V微动摩擦磨损试验机(德国Optimol公司)进行评价.摩擦副之间的运动方式为球-盘点接触往复运动,上试样采用硬度为700 HV~800 HV、直径为10 mm的AISI52100钢球;下试样采用硬度为750 HV~760 HV、直径为24 mm、厚度为7.9 mm的轴承钢块.测试条件:载荷为100 N、频率为25 Hz、振幅为1 mm、温度为25 ℃、时间为30 min.使用与SRV-V测试仪相连的数据采集系统,自动记录相应的摩擦曲线.在变频试验中,频率变化为5 Hz/5 min (5~50 Hz),每组试验重复测量3次.在试验开始前,钢球和盘分别在丙酮溶液和无水乙醇溶液中超声清洗30 s,并通过高速N₂吹干.

在摩擦试验结束后,将钢块放入无水乙醇中超声清洗30 s,并通过高速N₂吹干.使用DCM8全自动真彩共聚焦显微镜观察钢块上磨斑的表面形貌并计算磨损体积.通过钨灯丝扫描电子显微镜(SEM, TESCAN-

VEGA)对磨斑的表面微观形貌进行表征,并通过X射线光电子能谱仪(XPS)分析磨斑表面的元素组成。

1.5 石英晶体微天平试验

为进一步探究离子液体在金属表面的吸附能力,借助石英晶体微天平(QCM)在室温和流速为300 $\mu\text{L/s}$ 的条件下,测试了质量分数为0.5%的离子液体水溶液在市售的镀金石英芯片(QSX-301, Q-Sense)表面上的吸附行为。

2 结果与讨论

2.1 结构与表征

分别通过核磁共振氢谱(^1H NMR)和ATR-FTIR测试表征了2种离子液体添加剂的分子结构。Lys-LS和Arg-LS的 ^1H NMR谱图分别如图2(a)和图2(b)所示,2种离子液体中阴离子- CH_3 的积分面积与氨基酸 α 位H的积分面积比为3:1,表明N-LS与氨基酸的反应定量进行。采用ATR-FTIR进一步对2种离子液体结构进行表征,结果如图2(c)所示,2226~3422 cm^{-1} 之间对应了2种离子液体中阳离子氨基N-H的伸缩振动峰,1576~1583 cm^{-1} 对应的是C=O的伸缩振动峰,在1015~

1130 cm^{-1} 之间对应了分子结构中C-N的伸缩振动峰。 ^1H NMR和ATR-FTIR测试结果表明2种氨基酸基离子液体被成功合成。使用TGA对2种氨基酸基离子液体的热稳定性进行了表征。图2(d)所示为Lys-LS和Arg-LS的热重分析图。Lys-LS和Arg-LS热分解5%的温度分别达到了219.8和217.5 $^{\circ}\text{C}$,表明2种氨基酸基添加剂在低于200 $^{\circ}\text{C}$ 时具有优异的热稳定性能。

2.2 腐蚀性能

水基润滑易腐蚀的问题是水基润滑剂关注的焦点,因此对Lys-LS和Arg-LS作为水润滑添加剂时的抗腐蚀性进行了表征。图3所示为在 55 ± 2 $^{\circ}\text{C}$ 条件下,一级灰口铸铁片浸泡于不同浓度的Lys-LS和Arg-LS水溶液中24 h后的表面状况图片。结果表明,与浸泡于去离子水中的铸铁片相比,浸泡在质量分数为0.5%的Lys-LS和Arg-LS水溶液中的铸铁片,腐蚀面积和腐蚀点的数量均有明显降低。当Arg-LS溶液的浓度升高至为1%时,铸铁片表面与空白对照样相比没有明显的变化,具有最佳的抗腐蚀性能。离子液体添加剂良好的抗腐蚀性能主要归因于月桂酰肌氨酸阴离子在铸铁表面形成了吸附膜,其阻碍了水与铸铁表面的直接

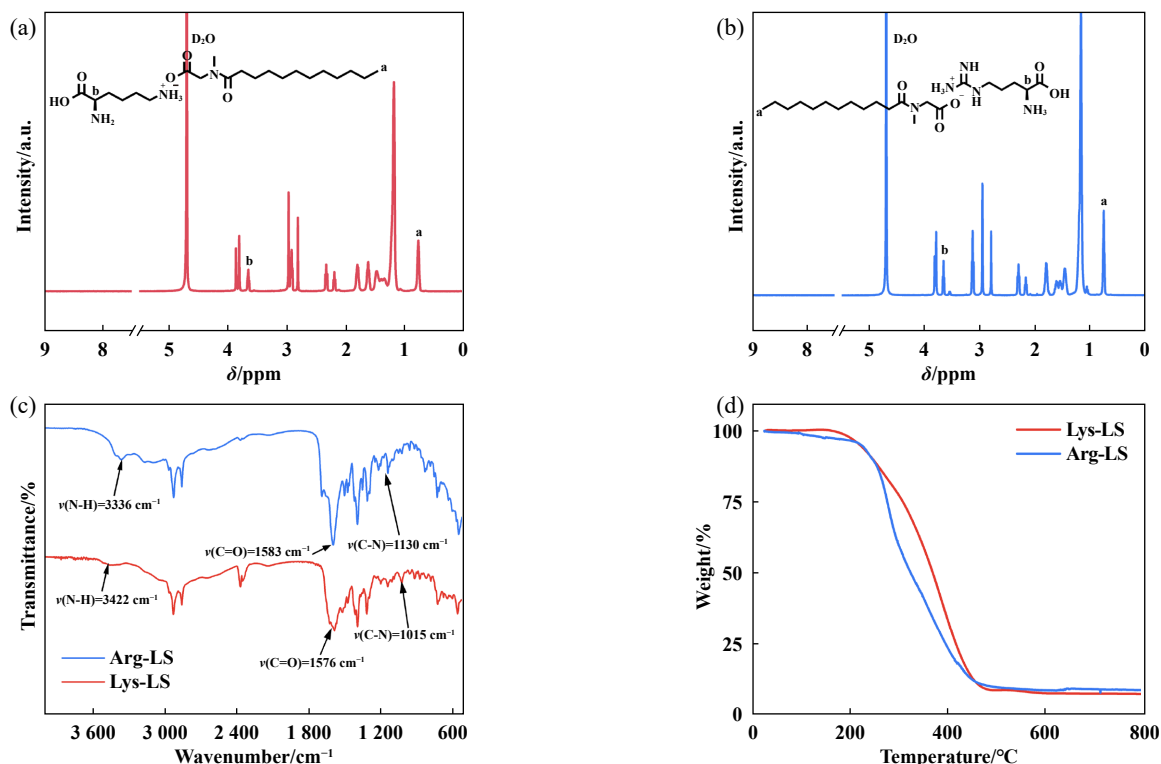


Fig. 2 (a) The molecular structure of Lys-LS and Arg-LS, spectra of (a) Lys-LS, (b) Arg-LS, (c) FT-IR spectra of Lys-LS and Arg-LS, (d) TGA curves of Lys-LS and Arg-LS

图2 (a) Lys-LS的 ^1H NMR谱图, (b) Arg-LS的 ^1H NMR谱图, (c) Lys-LS与Arg-LS的红外光谱图, (d) Lys-LS与Arg-LS的热失重曲线

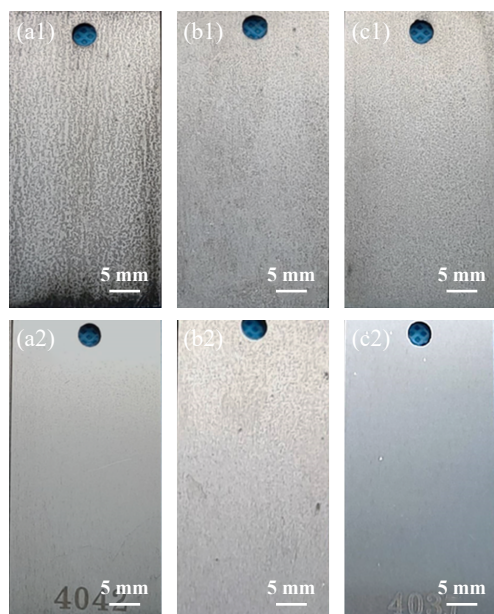


Fig. 3 Photographs of cast iron sheets after soaking in two amino acid-based ionic liquids aqueous solutions with different concentration for 24 h: (a1) H_2O ; (a2) blank cast iron sheet; (b1) 0.5% Lys-LS; (b2) 0.5% Arg-LS; (c1) 1.0% Lys-LS; (c2) 1.0% Arg-LS

图3 不同溶液浸泡24 h后的铸铁片: (a1)去离子水; (a2)空白铸铁片; (b1) 0.5% Lys-LS; (b2) 0.5% Arg-LS; (c1) 1.0% Lys-LS; (c2) 1.0% Arg-LS

接触。此外,随着离子液体浓度的增加,吸附膜的厚度不断增大,使其具有更优异的抗腐蚀性^[24-27]。

2.3 黏度测试

分别测试了不同浓度的离子液体水溶液在25和40 °C条件下的运动黏度,结果如图4所示。与去离子水相比,加入Lys-LS和Arg-LS后,溶液的黏度均有所增加,并且随着添加剂浓度的升高,黏度呈上升趋势。在25 °C时,去离子水、1% Lys-LS和1% Arg-LS润滑液的运动黏度分别为0.887、0.991和0.974 mm²/s。当温度升高至40 °C时,水溶液的黏度均降低,符合黏温变换效应,去离子水的运动黏度为0.682 mm²/s, 1% Lys-LS和1% Arg-LS运动黏度仍最高分别为0.730和0.722 mm²/s。由于离子液体为小分子,因此水基润滑体系的黏度改善幅度较小。黏度的升高有利于摩擦过程中离子液体在金属表面形成稳定的润滑膜,从而进一步提高溶液的摩擦学性能。

2.4 摩擦学性能评价

在适宜的添加剂浓度下,润滑液可以同时具备优良的润滑性能、抗腐蚀性能和溶解性能。利用SRV-V摩擦磨损试验机,对添加不同质量分数Lys-LS和Arg-LS的水溶液进行摩擦学性能测试,结果如图5所示。图5(a)和(b)所示分别为不同质量分数的Lys-LS和Arg-LS

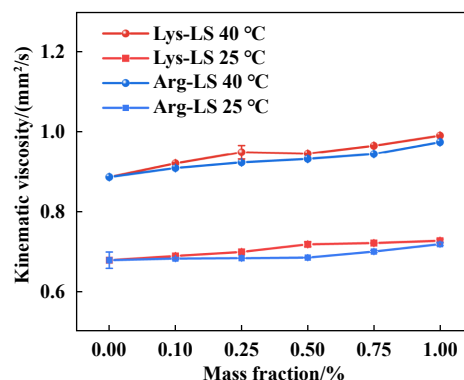


Fig. 4 Kinematic viscosities of deionized water and two ionic liquids aqueous solutions with different mass fraction at 25 °C and 40 °C.

图4 去离子水和不同质量分数的两种离子液体水溶液在25 °C和40 °C时的运动黏度。

水溶液摩擦系数随时间的变化曲线,图5(c)所示为不同质量分数的Lys-LS和Arg-LS水溶液作为润滑剂时的平均摩擦系数随浓度的变化趋势。去离子水对照组具有最高的摩擦系数,高达0.37。而Lys-LS和Arg-LS水溶液的摩擦系数显著低于去离子水对照组,大致稳定在0.100~0.110之间。当Lys-LS和Arg-LS水溶液的质量分数为0.5%时,其摩擦系数分别为0.109和0.105。2种添加剂均表现出优异的减摩性能,原因可能是在摩擦过程中,添加剂分子与钢块基底发生摩擦化学反应,生成了化学反应膜,避免了钢-钢摩擦对偶之间的直接接触,使得摩擦系数大幅度降低。与此同时,含Arg-LS的水溶液的平均摩擦系数均略低于含Lys-LS的水溶液,这可能与它们的化学组成有关,Arg-LS分子中含有更多的活性氮元素,更容易与基底发生摩擦化学反应。图5(d)所示为经过含有不同浓度Lys-LS和Arg-LS的水溶液摩擦后的下钢盘的磨损体积。含质量分数0.5%的Lys-LS和Arg-LS的水溶液的磨损体积分别为 56.77×10^{-5} 和 52.73×10^{-5} mm³,与去离子水的磨损体积(346.65×10^{-5} mm³)相比,分别降低了84%和85%,具有显著的抗磨损效果。

当Lys-LS和Arg-LS的添加质量分数为0.5%时,水基润滑液具有低摩擦系数和磨损体积,综合性能优异,因此选其作为代表性浓度进行后续试验,通过考察0.5% Lys-LS和0.5% Arg-LS水溶液在不同频率下的摩擦学性能[图5(e)],发现去离子水的摩擦系数随频率的升高不断增大,在高频率时失效明显。当使用含质量分数0.5%的2种离子液体的水溶液做润滑剂时,摩擦系数大幅度降低且走势平稳,无明显波动,显示出良好的频率抵抗性能。

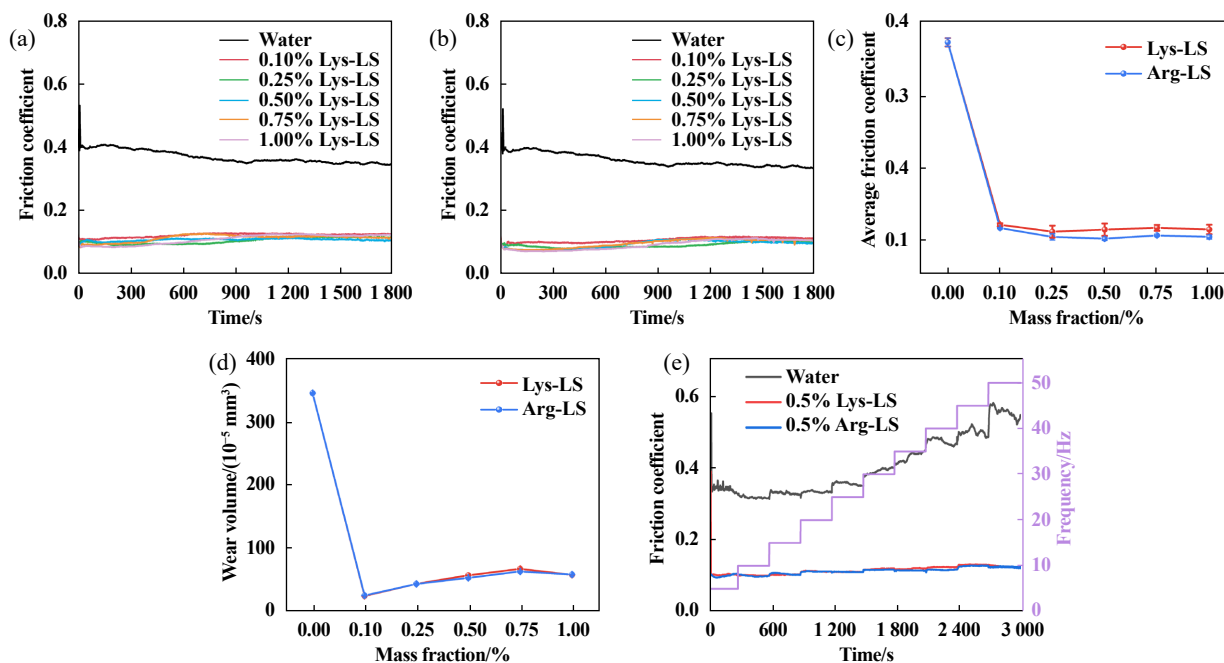


Fig. 5 (a) Friction coefficient curves for different concentrations of Lys-LS lubricants; (b) Friction coefficient curves for different mass fraction of Arg-LS lubricants; (c) Average friction coefficient for lubricated by Lys-LS and Arg-LS aqueous solutions with different mass fraction; (d) Wear volume of steel block after lubrication with Lys-LS and Arg-LS lubricants; (e) Wear volume of steel block after lubrication with Lys-LS and Arg-LS lubricants

图 5 (a)不同浓度Lys-LS润滑液的摩擦系数曲线; (b)不同浓度Arg-LS润滑液的摩擦系数曲线; (c)不同浓度的Lys-LS和Arg-LS水溶液的平均摩擦系数值; (d)经含不同浓度的Lys-LS和Arg-LS水溶液润滑后钢块的磨损体积; (e)摩擦系数随频率的变化曲线图

2.5 表面形貌分析

采用全自动真彩共聚焦显微镜研究了摩擦副接触区域的摩擦磨损状况, 如图6所示. 图6(a~c)所示分别为去离子水、0.5% Lys-LS和0.5% Arg-LS水溶液润滑后对应磨斑的横截面轮廓图. 对照组去离子水摩擦后的钢块产生的磨斑更深, 由刮擦产生的划痕非常明显. 从剖面图中可以更直观的对摩擦磨损情况进行分析, 水润滑后的磨斑的长度、宽度和深度分别达到了15.1 mm、0.82 mm和 7.81×10^{-3} mm, 这些结果表明去离子水的润滑效果较差, 发生了严重的磨损. 经0.5% Lys-LS和0.5% Arg-LS水溶液润滑后的磨斑深度明显变浅, 且宽度更窄, 磨斑的长度、宽度和深度与水相比得到了显著的降低, 宽度和深度分别降低了约45%和60%, 表明2种氨基酸基离子液体添加剂的加入可以有效抑制黏着磨损和犁沟, 显著提高了水基润滑液的抗磨损性能.

采用SEM对磨斑表面进行形貌分析, 观察了磨斑表面的微观状态, 如图7所示. 从图7中可以发现, 使用去离子水作为润滑剂时, 磨斑表面黏着磨损明显, 磨损轨迹直径大, 磨斑表面出现了多而深的犁沟, 并伴

随着许多因黏着磨损导致的磨斑和腐蚀斑. 与之对比, 当向水中加入2种离子液体后, 磨损轨迹直径明显减小, 如图7(b)和(c)所示. 从磨损轨迹对应的放大照片可以清楚地观察到含离子液体添加剂的水溶液润滑后的磨损表面更加光滑, 表明离子液体的加入有效地抑制了黏着磨损和腐蚀磨损, 这些结果与三维轮廓图的测量结果是一致的.

2.6 润滑机理分析

为了进一步研究2种氨基酸基离子液体作为水润滑添加剂时的减摩抗磨作用机理, 对添加质量分数为0.5%的Lys-LS和Arg-LS水溶液润滑后的磨斑表面的元素和化学组成进行XPS分析. 图8(a1~a4)和图8(b1~b4)所示分别为Lys-LS和Arg-LS对应磨斑的C 1s、N 1s、O 1s和Fe 2p谱图. 从图8可以看出, 添加2种离子液体时磨斑表面相应元素的峰型和结合能基本相同, 证明2种离子液体作为添加剂时, 均经历了相似的摩擦化学反应过程. C 1s谱的结果表明磨斑表面的碳元素主要以3种化学价态存在, 分别为284.8 (C-C)、286.2 (C-N)和288.86 eV (C=O)^[28], 其主要来源为离子液体或摩擦过程中在摩擦对偶表面形成的润滑膜. N 1s谱图在

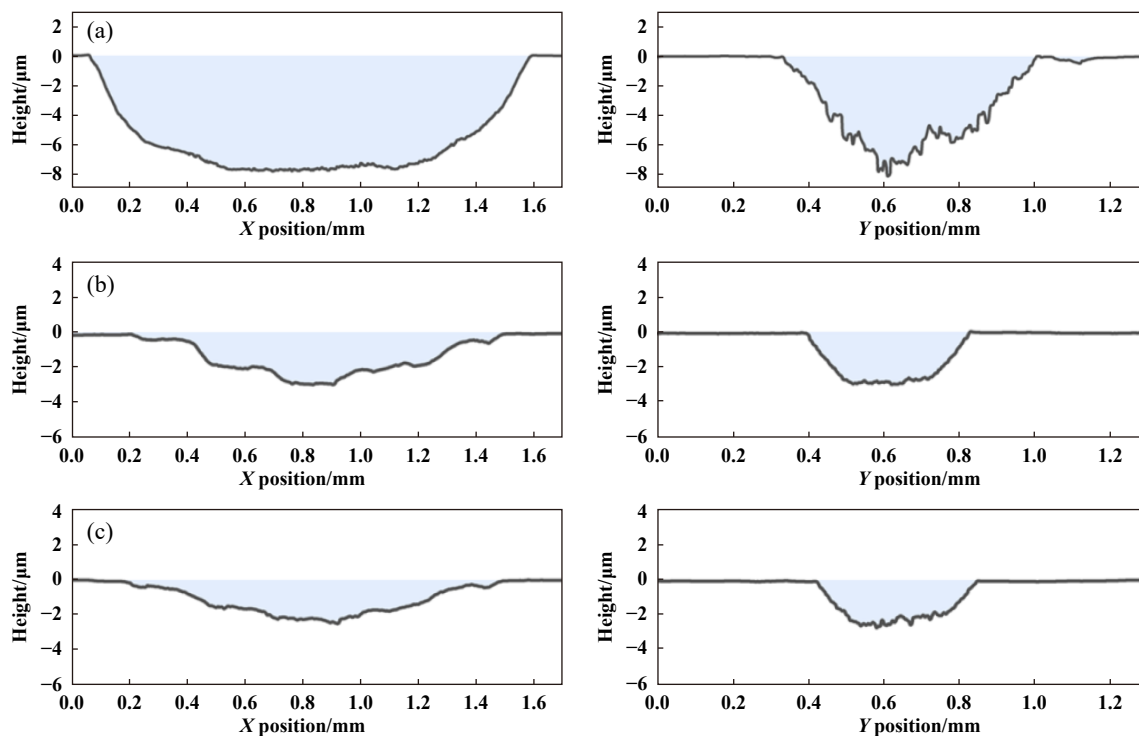


Fig. 6 3D morphology of the wear scar after the friction test of deionized water, 0.5 % Lys-LS and 0.5 % Arg-LS aqueous solution corresponds to the cross-sectional profile of the X and Y directions: (a) deionized water; (b) 0.5% Lys-LS; (c) 0.5% Arg-LS

图6 去离子水、0.5% Lys-LS和0.5% Arg-LS水溶液摩擦试验后磨斑的三维形貌对应 X 和 Y 方向的横截面轮廓图:
(a)去离子水; (b) 0.5% Lys-LS; (c) 0.5% Arg-LS

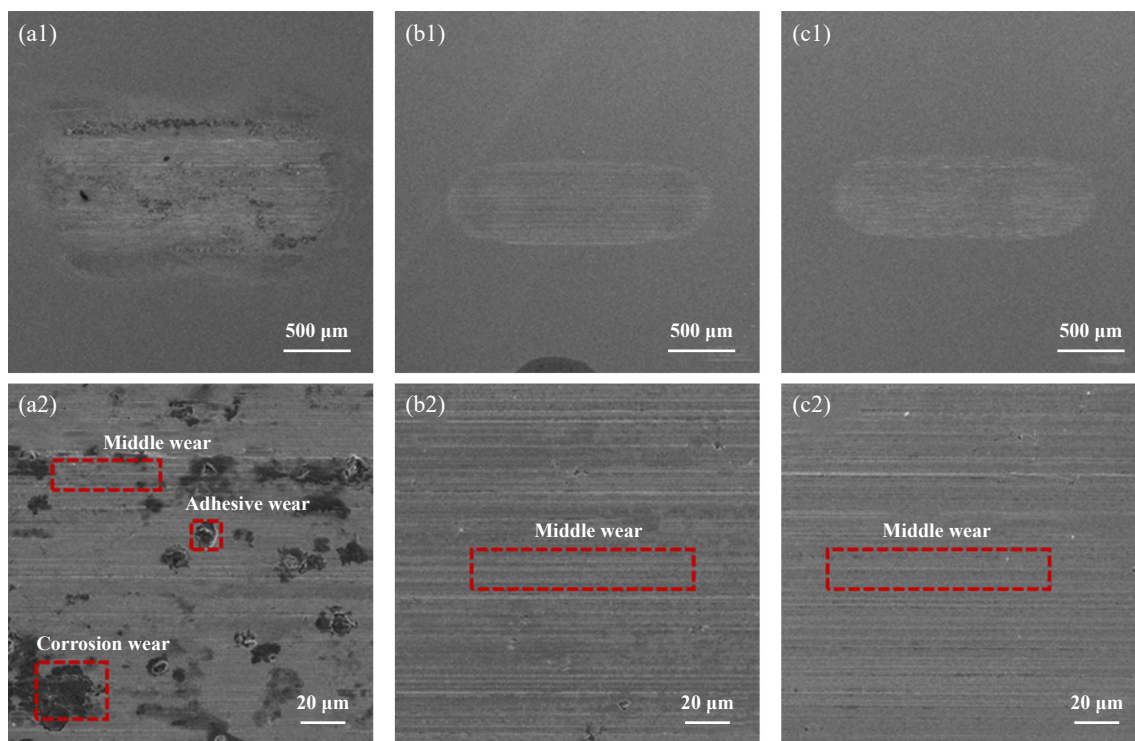


Fig. 7 SEM micrographs of the grinding surface of the worn spots lubricated by distilled water and Lys-LS aqueous solutions with different mass fraction: (a) deionized water; (b) 0.5% Lys-LS; (c) 0.5% Arg-LS

图7 去离子水、0.5% Lys-LS和0.5% Arg-LS水溶液摩擦试验后磨斑表面的SEM照片: (a)去离子水;
(b) 0.5% Lys-LS; (c) 0.5% Arg-LS

400.35和402.43 eV出现特征峰, 分别对应C-N^[29]和N-O键, 可能由于摩擦过程中离子液体中的N元素与摩擦副发生摩擦化学反应, 生成氮化物^[30-31]. O 1s的结合能峰值位置分别为530.43、531.81、532.65和533.93 eV, 表明O元素主要以金属氧化物、C-O、C=O和N-O的化学态形式存在^[32]. Fe 2p的结合能峰值位置分别为709.47、710.60、711.48和712.24 eV, 表明磨斑表面Fe元素主要以FeOOH^[33]、Fe(NO₃)₃^[31]、Fe₃O₄^[34]和Fe₂O₃^[35-36]形式存在. 以上分析表明, 2种氨基酸型离子液体作为添加剂具有优异的摩擦学性能的原因可能是在摩擦过程中, 离子液体与摩擦副表面反应生成1层致密的化学反应膜, 从而有效的隔绝上下摩擦副直接接触, 进而表现出良好的减摩抗磨性能.

通过QCM试验进一步研究了2种离子液体水基润

滑添加剂在金属表面的吸附能力. 图9(a)和(b)所示分别为质量分数为0.5%的Lys-LS和Arg-LS水溶液在金界面的吸附频率随时间的变化曲线(在所有试验中使用去离子水作为溶剂基线和金作为芯片). Lys-LS和Arg-LS水溶液的吸附频率分别为90和66 Hz, 表明2种离子液体均能有效吸附在金界面上. 可能是离子液体分子结构中的羧酸根离子具有很强的电负性效应, 使其很容易与金属表面发生相互作用, 进而形成吸附膜. 此外, 用去离子水冲洗之后吸附频率明显减小, 但不能恢复其原始值, 说明2种离子液体添加剂在钢块表面不仅存在物理吸附, 还存在化学吸附. 上述试验结果表明2种氨基酸基离子液体在摩擦过程中可以有效吸附在摩擦界面上, 形成稳定的吸附膜, 避免摩擦副之间的直接接触.

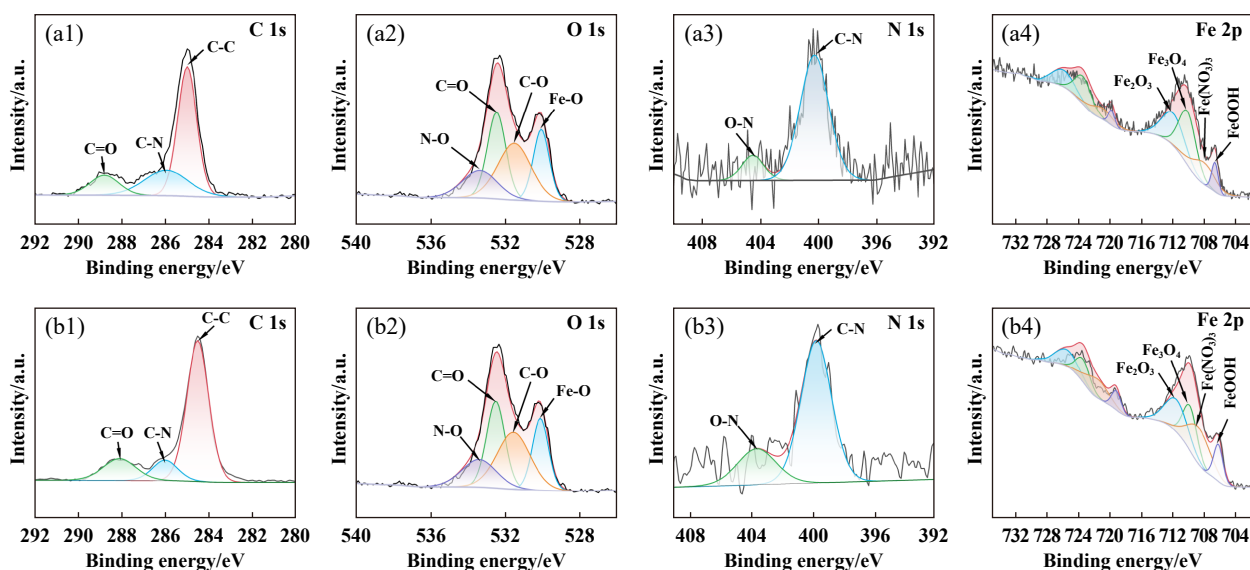


Fig. 8 XPS spectra of grinding spot surface lubricated by Lys-LS and Arg-LS solutions (0.5%): (a1~a4) Lys-LS; (b1~b4) Arg-LS

图 8 质量分数为0.5%的Lys-LS和Arg-LS水溶液摩擦后的磨斑表面的XPS谱图: (a1~a4) Lys-LS; (b1~b4) Arg-LS

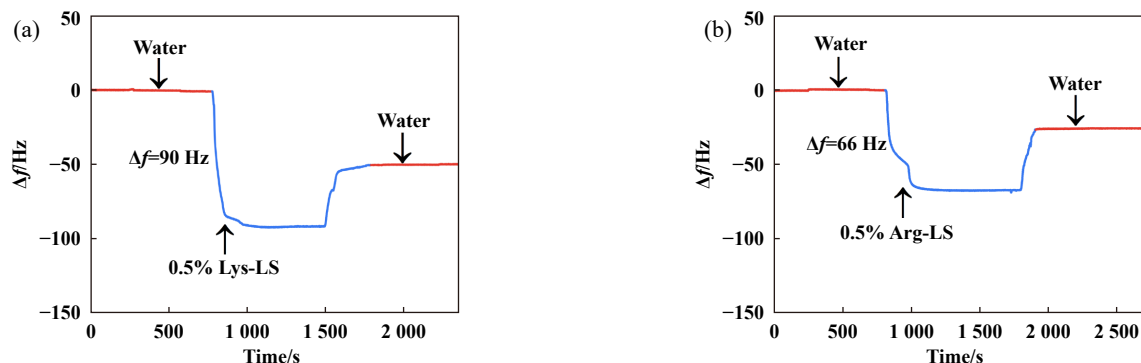


Fig. 9 Adsorption frequency as a function of time for (a) Lys-LS and (b) Arg-LS aqueous solutions on QCM gold chips (deionized water as the baseline)

图 9 (a) Lys-LS和(b) Arg-LS水溶液在QCM金芯片上的吸附频率随时间变化曲线(以去离子水为基线)

结合XPS分析和QCM测试结果,可推测2种氨基酸基离子液体的润滑机理如图10所示,在摩擦试验前钢块摩擦副之间实际接触的微凸起上由于电子逃逸而布满了正电荷^[37],离子液体中带负电基团的羧酸根阴离子与钢块表面的正电荷发生静电相互作用^[38],在界面处形成1层阴离子吸附层,这种稳定的吸附膜有效地阻断了摩擦副直接接触.在摩擦试验过程中产生的局部高温和机械力的作用下,离子液体会与钢块表面发生摩擦化学反应,形成了含有C、Fe、O和N等元素组成的复杂的摩擦化学反应膜.这些形成的摩擦化学反应膜与界面吸附膜共同相互作用,有效地阻止了滑动摩擦副之间的直接接触,起到减摩抗磨的作用,赋予水基润滑液优异的润滑性能.

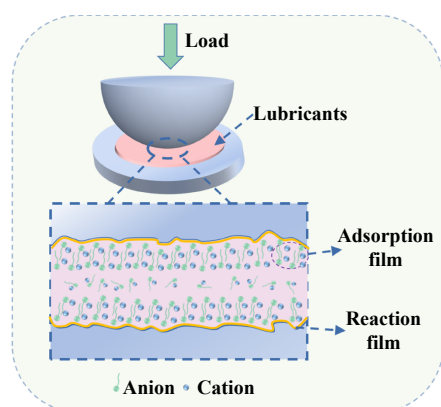


Fig. 10 Lubrication mechanism model
图10 润滑机理模型

3 总结

a. 以完全无毒且可生物降解的N-月桂酰肌氨酸和天然氨基酸为原料,通过简单的质子交换反应制备得到了2种绿色的氨基酸基离子液体, Lys-LS和Arg-LS,并将其用作水基润滑添加剂. Lys-LS和Arg-LS热分解5%的温度分别达到了219.8和217.5℃,具有优异的热稳定性.

b. 2种氨基酸离子液体均可小幅度提高水基润滑剂的黏度,且在水中添加质量分数 $\geq 0.5\%$ 时,能显著提高铸铁在水中的抗腐蚀性能.与纯水润滑液相比,含质量分数为0.5%的2种离子液体水溶液作为润滑剂时的摩擦系数和磨损体积分别降低了约70%和85%,显著提高了水基润滑液的摩擦学性能.

c. QCM测试及XPS分析结果表明,在摩擦过程中,添加剂在摩擦热和机械力作用下,与金属基底发

生摩擦化学反应,生成了1层富含C、Fe、O和N元素的摩擦化学反应膜.该反应膜与离子液体在界面处形成的稳定的物理/化学吸附膜协同作用,有效地阻止了滑动摩擦副之间的直接接触,进而赋予水基润滑液优异的摩擦学性能.2种氨基酸基离子液体润滑添加剂制备简单,安全无毒,绿色环保,有望作为金属加工液和难燃液压液的关键添加剂使用.

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