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# 香港表面處理



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## 香港表面處理學會

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## 編輯的話

#### 《編輯的話》是編者個人的觀點想法,並不代表學會的立場。

香港表面處理學會新一屆理事會會長於新春聯歡晚會,由會員投票選舉出 來,理事會理事亦已於六月正式上任。現今這個年代被稱為「新經濟模式」 的年代,90年代移動通訊普及,00年代互聯網的興起,到現今雲端服務及 人工智能被大眾所注視。在這個「新經濟模式」下,人們的生活和以往有著 巨大的分別,對書刊的需求相對減少,對電子媒體的需求隨之增加。新理事 會成立將更加積極推進新互動互聯模式,例如微信公眾號,相信第71期會 刊將有更多微信公眾號的資訊。

本屆理事會亦加入了多位「新血」,他們都是表面處理行業的從業員,對表面處理行業有深入的認識及廣闊的人際網絡,名副其實是強而有力的新力軍,往後日子會刊將逐一介紹他們給讀書認識。除了理事會的改變,最近學會加入了「學生會員」這一會員類別,主要是希望可以讓在學學生更多的接觸行業實況,增加彼此之間的聯繫,有關學生會員的查詢可直接聯絡學會秘書處。

說完學會內部環境,說說外部經濟環境。全球經濟不穩,中美貿易戰持續, 影響人們的消費意欲,香港作為以金融業、旅遊業、服務業為主的轉口港, 影響將會逐步浮現。但過去的歷史亦證明,每當「危」出現的時候,「機」 亦會一同出現。筆者並不鼓勵高風險投資,但亦不主張悲觀消極,更多的是 希望讀者們在這個陰晴不定的環境裏,更好的裝備自己,因為投資在自己身 上(例如:鍛鍊身體、學習知識)是永不虧本的。

筆者作為學會一員,知道學會將在不久的將來舉辦國內考察團、國外考察 團、表面處理相關課程、員會活動等等,暫時都在組織階段,更多資訊請留 意學會電郵,學會網頁,以及將來學會微信號。請多多支持。

最後希望各位讀者在這個容易浮躁不安的大時代裏,能夠穩住心態,深耕細 作,砥礪前行。



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# 己亥年中港同業新春聯歡晚會

本學會於2019年3月4日, 假粵品 匯舉行之「己亥年中港同業新春聯 歡晚會」已完滿結束。今年的聯歡 晚會除了得到本會會員、同業友會 及各方好友鼎力支持外,亦有幸邀 得香港和國內有關的政府機構官員 一同參與,實在不勝榮幸。

晚宴開始,先由本學會會長劉利強 先生致歡迎詞,接著由晚宴籌委會 主席黃順勳博士致謝詞,答謝協助 籌備是次聯歡晚會的理事及會員。 經過大家數個月的協助和努力,今



全體理事大合照

年的聯歡晚會仍有「拍賣」環節,為各位來賓增添了一些新鮮感。

晚會流程相當緊湊,項目環節一環扣一環。司儀胡學 聰先生聯同新男子組合胡中和先生與張智恆先生介紹來 賓,再來抽檯獎,有拍賣有遊戲有抽獎。正當來賓享用 第一道菜的時候,司儀開始了聯歡晚會第一個環節,邀 請陳祖貽先生講述製作新麥兜銅像及運送至星光大道過 程,感謝麥兜公司送出一幅麥兜畫拍賣,當晚拍賣的 Alice親筆簽名麥兜畫,來賓為競投熱烈,競投出價都 十分踴躍,會場的氣氛亦變得十分熱鬧,最後由名譽會 長李遠發先生以港幣66,888元投得至愛麥兜畫。

今年適逢理事會會長換屆,新會長選舉於當晚同時進 行,經過會員投票後,由會計師現場監票,在沒有反對 票下一致通過,張志恒先生當選為新一任會長。



麥兜公司代表與銅像專責小組合照



李遠發名譽會長投得名畫 - 眾嘉賓同慶賀



張志恒先生 (2019-2021年度理事會會長)

晚會遊戲以人人有份參與的 BINGO 來增加氣氛,今年 的「幸運大抽獎」由多家贊助公司及贊助人提供,獎品 數量和種類都相當豐富。為使每檯都有機會中獎,故以 「波波」來代替檯號來抽獎,每當抽獎嘉賓喊出得獎檯 號時,來賓都情緒高漲,氣氛非常熱烈。除「幸運大抽 獎」的獎品,學會也為各位來賓準備了各式各樣的檯 獎。聯歡晚會在一片熱鬧歡呼聲中完滿結束,期待來年 的聯歡晚會舉辦得更加熱鬧成功。

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<u>鳴謝 Bliss Concepts Ltd.贊助麥兜畫</u>

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# 2019年第十屆高爾夫各界友好聯誼賽

第十屆高爾夫各界友好聯誼賽於 2019年4月26日在東莞鳳凰山高 爾夫球會舉行。比賽當天已踏入初 夏,雖然稍微有涼風,當天間中有 雷暴,有點烏雲蓋天,尚幸沒有下 雨。非常感謝39位好友報名參加打 球,場面熱鬧。

大家一早就到了球會,先享用午餐,整裝待發,各人到B場1號洞來拍大合照。會員部理事黃順勳博 士講解比賽規則,期待開球時刻來 臨。今年選在中午12時開球,邀請 學會候任會長張志恒先生、名譽會 長陳禮信先生、榮譽會長楊利堅博 士一同主持開球禮。之後分組駕駛 球車往球洞出發,同步開球。

學會規則按新新貝利亞計分,經過 四個多小時的角逐,各項獎於晚餐 時揭曉,並將獎盃頒授予得獎者。 本次比賽總桿冠軍獎由陳雅萍小 姐摘得,學會特別製造了一台捷克 宮廷杯,把每屆冠軍名字刻上獎杯 延續下去。為感謝各位參賽者的努 力,晚餐時進行了抽獎,讓本屆高 球聯誼賽在一片歡樂聲下完滿結束。

是次比賽得到了以下公司大力支 持,贊助場地廣告及贊助高球,在 此特別鳴謝:

正邦國際控股有限公司 永星化工有限公司 東莞市領升等離子抛光設備有限公司 香港錶面廠有限公司 嘉瑞國際控股有限公司 劉國才先生 (以上排名以筆劃序)



賽前大合照



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淨桿冠軍	楊利堅博士
淨桿亞軍	黃維柏先生
淨桿季軍	郭嘉君先生

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最遠發球獎 一 陳雅萍小姐

最近旗桿獎 - 陳校雄先生

# 2019年會員週年大會

2019年會員週年大會於2019年5月 10日(粵品匯)舉行,悉藉當天是楊 達生理事的生日,兩位會長與楊達 生理事先來慶祝生日切蛋糕,眾人 同唱生日頌,樂也融融!



慶賀楊達生理事生日

2017-2019年理事會劉利強會長宣 佈2019年會員週年大會開始。張 志恒副會長兼司庫匯報2017/2018 年度財務報告盈餘及通過由榮譽會 計師審核的2017/2018年度財務報 告,大會一致通過委任張叔千會計 師為下一屆核數師,會員全體通過 動議。劉利強會長匯報2018/2019 年學會的會務概況:會員數字、學 會活動、會刊出版、參予友會的活 動、對友會支持及協辦的活動等。

2019-2021年理事會張志恒會長報 告新理事名單,沒有其他動議及事 項,宣佈會議於下午七時五十分完 結。









## 第五屆國際表面處理發展高峰論擅 主題:表面處理緣色生產新進程

由中國表面工程協會電鍍分會、中國表面工程協會塗裝分會、廣東省塗料行 業協會聯合主辦的2019國際(廣州)表面處理 電鍍 塗裝展覽會於2019年5 月21-23日在廣州保利世貿博覽館隆重舉行!在廣州保利世貿博覽館,迎接 來自表面處理、電鍍、塗料、塗裝、環保技術、汽車、機械、電子五金、鋁 型材等相關行業人士!



同期由香港表面處理學會與廣東智展展覽有限公司聯合舉辦的論壇於2019 年5月21日,廣州保利世貿博覽館 (1.5F薔薇廳)舉行。

今屆主題主要對國內外表面處理現狀及發展趨勢、國外對廢水、廢氣治理的 最新進展,金屬工業、加工處理、產生廢水、合格排放(如有標準)處理。共 邀請四位講者嘉賓分享題目:

演講題目	嘉賓
大灣區五金行業污水零 排放 — 技術及案例分享	香港環保產業協會 (會長) 正昌科技(集團)有限公司 (董事總經理) 鄭文聰教授
智慧環保清洗 +	深圳市鑫承諾化工有限公司 (總經理) 李輝先生
脱脂槽液在綫循環凈化技 術及新型重金屬捕捉劑在 廢水處理中的應用	深圳慧欣環境技术有限公司 周友元先生 (由於孫臨泉先生因要事未能出席,由他同 事代替)
工業廢水零排放產業鏈研 究、難題講解、技術難點 與對策	《國家城市汙水處理與資源化工程技術研究 中心》專家委員/廣東區主任 袁偉光先生





2019第五届国际表面处理发展高峰论坛

鄭文聰教授



周友元先生

袁偉光先生

論壇於下午13:30開始,先由劉利強會長發表序言舉辦論壇的始末,其後由 主持人黃順勳博士介紹演講嘉賓及題目,四位嘉賓演講完畢後回到台上進行 Q&A環節,當日出席者非常踴躍發問問題,最後由劉會長頒發紀念品給四 位嘉賓,表示謝意,在下午大約17:00完結。





答問環節



講者與學會理事合照

## 展會前膽

日期	展覽會	地點
2019年8月28-30日	2019武漢國際汽車製造暨工業 裝配博覽會	武漢,國際博覽中心
2019年9月3-7日	香港鐘表展 Hong Kong Watch & Clock Fair	香港會議展覽中心 Hong Kong Convention and Exhibition Centre
2019年9月18-20日	第2屆名古屋國際汽車工業技術展	日本,名古屋國際展覽中心 Nagoya International Exhibition Hall, Japan
2019年9月20-22日	2019深圳國際高性能薄膜製造技術 科技創新博覽會	深圳會展中心
2019年10月9-11日	2019日本東京現代農業展覽會 AGRI WORLD 2019	日本,東京千業幕張國際展覽中心 Makuhari Messe, Japan
2019年10月10-12日	2019越南國際機床及金屬加工展覽會 2019 Metalex Vietnam	越南,胡志明西貢會展中心 Saigon Exhibition and Convention Center, Ho Chi Minh, Vietnam
2019年11月14-17日	SIA CHINA 2019 2019東莞智慧製造博覽會暨工業 自動化及機器人展覽會	廣州現代國際展覽中心
2019年11月18-20日	2019 第三十二屆「中國國際表面 處理展」	上海新國際博覽中心 (SNIEC)
2019年11月26-29日	DMP大灣區工業博覽會 第22屆DMP國際模具、金屬加工、 塑膠及包裝展	深圳國際會展中心
2019年12月4-6日	2019國際電子電路(深圳)展覽會	深圳會展中心1、2、4及9號館

## 環境政策資訊

# 通過《中華人民共和國固體廢物 污染環境防治法(修訂草案)》

國務院總理李克強6月5日主持召開國務院常務會議,確定按照創新驅動發 展戰略要求把大眾創業萬眾創新引向深入的措施;部署抓好農業生產、保障 農產品有效供給,要求全面做好防汛抗旱工作;通過《中華人民共和國固體 廢物污染環境防治法(修訂草案)》。

按照黨中央、國務院部署,為進一步實施創新驅動發展戰略,更大激發市場 主體活力,會議確定了把"雙創"引向深入的措施。一是發揮"雙創"支撐 就業的重要作用,提供更多適應高校畢業生、退役軍人等重點群體就業需求 的崗位。深化"放管服"改革,制定《優化營商環境條例》,降低創業創 新成本。二是發揮"雙創"促進科技創新的獨特作用。支持"雙創"示範基 地在科研立項實施、成果確權和轉化等方面先行先試。加快落實研發費用 按75%比例税前加計扣除的政策,並研究加大政策力度。三是支持打造" 雙創"平台,推動大中小企業融通發展。完善股權、薪酬等激勵機制,促進 各類企業協同創新。四是推動"互聯網+"升級。加快發展工業互聯網,拓 展"互聯網+"在醫療、養老、教育等社會領域的應用。五是引導金融機構 降低小微企業融資實際利率和綜合成本,將小微企業不良貸款容忍度從不高 於各項貸款不良率2個百分點放寬到3個百分點。鼓勵風投、創投加大對" 雙創"的支持力度。支持創業孵化機構、創投企業發債融資。

會議通過《中華人民共和國固體廢物污染環境防治法(修訂草案)》。草案 強化工業固體廢物產生者的責任,完善排污許可制度,要求加快建立生活垃 圾分類投放、收集、運輸、處理系統。會議決定將草案提請全國人大常委會 審議。

來源:【中國法院網】https://www.chinacourt.org/article/detail/2019/06/id/4007702.shtml

# 麥兜誕生的故事2019

## 學會與麥兜結緣於2011

早在2014年,學會會刊曾刊登過一篇《麥兜的新衣》 的專題,記錄了學會向麥兜創作人麥家碧小姐(以下 以Alice稱呼)提供關於麥兜銅像復修及保護的技術方 案。尖沙咀星光大道上的麥兜銅像於2011年07月28日 正式揭幕,但可惜好景不長,短短數月時間,銅像已經 出現嚴重的腐蝕問題,在2011年年底Alice向學會諮詢 有關銅像腐蝕方面的技術方案。

學會特此成立了一個專責小組,由前會長莊龍三先生帶 領,進行背景研究及實地視察,總結調查所得結論,提 供具可行性的方案,當時專責小組總結麥兜銅像短時間 出現腐蝕問題,主要原因:

- 一)銅合金質量較次與平均銅壁很薄;
- 二)銅像表面處理方法和程序存在不當;
- 三)星光大道靠近海邊,受嚴峻的大自然侵蝕,和遊客 觸摸等人為因素。

學會向Alice提供了兩組技術解決方案:

- 一)整個麥兜銅像搬遷到工場進行全的修復工程(難度 較低);
- 二)原地原址對麥兜進行修復工程(難度較高)。

最終Alice團隊擔心銅像在搬遷的時候會 出現損毀等可能性,選擇了原地原址進行 修復工程。經歷一年多與多方合作,麥 兜的新衣在2013年06月04日完成修復工 程,新衣並不能解決原本的製造缺憾,只 能作有限度的延續,但情況已有所改善。

完整文章《麥兜的新衣》可參閱《香港表 面處理學會40週年特刊2014》。香港公 共圖書館系統索書號為472.06.2351。

## 新麥兜誕生2019

尖沙咀星光大道於2015年年底,因為 「優化尖沙咀海濱計劃」而需要暫時關 閉,原本在星光大道上眾多的銅像都遷移



專責小組檢測銅像





遊人圍觀



遊人圍觀

到尖沙咀東海濱平台花園展出,安靜地 等待全新的星光大道到來。

2018年年中學會收到Alice團隊關於重 新鑄造麥兜銅像的查詢。正如上文提 到,因為麥兜銅像的製造缺憾是無法透 過表面處理解決,所以Alice團隊希望 在2019年星光大道重開前,可以鑄造 一個全新的銅像,讓市民及遊客可以欣 賞到更完美的麥兜銅像。於是學會成立 了專責小組,並由時任會長劉利強先生 及外務部部長陳祖貽先生帶領,於2018 年4月26日一行八人來到位於北角Alice 團隊的辦公室。古語雲:「金無足赤,

人無完人」,每一種表面處理技術都會存在著優點及缺點,在這次拜訪Alice團隊,是希望聆聽他們對新麥兜 銅像的要求及想法,而在場的學會專家成員亦即場提供 相關的技術介紹及限制,希望在討論的過程中,得到一 個確實可行的方向。

一般銅像戶外保護都是用化學發黑,做成不同色調的 古銅外觀,如匯豐銀行外的銅鑄件及各處的銅雕像皆如 如此,好處是比較耐久,及不需要頻繁的補修,但麥兜 銅像是動漫主角,Alice團隊對此有不同的要求,鑑於 2011年所做的銅像,化學發色後外觀黝黑,對兒童觀 感甚為不討好,Alice團隊要求要保持原有鑄造的黃銅 原色,作為銅像的底色,經過與他們團隊交流後,所得 技術要求如下:

- 新銅像顏色盡量保持黃銅底色,所以表面漆層是透明為主。
- 新銅像放置的地方較接近海邊,表面漆的耐腐能力 要求高。
- 新銅像放在星光大道地面,以便遊人隨意觸摸,所
   以表層的耐磨性有要求,並且可以修補及維護。

學會專家成員會如何回應Alice團隊的要求?而製作新 麥兜銅像有沒有遇到甚麼困難?怎樣面對和解決?

因為要達到第一點的要求,所以鑄造黃銅的成份有規格

的要求。第一是流動性要求稍高,及銅像要以原色示人,盡量不可以分段鑄造之後再焊合。因是焊合綫的結晶與之後再焊合綫的結晶與之後,原因是焊合綫的結晶與之後,因是焊合綫的結晶有差異。日後必會在銅像上顯示出來,做成分格的外觀,對一體鑄造比較相關。一體鑄造比較相配。一體鑄造的人類。有不良影響有錫。一體鑄造的人類。其間和液的的現象。其間和液的的現象。其間我們建議一個人類的



保護塗層的帳幕

成白色的,我們便可以改用不鏽鋼來製作,這樣便可以 用模鍛方式焊接成像,效果更有保證。及不鏽鋼的抗海 水鏽蝕的能力比黃銅強得多,但Alice是要求麥兜銅像 必須是一個可以給人們一個溫暖的感覺,因不鏽鋼是白 色的,色溫比較冷而不被採用。

在如此多的不利環境下,即使我們用上了各式各樣保護 銅像的方法,最後都會必定會被鏽蝕的。因為我們在考 慮製作新的銅像時,必須要考慮如何維護銅像,所以在 新製造銅像時,必須要考慮在大修時,銅像可以比較 容易拆卸,運送回廠來進行大修;而平時也必須製訂

一個合理的維修方案,使銅像可以有一個較長的時間可以呈現一個比較光亮的 表面,其實這是最困難的,原因是全世 界都沒有一個類似的案例。首先是銅像 的放置的位置是在海邊;二來是在一個 空曠及有十分猛烈陽光,即是暴露在強 UV照射的地方;三來十分多遊人會觸摸 到,尤其是一些特定的位置,磨損的速 度都會不同的。

在後來銅像交付後,麥兜團隊對於初次 所做的底座有意見,並對凸起的星星提 議出有關安全的耽心,建議再設計了一 個以馬賽克堆砌的底座以增加安全及美



於麥兜銅像位置視察



包裝銅像趕赴星光大道



原創者謝立文噴塗時到訪

觀,但不可拆開,這便使得日後的 維修保養必須在現場進行。

針對以上的問題,我們從舊的銅像 的磨損情況,我們最好製訂每隔一 段時間最好在不同的最嚴重磨損的 位置,進行保護層厚度的測量,尤 其是新開始開放給遊人可以觸摸 時,從而估算遊人觸摸對保護層磨 損的速度是多少,在保護層厚度下 降至某一個厚度時,必須進行保護 層的加厚,而保護層的加厚,最理 想是可以十分簡單地進行補油。保 護層用上了全透明的PU膜層,雖然 已經對此UV漆做了防UV的處理, 但是在如果嚴苛的環境及極高UV照 射的情況下,此層全透明的PU膜層 都會出現變化,在此情況下,我們 便必須將所有舊的保護膜層脱掉, 再重新再做保護處理。



2019年6月補修銅像



2019年6月補修銅像

# 《IUSF,Interfinish與你》

上回提到,約在1909年左右,世界上開始出現一些專業的、著重科學研究 的表面處理組織,例如:美國的American Electroplaters Society (AES) 和英國的Electrodepositors Technical Society (EDTS)。它們成立的主要 目的是聯繫當地的業界人員,舉行會議進行技術交流,和提升表面處理技術。

## IUSF的成立:

之後世界經歷兩次世界大戰(第一次世界大戰[1914-1918];第二次世界大戰[1939-1945]),造成了大量人命傷亡,戰爭對社會、經濟、科技亦產生

巨大的影響。電子技術群因 戰爭的需要得到發展,電子 通訊器材改進及應用亦逐漸 普及。戰爭結束後不久,多 個國際性組織成立,例如: 聯合國、國際貨幣基金組織 等,確立了維護戰後世界秩 序的國際制度,世界也逐步 恢復原來的面貌。

戰爭結束後,作為EDTS founding assistant secretary

(不懂正確英譯中)的Simon Wernick博士,打算繼續進 行之前建立的三邊會議(英 國、荷蘭和比利時),進行 技術交流,並希望將會議擴 展到整個歐洲。當時正值是 社會經濟復甦期,對國際性 會議的需求殷切,順理成章 EDTS提出主辦相關會議,並 提出成立一個國際性協會, 將世界各地的表面處理組織 聯會一起。IUSF在這個背景 下正式成立。



## International Union for Surface Finishing

President : Prof. Nagahin Immediate Past President : MA Jie, Vice-President: Prof. Sungmo Secretary General : Madhav Singh Treasuret : Dr. Lo Wai Yi Honorary Vice-President : Clive M. Whit

gmo Moon, Korea ingh, India ai Yin, Hong Kon Whittington, Australia

Dear Surface Finishing Friends,

Last September, I was elected President of the International Union for Surface Finishing (IUSF) for the years 2018-2022, which will feature the 4-Yearly 2020 Interfinish Congress, to be held in Nagoya, Japan.

Along with fellow members of the Executive Council, I am pleased to introduce the new IUSF website kindly prepared by Mr Madhav Singh, Secretary General: https://www.iusf.world/

We trust this provides a complete insight into the long history and well-established activities of the Union, whose singular objective is the betterment of the surface finishing industry worldwide. All of us are volunteers drawn from National technical organisations who are accredited Members of the IUSF, focused upon freely sharing the latest ideas on products and processing technology.

All current IUSF Member organisations are invited to use this site to publicise their latest news of events and educational programs. While sponsorship and advertising will be available for individuals and companies who wish to promote their commercial activities globally.

We trust you find this new website beneficial, and welcome your comments and suggestions.

Yours in surface finishing.

Nagatin Sars

Prof. Nagahiro Saito Dr.Eng IUSF President

> Secretariat: Madhav Singh c/o Metal Finishers' Association of India, 202- 203, Atlanta Estate, Vibbatti, Goregaon-Mulund Link Road, Off W. E. Highway, Goregaon (E), Mumbai - 400063. Malamashtra, India. Tel :+91-22-29277291, +91-22-49240693 • Email: relianceatotech@yahoo.com • Website: www.iusf.world

# 《金屬腐蝕的原理》

本專題的目的是希望將金屬腐蝕的原理,從學術的 角度,以簡單明瞭的方式向讀者進行解説。如讀者 對此題目有興趣或疑問,希望有更深入的瞭解,可 聯絡本會專家學者。

日常生活中隨處可見「腐蝕」的影響,很久以前就已經引起了科學家的興趣,並進行深入的研究。時至今日,「腐蝕」已經發展成為一獨立的科學 ——「腐蝕科學(Corrosion Science)」。上期《金屬腐蝕的原理》非常 粗略的解説了「吉布斯能(Gibbs Free Energy)」、「化學腐蝕」和「電 化學腐蝕」。本期我們將聊聊保護金屬表面的氧化膜。

## 既是魔鬼,又是天使的「氧氣」

「讓金屬腐蝕是氧氣,讓金屬耐腐蝕也是氧氣。」這句話的前半部分,我相 信各位讀者都理解的(可以參考上期內容),但是後半部分該怎麼理解呢? 為什麼説氧氣能讓金屬耐腐蝕呢?

當金屬與空氣接觸就會發生腐蝕反應,形成氧化物,這是很正常的反應。關 鍵是這個氧化物是否具備良好的保護性能,這就取決於金屬材料和腐蝕反應 的環境條件。接下來,我們以鐵、鋁為例,説明這個具保護性能的氧化物。

假設我們準備好2片打磨至相同光潔度的鐵片,之後做以下的實驗:

	鐵片1:	鐵片2:
步驟1:	放在恆溫~25℃和恆濕~90% 的箱裏	放在乾燥箱中24小時
步驟2:	不適用	放在恆溫~25℃和恆濕~90% 的箱裏
測試:	觀察和量度生鏽出現的時間	觀察和量度生鏽出現的時間

經過以上的小實驗,我們會發現鐵片2的耐腐蝕能力比鐵片1高,需要更長 的時間才出現腐蝕現像。這是因為放在乾燥箱中的24小時裏,鐵片的表面 生成了一層氧化物,這層氧化物保護著底層鐵片,緩慢了金屬腐蝕的速度。

雖然說鐵片表面在空氣中形成了一 層具有保護性的氧化物,但是其保 護能力不強,只能勉強緩慢腐蝕速 度而已,接下來讓我們一起看看保 護性能強的金屬 — 鋁。



## 能自愈的氧化物保護膜?

不同金屬材料表面的氧化物對基底保護能力都是不一樣,有的保護能力很強 (例如:鈦和鋁),有的保護能力很弱。在進行強弱對比解説之前,先回顧 一下69期提到常用金屬的電負性排序(從活潑至不活潑):

鉀、鈉、鋰、鈣、鎂、鈦、鋁、鋅、鉻、鐵、鈷、銅、鎳、銀、錫、汞、鈀、鉑、鎢、金

在這個排序當中,讀者也許會發現,鈦和鋁的電負性排序都比鐵活潑,那就 是說鈦和鋁金屬更容易失去價電子,更容易與氧生成氧化物。但是,我們在 日常生活中鋁製品比鐵製品更能抵抗腐蝕保持光澤?就像鋁製浴室用具,鋁 製窗框等,就算它們是經常曝露在戶外或者潮濕的環境,都沒有明顯的生鏽 情況。這是為什麼呢?

這是因為鋁製品的表面也覆蓋了一層氧化物膜,這層氧化物膜很薄很薄(納 米級別),對製品起到了保護的作用,因為很薄所以我們眼睛是看不出這層 氧化膜。有這層氧化膜保護基底金屬,延緩了腐蝕的速度,使得鋁製品在空 氣中不能表現出它原有的化學活潑性。

鐵製品表面可以生成氧化物膜, 鋁製品表面也可以生成氧化物膜, 不同的地 方在於鋁製品的氧化物膜具有自愈能力。一般的鐵製品就算是表面覆蓋著一 層氧化物膜,但是當這層氧化物膜遭遇到劃破,就失去了保護能力,氧化生 鏽就會從劃破的裂縫開始出現。就算是沒有遭到劃破,鐵表面上的氧化物膜 保護能力也是很弱,過一段時間後還是會出現氧化生鏽的情況。

鋁製品就有點不一樣了,鋁製品表面的氧化物膜保護能力比鐵強,而且鋁製品的氧化物膜具有自愈能力。當表面遭到劃破,被劃破的地方會生成新的具 有保護能力的氧化物膜,保護基底金屬不被氧化腐蝕,這就是鋁氧化物膜的 自愈能力。鈦金屬的自愈能力更為強大。

## 下期再會

本期的內容主要是為大家解説了氧氣對金屬的兩重作用,以及解説了為甚麼化學活潑性更高的鋁比鐵有更強的防腐蝕能力。下期我們會繼續深入探討腐蝕這個話題。如對本期的內容感興趣,可以在網絡上搜索:氧化物膜 (Oxidation film)、鈍化膜(Passivating film),作深度學習。

# 如何應對新法規下的鉻霧管控

這些年,國家全方面推廣表三排放標準,實施了最嚴格的新環保法,對廣大 電鍍企業提出了更加嚴峻的考驗。而在電鍍銘時,因為鍍銘溶液電流效率極 低,一般只有12-30%,大部分的電流用於電解水,在陰陽極周圍會產生大 量的氫氣和氧氣,氣體的析出形成了一種含有鉻酸的有毒霧氣,對電鍍生產 線的操作人員造成了健康危害。同樣情況亦發生在塑膠電鍍前處理的粗化工 藝和含鉻的陽極氧化工藝,所以需要一些手段去抑制這種危害並達到排放標 準。



目前市面上有以下幾種方式來抑制銘霧:



1. 使用完全封閉的電鍍線加抽風噴淋回收系統來抑制銘霧,如下圖:

整個電鍍線都是完全封閉的,車間沒有銘霧,另外經過兩級噴淋回收, 最終排放的銘霧能夠達到0.006mg/m3以下,遠遠低於國標(III)環保 要求的0.05mg/m3。但設備成本較高,一般電鍍廠家很難承受。

 使用一種乒乓球類型的塑膠球。這種方式可以抑制一部份銘霧,但效果 並不理想,很難達到國標(Ⅲ)環保要求。

 使用專門的鉻霧抑制劑。 鉻霧抑制劑主要分2大類,分別是高泡型和低 泡型。高泡型主要用於塑膠粗化工藝,好處是操作簡單、易於管控。而 低泡型多用於電鍍鉻工藝,尤其是功能性鍍鉻工藝。

最早的鉻霧抑制劑都含有一種叫做全氟辛烷磺醯基化合物(PFOS)的物質,而近幾十年PFOS一直是鉻霧抑制劑的主要成分。



全氟辛烷磺醯基化合物 (PFOS)

PFOS是一種非常穩定的化學物質,能在高溫鉻鍍液的環境下保持穩定,不易分解。

PFOS也是一種可在生物體內持續積累的有毒物質,大多數國家已在多個應用領域上禁止使用該物質。

以下國家已相繼出臺針對PFOS的法規,禁止在鉻鍍液使用該物質:日本-於2010年禁止使用;加拿大-於2013年5月底禁止使用;美國-於2015年9月21日禁止使用;我國-於2019年3月26日亦已禁止生產流通使用(見公告)。

生態環境部,外交部,國家發展和改革委員會,科學技術部, 工業和信息化部,農業農村部,商務部,國家衛生健康委員會, 應急管理部,海關總署,國家市場監督管理總局

#### 公 告

公告 2019年 第10號

關於禁止生產、流通、使用和進出口林丹等持久性有機 污染物的公告

為落實《關於持久性有機污染物的斯德哥爾摩公約》履約要求,現就林 丹、硫丹、全氟辛基磺酸及其鹽類和全氟辛基磺酰氟管理的有關事項公 告如下。

- 一、自2019年3月26日起,禁止林丹和硫丹的生產、流通、使用和進出口。
- 二、自2019年3月26日起,禁止全氟辛基磺酸及其鹽類和全氟辛基磺 酰氟除可接受用途(見附件)外的生產、流通、使用和進出口。
- 三、各級生態環境、發展改革、工業和信息化、農業農村、商務、衛 生健康、應急管理、海關、市場監管等部門,應按照國家有關法 律法規的規定,加強對上述持久性有機污染物生產、流通、使用 和進出口的監督管理。一旦發現違反公告的行為,嚴肅查處。
- \* 附件:全氟辛基磺酸及其鹽類和全氟辛基磺酰氟可接受用途

## 生態環境部,外交部,發展改革委,科技部,工業和信息化部, 農業農村部,商務部,衛生健康委,應急部,海關總署,市場監管總局 2019年3月4日

\* 附件;全氟辛基磺酸及其鹽類和全氟辛基磺酰氟可接受用途 (生態環境部辦公廳2019年3月11日印發)

依據《關於持久性有機污染物的斯德哥爾摩公約》,全氟辛基磺酸及其 鹽類和全氟辛基磺酰氟的可接受用途是用於下列用途的生產和使用:

- 一、 照片成像;
- 二、 半導體器件的光阻劑和防反射塗層;
- 三、 化合物半導體和陶瓷濾芯的刻蝕劑;
- 四、 航空液壓油;
- 五、 只用於閉環系統的金屬電鍍(硬金屬電鍍);
- 六、某些醫療設備(如乙烯四氟乙烯共聚物(ETFE)層和無線電屏蔽 ETFE的生產,體外診斷醫療設備和CCD濾色儀);
- 七、 滅火泡沫。

為了應對新環保法規下的鉻霧管理,市場上出現了一些不含PFOS的鉻霧抑 制劑。它通過降低鍍液的表面張力,減小溶液中氫氣和氧氣氣泡的大小,從 而減少氣體上升的浮力和速度,降低破裂時噴射的力度,從而減少銘霧形

成;另外也降低了氣泡在溶液表面向空氣噴射液滴的力度,減少鉻霧形成; 同時也會在陽極和陰極周圍形成泡沫,有助於抑制破裂噴射的液滴形成鉻 霧,從而減少鉻霧形成。



這種環保型不含PFOS的鉻霧抑制劑,通常依靠安培小時消耗來添加,並使 用溶液的表面張力來控制,而不是像以往那些電鍍師傅或操作工通過鍍液表 面泡沫量來控制。一般要求表面張力控制在35達因/釐米以下,才有較好的 抑制鉻霧效果。表面張力可以通過一種玻璃管表面張力滴重計來檢測,有條 件的廠家也可以購買表面張力檢測儀檢測,或者目前一些國際大型的化學品 供應商都有自己的檢測中心,可以定期給廠家檢測表面張力。



表面張力滴重計



表面張力檢測儀



使用鉻霧抑制劑有以下幾個方面的好處:

- 減少鉻霧的形成
- 減少空氣污染
- 减少六價鉻吸入排氣系統
  - 降低排氣系統負荷
  - 排氣系統能更久地保持潔淨
    - ◆ 維護頻率降低
- 降低操作者接觸六價鉻的機會
  - 減少化學品的消耗
  - 減少化學品帶入清洗槽
  - 減少化學品吸入排氣系統
  - 降低帶出損失
  - 設備污染程度減弱
  - 維護頻率降低

總體來說,使用不含PFOS的鉻霧抑制劑是最合適的抑制鉻霧的手段,它既 能有效的抑制鉻霧,減少空氣污染,也能滿足新型環保法規的要求。這種 鉻霧抑制劑也能應用於電鍍硬鉻,裝飾六價鉻,塑膠鉻酸粗化以及鉻酸陽 極氧化中。

面臨越來越嚴峻的環保法規,也為了保護我們的環境和操作者的健康,越 來越多的行業,以往都不使用鉻霧抑制劑,比如工程機械活塞桿鍍硬鉻以 及印刷輥筒鍍硬鉻,但目前因為環保要求,也有部分廠家開始陸續使用鉻 霧抑制劑。這是一種趨勢,不然很難達到環保要求。

總之,使用銘霧抑制劑是電鍍六價銘塑膠粗化以及陽極氧化最經濟實惠的 選擇。

# 雙重激光混合抛光技術 優質・環保・經濟・快速

黎少斌

香港生產力促進局首席數碼總監

金屬表面打磨拋光可以提高產品的表面光潔度、改善光學和耐腐蝕能力、降 低磨擦阻力,也會影響消費者對產品的觀感。香港生產力促進局(生產力 局)在香港特區政府創新及科技基金的支持下,開發了創新的「雙重激光混 合拋光技術」,混合了粗拋光和精細拋光的兩種模式,集「優質、環保、經 濟、快速」四大優點於一身。處理精密零件的時間更可由三小時,大幅縮短 至15分鐘,生產效率顯著提升。

## 傳統機械式打磨拋光局限

傳統的打磨拋光方法需要大量人手和相對耗時,處理一些形狀複雜的零件往 往可佔生產週期的30%至50%。隨著不少消費電子產品或醫療設備走向複 雜化,大大增加市場對複雜零件的需求;然而,複雜零件的高精度打磨拋光 難度極高,因為其打磨加工餘量已接近公差,需要熟練的技術人員才可打磨 出如此精密的效果。對於模具製造業而言,打磨拋光更是一絲不苟,稍一不 慎便會損壞成本高昂的模具。

現時已有研究將打磨拋光系統跟機械手或數控加工中心整合為自動化系統, 可降低加工成本和縮短交貨期,但始終未能克服傳統機械式打磨拋光的局限,難以有效處理形狀複雜、具有精細紋理、多面和利角的零件。

另外,在打磨抛光過程會產生懸浮粒子,造成環境污染,可能傷害呼吸系統,故難以吸引年輕一代入行。

### 粗抛光和精細抛光混合模式

隨著激光技術的進步,激光束近年已應用到金屬拋光的層面。激光束精準照 射到零件表面,使薄薄的表層材料瞬間熔化,然而在表面張力下流動,形成 光滑表面,達到拋光目的。由於激光束的軌跡、溫度和速度都便於控制,善 用不同能量密度和波長的激光束,形成光滑的拋光效果和精細的表面紋理, 過程毋須接觸材料表面。

生產力局新開發的激光拋光設備可提供兩種模式,分別使用連續激光進行粗 抛光(Ra = 0.4 - 10 μm),或混合使用連續激光和脈衝激光進行精細拋 光(Ra = 0.1 - 0.4 μm)。由於激光加工可瞬間加熱和冷卻,零件表面的 加熱範圍和熔化深度均嚴格受控,有助減少加工過程對工件物理性質和精度 的影響,可處理傳統方法難以拋光的複雜曲面。由於激光本身經電腦控制, 為生產管理流程數碼化奠下基礎。

## 雙重激光混合抛光技術四大優點

優質	<ul> <li>光滑度可高達Ra = 0.1 µm</li> <li>尺寸精準,品質穩定</li> <li>可處理錯綜複雜的幾何面</li> <li>可局部拋光,營造精細的表面紋理</li> <li>不會在工件表面留下雜質</li> <li>減少微孔或裂紋缺陷</li> </ul>
環保	<ul> <li>不會產生懸浮粒子</li> <li>不使用化學試劑</li> <li>不會產生污水</li> </ul>
經濟	• 節省人力成本
快速	● 自動化加工 ● 大幅縮短加工時間

### 實例圖示Experimental Results



**模具鋼試件** 經過雙重激光抛光,表面光潔度由 Ra≈2.6µm提升至Ra≈0.12µm

Tooling Steel Plate Surface roughness enhanced from Ra≈2.6µm to Ra≈0.12µm after dual laser polishing





**熱作鋼玻璃杯模具試件(激光抛光)** 模腔內的陝長形狀,人手不易打磨,經 激光拋光處理後,光潔度為Ra≈0.15

Hot-work Die Steel for Wine Glass The long shaped cavity is laser polished to a fine roughness of Ra≈0.15 which was difficult to achieve by manual polishing



**鈦合金心臟起搏器零件** (德國Fraunhofer ILT提供) 抛光過程毋須使用化學品, 避免污染醫學零件; 相比傳統打磨拋光工藝,加工時間可 由三小時大幅縮短至15分鐘

Implant Medical Part Made of Titanium Alloy (Courtesy: Fraunhofer ILT) Requires no chemicals for polishing and shortens lead-time significantly from 3 hours to 15 mins



透鏡注塑模具 粗銑削加工後,直接以激光抛光去除刀紋,可節 省人手粗打磨工序,光潔度為Ra~0.15

Injection Mould for Lens The cutting face is polished to a fine roughness of Ra≈0.15 by laser right after rough milling which saves the rough grinding process



**不鏽鋼錶零部件** 利用電腦輔助設計軟件, 以電腦編程進行自動化激光抛光, 處理複雜曲面和利角效果佳

Stainless Steel Watch Parts Automated laser polishing with computer-aided design software for parts with complicated geometries and sharp ends

## 發展計劃

速度和效率兼備的激光抛光技術,可大大提高抛光效果,適用於本地多個工業,包括:模具、汽車零部件、醫療植入件、珠寶、鐘錶等,也可應用於改善者3D金屬打印產品的「粗糙面」,極具發展潛力。生產力局通過是次研發

項目,開發了一部雙重激光混合拋光設備,將激光拋光技術的加以發揮,可 處理形狀複雜的零部件。研發團隊已將當中的經驗,例如各技術參數對拋光 情況的影響,並編製成技術指南,詳細説明激光拋光系統設計、原理、工藝 設計、參數配置等關鍵要素,協助本地工業掌握當中的技術重點,推動雙重 激光混合拋光技術的發展應用。

生產力局正為這創新的混合式激光拋光技術申請專利,下一步計劃與汽車 零部件行業合作,率先將有關設備應用到汽車輪圈壓鑄模具打磨方面。未 來,研發團隊會利用數控的雙激光拋光機,通過感應器收集工藝參數,融入 「工業4.0」的工業物聯網(IIoT),自動收集和分析生產數據,提高生產 效率。

以上資訊由香港生產力促進局提供。如有查詢,請致電2788 5555或 電郵至service@hkpc.org。

## Dual Laser Polishing Technology -A Better Quality, Eco-friendly, Cost-effective and Efficient Solution

Edmond Lai Chief Digital Director, Hong Kong Productivity Council

Metal Surface Finishing could significantly reduce surface roughness and friction, improve optical properties, enhance corrosion resistance, as well as uplift visual impression of the end product. The Hong Kong Productivity Council (HKPC), with the support of the Innovation and Technology Fund of the Hong Kong SAR Government, has developed a novel "Dual Laser Polishing Technology", a combination of rough and fine polishing that provides a better quality, eco-friendly, cost-effective and efficient metal surface finishing solution to the industry. The lead-time of precision part polishing could be drastically shortened from 3 hours to 15 minutes, the production efficiency is then significantly improved.

## Limitations of conventional mechanical polishing

The conventional mechanical polishing process is labour-intensive and timeconsuming, for parts with complicated geometries could take up 30% to 50% of the production cycle. The demand on complex parts is significantly increased due to the trend of highly integrated consumer electronics or even medical device. Since the polishing allowance is very close to its tolerance, achieving precision micro-polishing on micro-parts is yet challenging which could only be handled by skillful technicians. Particularly for the mould and die industry, any tiny error or defect can make irreversible damage on the costly toolings.

Nowadays, some surface finishing systems are integrated with robotic arm and CNC machine centre to provide an automated metal polishing solution at lower cost and shorten lead-time, without overcoming the inherent limitations of conventional mechanical polishing process, not applicable for parts with complicated geometries, fine surface texture and sharp ends.

The suspended particulate generated in the process might be damaging to the environment, and could be harmful to the respiratory systems of human beings. These could be a barrier to engage young generation in the metal polishing industry.

## **Combination of Rough and Fine Polishing**

With the advancement of laser technology, laser beam is made applicable to metal surface finishing. A thin layer of material is molten to flow under surface tension by a laser beam with controllable path, temperature and speed to form a smooth surface. It helps achieving the purpose of metal polishing for intricate surface and fine surface

texture under a contactless process.

The novel laser polishing system, developed by HKPC, offers dual mode processing of rough polishing ( $Ra = 0.4 - 10 \mu m$ ) by Continuous-Wave (CW) lasers and fine polishing ( $Ra = 0.2 - 0.4 \mu m$ ) by combining CW lasers with pulsed lasers. Due to the rapid heating and cooling in the laser polishing process, the heating area and melting depth of the workpiece are strictly controllable. This helps minimise the influence of the machining process on the physical properties and precision of the workpiece, making this innovative process applicable to intricate surfaces that were difficult to be polished by conventional methods. The computer-controlled laser builds a strong foundation for the digitalisation of production management processes.

Better Quality	<ul> <li>Fine surface finishing up to Ra = 0.1 μm</li> <li>High dimensional accuracy and repeatability</li> <li>Capable of polishing intricate surface</li> <li>Enable selective polishing for excellent surface finish on fine surface texture</li> <li>Enhanced accessibility</li> <li>No contaminant left on the surface</li> <li>Reduce surface pores and cracks</li> </ul>
Eco-friendly	<ul> <li>No suspended particulate generation</li> <li>Chemical-free</li> <li>No waste water discharge</li> </ul>
Cost-effective	Reduce labour costs
Efficient	<ul><li>Automated process</li><li>Shorten lead-time</li></ul>

## **4 Major Competitive Advantages**

## **Further Development**

Laser polishing, as a fast and efficient innovative technology, can greatly enhance the surface quality and productivity. It demonstrates great potentials for various local industries, including mould and die, automotive parts, medical implants, jewellery,

watch and clock, etc. The technology can also be used to improve the surface quality of 3D metal printing products. Through this R&D project, HKPC has developed a dual laser polishing system, making good use of the advantages of laser polishing for parts with complicated geometries. The R&D team has compiled a guidebook to incorporate the key findings, such as the detailed laser polishing system design, physical mechanism, process design, parameter configuration, etc., assisting the local industry to deploy the dual laser polishing technology.

Patent for this novel hybrid laser polishing technology is pending. HKPC plans to collaborate with automotive parts industry to apply the system in wheel rim die casting mould polishing process. In the future, the R&D team will make use of the CNC dual laser polishing system to collect process parameters through sensors, enabling the integration of the Industrial Internet of Things (IIoT) for automatic production data collection and analysis, aiming at better productivity and efficiency.

Above information is provided by Hong Kong Productivity Council. For details, please call 2788 5555 or email to service@hkpc.org.

## Influence of cerium oxide (CeO<sub>2</sub>) nanoparticles on the microstructure and hardness of tin-silver-copper (Sn-Ag-Cu) solders on silver (Ag) surface-finished copper (Cu) substrates

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Abstract Nano-sized, non-reacting, non-coarsening CeO<sub>2</sub> particles with a density close to that of solder alloy were incorporated into Sn-3.0 wt%Ag-0.5 wt%Cu solder paste. The interfacial microstructure and hardness of Ag surfacefinished Cu substrates were investigated, as a function of reaction time, at various temperatures. After the initial reaction, an island-shaped Cu<sub>6</sub>Sn<sub>5</sub> intermetallic compound (IMC) layer was clearly observed at the interfaces of the Sn-Ag-Cu based solders/immersion Ag plated Cu substrates. However, after a prolonged reaction, a very thin, firmly adhering Cu<sub>3</sub>Sn IMC layer was observed between the Cu<sub>6</sub>Sn<sub>5</sub> IMC layer and the substrates. Rod-like Ag<sub>3</sub>Sn IMC particles were also clearly observed at the interfaces. At the interfaces of the Sn-Ag-Cu based solder-Ag/Ni metallized Cu substrates, a (Cu, Ni)-Sn IMC layer was found. Rod-like Ag<sub>3</sub>Sn and needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC particles were also observed on the top surface of the (Cu, Ni)-Sn IMC layer. As the temperature and reaction time increased, so did the thickness of the IMC layers. In the solder ball region of both systems, a fine microstructure of Ag<sub>3</sub>Sn, Cu<sub>6</sub>Sn<sub>5</sub> IMC particles appeared in the  $\beta$ -Sn matrix. However, the growth behavior of the IMC layers of composite solder doped with CeO<sub>2</sub> nanoparticles was inhibited, due to an accumulation of surface-active CeO<sub>2</sub> nanoparticles at the grain boundary or in the IMC layers. In addition, the composite solder joint doped with CeO<sub>2</sub> nanoparticles had a higher hardness value

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than the plain Sn–Ag–Cu solder joints, due to a well-controlled fine microstructure and uniformly distributed CeO<sub>2</sub> nanoparticles. After 5 min of reaction on immersion Agplated Cu substrates at 250 °C, the micro-hardness values of the plain Sn–Ag–Cu solder joint and the composite solder joints containing 1 wt% of CeO<sub>2</sub> nanoparticles were approximately 16.6 and 18.6 Hv, respectively. However after 30 min of reaction, the hardness values were approximately 14.4 and 16.6 Hv, while the micro-hardness values of the plain Sn–Ag–Cu solder joints and the composite solder joints on Ag/Ni metallized Cu substrates after 5 min of reaction at 250 °C were approximately 15.9 and 17.4 Hv, respectively. After 30 min of reaction, values of approximately 14.4 and 15.5 Hv were recorded.

#### **1** Introduction

To address the health and environmental safety concerns associated with lead and lead-containing alloys, research has been conducted over the past decade to find suitable lead-free solder alloys to replace the eutectic Sn-37Pb solder that has typically been used for interconnection in electronic assembly [1-4]. Much of this research has focused on the development of lead-free, Sn-based, binary and ternary systems-including those associated with Sn-Bi, Sn-Zn, Sn-Zn-Bi, Sn-Ag, Sn-Ag-Zn, Sn-Zn-In, Sn-Bi-Ag, and Sn-Ag-Cu [5-8]. Of these, ternary Sn-Ag-Cu solder alloys, with near eutectic compositions and melting temperatures of around 217 °C, have been regarded as possible replacements for the traditional Sn-Pb solder used in the electronic packaging industry [9, 10]. However, minimizing the excessive growth behavior of the intermetallic compound (IMC) layers at their interface with the mechanical properties of the solder joint reduces the

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reliability and lifespan of the electronic packaging systems [11]. The formation of coarse primary dendrite-shaped  $\beta$ -Sn grains in the Sn–Ag–Cu solder also retards the resistance to thermal–mechanical fatigue [12].

As electronic and optical devices become more integrated and miniaturized, electronic packaging is crucial for achieving a higher input/output density, higher speed, smaller, thinner and more portable features, and to increase performance and improve the thermo-mechanical characteristics. The extremely small size of advanced electronic devices, combined with the size of the solder bump, can significantly increase the current density [13]. Since Joule heating is proportional to the square of the current density, the local temperatures of conductive lines and solder bumps will increase substantially which minimize the lifetime of electronic devices. In general, several factors can affect the reliability of solders, such as creep resistance, yield strength, thermo-mechanical fatigue resistance—and electrical conductivity [14]. During the reflow process, IMC layers will inevitably form at the interface between the solder and the substrate and, due to solid-state diffusion, these layers increase in thickness over successive reflow cycles and thermal aging stages [15]. Both the properties of solder joints and the reliability of the whole system are sensitive to the thickness and morphology of the IMC layers at the interfaces of the joints [16].

Studies have shown that the development of composite lead-free solders by mechanically adding micro/nano-sized particles into Sn-based lead-free solder matrices enhances their wettability and mechanical properties [17]. Metallic micro/nano-sized alloys of elements such as silver, copper, nickel, antimony, and bismuth improve the mechanical properties of a lead-free solder, and simultaneously reduce the melting point. Moreover, various nano-sized, nonreacting, non-coarsening oxide dispersoids incorporated into solder alloys create a new improved solder structure, significantly enhancing creep resistance and increasing strength [18]. Mavoori and Jin reinforced a conventional Sn-Pb solder with 5 nm TiO<sub>2</sub> and 10 nm Al<sub>2</sub>O<sub>3</sub> particlesand reported significant improvements in creep resistance and mechanical properties [19]. Tsao and Chang [20] prepared a series of Sn-3.5Ag-0.25Cu composite solders reinforced with different weight percentages (0, 0.25, 0.5 and 1 wt%) of TiO2 nanoparticles, and measured their mechanical properties. Those containing 1 wt% TiO<sub>2</sub> nanoparticles exhibited significant improvements in the yield strength, micro-hardness, and ultimate tensile strength. Roshanghias et al. [21] recently developed Sn-3.8Ag-0.7Cu-x(nano-CeO<sub>2</sub>) composite solder alloys through a rolling process, and found that the Sn-3.8Ag-0.7Cu-1 wt%CeO<sub>2</sub> composite solder significantly improved the material properties, such as the micro-hardness and ultimate tensile strength. Cerium oxide (CeO<sub>2</sub>) particles at the nanometer length were used in this study. The main advantages of these nanoparticles are: (a) a density that is close to that of Sn–Ag–Cu, where the density,  $\rho$ , of Sn–3Ag–0.5Cu is 7.11 and  $\rho$  for CeO<sub>2</sub> is 7.65 g/cm<sup>3</sup>, compared with densities of ceramic particles—where  $\rho$  of Al<sub>2</sub>O<sub>3</sub> is 3.97 g/cm<sup>3</sup> and  $\rho$  for TiO<sub>2</sub> is 3.89 g/cm<sup>3</sup>, and (b) a greater hardness compared with that of a Sn-3Ag-0.5Cu matrix.

No previous efforts have been made to develop lead-free  $Sn-Ag-Cu-1CeO_2$  composite solder joints on Ag surface-finished Cu substrates. This study is primarily concerned with the morphology of the IMC layer resulting from the interaction between lead-free plain Sn-Ag-Cu and  $Sn-Ag-Cu-1CeO_2$  composite solders on Ag surface-finished Cu substrates, at various temperatures, depending on the interaction time. The micro-hardness of plain Sn-Ag-Cu and Sn-Ag-Cu and

#### 2 Experimental procedure

#### 2.1 Preparation of the Ag/Ni metallized Cu pad

The Cu substrate was scrubbed with aluminum powder and washed with deionized water. Grease, oxide film, and fingerprints were removed using cleaning solution. The substrate was immersed in an electrolytic plating bath containing Charter ELSNIKE SM-1 solution. This is a sulfur-free, semi-bright nickel plating process solution that produces extremely ductile and uniform semi-bright deposits over a wide current density range. It is particularly suitable for electronic components, electroforming, and printed circuit boards. The substrate was then placed in an electrolytic silver plating bath containing an ELSTAR-A solution. This is an alkaline-cyanide bright to semi-bright, pure hi-speed silver process, suitable for either barrel or vat operations. The substrate was then rinsed with deionized water for 1 min and dried with a hairdryer.

#### 2.2 Preparation and characterization of solder joints

Composite solders were prepared by mechanically dispersing 1 wt% CeO<sub>2</sub> nanoparticles into a eutectic Sn– 3.0 wt%Ag–0.5 wt%Cu (AMTECH, USA) solder powder. The mixtures were manually blended for at least 30 min to create a uniform distribution of the nanoparticles in a water-soluble flux (Qualitek Singapore (PTE) Ltd). The paste mixture was then printed on the pre-fluxed, laboratory-prepared Ag/Ni metallized and immersion Ag-plated Cu substrates, [22] and reflowed at various temperatures



Fig. 1 SEM micrographs (a), EDS analysis (b), AFM micrograph (c) and XRD profile (d) of Ag/Ni metallized Cu substrate

from 230 to 270 °C, with different reaction times, in a convection reflow oven (BTU International, Pyramax-100N). The samples were then cooled to room temperature and each solder joint cleaned with isopropyl alcohol (IPA).

The reflowed samples were cross-sectioned using the metallographic sample preparation technique and mounted in resin to observe the microstructure characteristics. Emery paper with successively smaller grit sizes was used to grind the surface. The samples were then polished with 0.5 µm alumina powders, and the microstructures were observed with a scanning electron microscope (SEM, Philips XL 40 FEG) in the backscattered electron (BSE) imaging mode. An energy dispersive X-ray spectrometer (EDX) (EDAX International, model DX-4) was used to determine the phase compositions.

The melting characteristics of Sn–Ag–Cu–1CeO<sub>2</sub> composite solders were investigated using a differential scanning calorimeter (DSC Q 10). Here, 10 mg of each solder was placed in an aluminum pan and temperature-scanned over the range from 100 to 250 °C, with the temperature increasing at a rate of 5 °C per minute—under a nitrogen atmosphere.

#### 3 Results and discussion

#### 3.1 Characterization of the Ag-plated Cu pad

Figure 1a shows backscattered SEM micrographs of Ag/Ni metallized Cu substrates, while Fig. 1b shows the EDS and elemental analysis. Figure 1c is an AFM micrograph and Fig. 1d is an XRD profile. The micrographs confirmed that the Cu substrates were well plated with the Ag and Ni phases. The average plated layer-thickness was approximately 7.7 µm. The EDS and elemental analysis were taken from the top surface of the plated layers, shown in Fig. 1a, demonstrating that the top plated surface contained the Ag element. The AFM micrograph in Fig. 1c clearly showed that the topplated Ag layer surface was very smooth. The XRD profile in Fig. 1d showed that crystalline Ag and Ni phases with sharp peaks occurred without a Cu phase, on the Ag/Ni metallized Cu substrates. These observations confirmed that Ag/Ni surface finish plated materials coated the Cu substrates with uniform layers. On the prepared immersion Ag-plated Cu substrates, the immersion Ag layer thickness was approximately 1.2 µm [22].

Fig. 2 TEM micrograph(a) and HRTEM micrograph(b) of CeO<sub>2</sub> nanoparticles





Fig. 3 DSC curves Sn–Ag–Cu-1CeO $_2$  composite solder alloy on heating

## 3.2 Examination of CeO<sub>2</sub> nanoparticles using a transmission electron microscope (TEM)

Figure 2 illustrates: (a) bright field TEM and (b) HRTEM micrographs of  $CeO_2$  nanoparticles. The TEM image shows spherical  $CeO_2$  nanoparticles, with an average diameter of about 30 nm. In the low-magnification TEM observation (Fig. 2a), the nanoparticles inside one cluster appear to be in contact. However, the high magnification image at the bottom right-hand corner of Fig. 2a reveals spaces between some of the particles. In the HRTEM micrograph (Fig. 2b), lattice distortions were clearly observed in the inner regions, indicated by the circles in Fig. 2b. However internal defects, such as twins or dislocations, were not found within the  $CeO_2$  nanoparticles.

## 3.3 Thermal analysis of Sn-Ag-Cu-1CeO<sub>2</sub> composite solders

Figure 3 shows the DSC curves of the Sn-Ag-Cu-1CeO<sub>2</sub> composite solders. The onset and offset temperatures of the DSC curve indicate the start and end melting temperatures

of the solders. The DSC analysis showed an onset temperature for the Sn–Ag–Cu–1CeO<sub>2</sub> composite solders of approximately 217.1 °C. For the Sn–Ag–Cu solders, the onset temperature was approximately 217.0 °C [9, 10]. The melting point of the composite solders changed slightly, as the second-phase reinforcement CeO<sub>2</sub> nanoparticles changed the surface instability and the physical properties of the grain boundary/interfacial characteristics. The DSC profiles confirmed that no change to the solder process parameters, such as the reflow temperature, were necessary when applying the Sn–Ag–Cu composite solder doped with CeO<sub>2</sub> nanoparticles.

## 3.4 Microstructure observation of Sn–Ag–Cu based solders on immersion Ag plated Cu substrates

Figure 4 illustrates the backscattered SEM micrographs of (a, c) plain Sn-Ag-Cu solder and (b, d) Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on immersion Ag-plated Cu substrates, depending on the reaction time; i.e., (a, b) 5 min and (c, d) 30 min at 230 °C. At the solder/Ag-plated Cu substrate interface, an island-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC layer was clearly observed in the plain Sn-Ag-Cu solder joints-and in those containing 1 wt% of CeO2 nanoparticles. Generally the top Ag layer was completely dissolved in the molten solder, leaving the Cu layer exposed during the soldering process. At the interface, the Ag layer completely disappeared. Previous studies have also reported this rapid dissolution of Ag in liquid solder, resulting in the complete consumption of the top Ag layer, and this was explained through thermodynamics and kinetics [23]. However, as the reaction time was increased in this study, rod-shaped Ag<sub>3</sub>Sn IMC particles were clearly observed, as marked in Fig. 4c, d. Additionally, a very fine Cu<sub>3</sub>Sn IMC layer between the Cu<sub>6</sub>Sn<sub>5</sub> IMC layer and the immersion Ag plated Cu substrate appeared, as shown in the figure. The thickness of the Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn IMC layers increased with the reaction time. Various steps led to the formation of the Cu<sub>3</sub>Sn IMC layer, including (1) the dissolution of Cu from the substrate, (2) the diffusion of Cu and Sn through



Fig. 4 SEM micrographs of  $(\mathbf{a}, \mathbf{c})$  Sn-Ag-Cu and  $(\mathbf{b}, \mathbf{d})$  Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on immersion Ag plated Cu pad depending on reaction time;  $\mathbf{a}, \mathbf{b}$  5 min,  $\mathbf{c}, \mathbf{d}$  30 min at 230 °C and  $(\mathbf{e}, \mathbf{f})$  EDS and elemental analysis as marked region 'P' and 'Q' in  $(\mathbf{b}, \mathbf{d})$ 

the existing Cu<sub>3</sub>Sn layer, and (3) the conversion of Cu<sub>6</sub>Sn<sub>5</sub> into Cu<sub>3</sub>Sn at the interfaces—and the reaction of Sn with Cu at the Cu substrate and Cu<sub>3</sub>Sn interface [24]. Figure 4e, f represents the EDS and elemental analysis, taken from the regions marked 'P' and 'Q' in Fig. 4b, d. The EDS analysis confirmed that the Cu<sub>6</sub>Sn<sub>5</sub> IMC layer formed between the plain Sn–Ag–Cu based solders on immersion Ag-plated Cu substrates had a phase composition specified by 25.8 wt% Cu and 74.2 wt% Sn (39.4 at% Cu and 60.6 at% Sn). This result clearly illustrates that the thin layer of Ag became

dissolved into the solder during the soldering process. The rod-shaped IMC particles near the interface, marked 'Q' in Fig. 4d, consisted of phases with 68.6 wt% Ag and 31.4 wt% Sn (70.6 at% Ag and 29.4 at% Sn).

Figure 5 illustrates the backscattered SEM micrographs of, in Fig. 5a, c, e, plain Sn–Ag–Cu solder and, in Fig. 5b, d, f, Sn–Ag–Cu–1CeO<sub>2</sub> composite solder joints on immersion Agplated Cu substrates, as a function of the reaction time. i.e., Figure 5a, b is for 5 min reaction time, Fig. 5c, d is for 15 min reaction time—and Fig. 5e, f is for 30 min reaction time—all

**Fig. 5** SEM micrographs of (**a**, **c**, **e**) Sn-Ag-Cu and (**b**, **d**, **f**) Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on immersion Ag plated Cu substrate depending on reaction time; **a**, **b** 5 min, **c**, **d** 15 min and (**e**, **f**) 30 min at 270 °C



reaction temperature at 270 °C. At the interfaces, an islandshaped Cu<sub>6</sub>Sn<sub>5</sub> IMC layer, as shown in Fig. 4, was clearly observed. The SEM observations, shown in Figs. 4 and 5, illustrated the point that the thicknesses of both the Cu<sub>6</sub>Sn<sub>5</sub> and the Cu<sub>3</sub>Sn IMC layer types increased substantially with the reaction temperature. By increasing the reaction time, the thickness of the island-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC layer substantially increased in the plain Sn-Ag-Cu solder joints-as well as in the composite solder joints containing 1 wt% CeO<sub>2</sub> nanoparticles. However, after the addition of CeO<sub>2</sub> nanoparticles, the growth rate of the IMC layers was significantly lower than for the plain Sn-Ag-Cu solder joints. The reinforcing CeO<sub>2</sub> nanoparticles promoted a high nucleation density during solidification. It is to be expected that the plane with the maximum surface tension grows most rapidly, since the amount of adsorbed, surface-active, material is maximized.

Figure 6 shows backscattered SEM micrographs of, in Fig. 6a, b, plain Sn-Ag-Cu solder and, in Fig. 6c, d, Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on immersion Agplated Cu substrates taken from the solder ball regions, as a function of the reaction time: of 5 min in Fig. 6a, c and 30 min in Fig. 6b, d-at 270 °C. In these regions, networktype needle-shaped Ag<sub>3</sub>Sn IMC particles were clearly observed in the  $\beta$ -Sn matrix of both types of solder joint. The  $\beta$ -Sn matrix grain size of the particles increased with the reaction time. Furthermore, the inserted EDS spectrum was taken from the marked region as shown in Fig. 6d. From this analysis, it was confirmed that the reinforcing ceramic nanoparticles exhibited in the solder matrix. After the addition of the CeO<sub>2</sub> nanoparticles, fine microstructures appeared. A comparison with the plain Sn-Ag-Cu solder joints is given in Fig. 6c, d. It was noted that the formation of coarse primary dendrite-shaped β-Sn grains in lead-free

Fig. 6 SEM micrographs of solder ball region of  $(\mathbf{a}, \mathbf{b})$  and  $(\mathbf{c}, \mathbf{d})$  Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on immersion Ag plated Cu substrate depending on reaction time;  $\mathbf{a}, \mathbf{c}$  5 min and  $(\mathbf{b},$  $\mathbf{d})$  30 min at 270 °C



Sn based solder retarded the resistance of thermalmechanical fatigue [12]. In addition, in the existing literature it was confirmed that the actual amount of adding second phase reinforcing nanoparticles do not incorporate in the solder matrix during the reflow process [25, 26]. Haseeb et al. [26] prepared Zn nanoparticles (1–2 wt%) doped Sn–3.5Ag composite solders and reported that for the addition of 1 and 2 wt% Zn nanoparticles in the Sn– 3.5Ag solder, the actual amount of Zn incorporated into Sn–3.5Ag is 0.13 and 0.34 wt% respectively.

## 3.5 Observation of the microstructure of Sn-Ag-Cu based solders on Ag/Ni metallized Cu substrates

Figure 7 shows the backscattered SEM micrographs of (a, b) plain Sn–Ag–Cu solder and (c, d) Sn–Ag–Cu–1CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu substrates, depending on the reaction time; i.e., (a, c) 5 min, and (b, d) 30 min at 230 °C. At their interfaces, a (Cu, Ni)-Sn IMC layer was clearly observed in both solder joints after a reaction time of 5 min. A very thin Ag<sub>3</sub>Sn IMC layer with bright contrast was found to be adhering to the top surface of the (Cu, Ni)-Sn IMC layer, as identified in Fig. 7a, c. Very fine, needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC particles were also found at the interfaces. However, after increasing the reaction time by up to 30 min, very thin rod-like Ag<sub>3</sub>Sn IMC appeared, as shown in Fig. 7b, d. Remarkably, the needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC particles grew in plain Sn–Ag–Cu solder joints and

solder joints containing CeO<sub>2</sub> nanoparticles. However, after CeO<sub>2</sub> nanoparticles were added, the (Cu, Ni)–Sn IMC layer appeared thinner than in the plain Sn–Ag–Cu—on the Ag/ Ni-metallized Cu-substrate system. The most interesting phenomenon observed in the Ag/Ni-metallized Cu substrate system was that, after a longer reaction time, no brittle Cu<sub>3</sub>Sn IMC layer was found between the (Cu, Ni)–Sn IMC layer and the Ag/Ni metallized Cu substrates. Generally, the formation of a Cu<sub>3</sub>Sn IMC layer depends on the phase stability of Cu<sub>6</sub>Sn<sub>5</sub> and the IMC, according to the reaction Cu<sub>6</sub>Sn<sub>5</sub> IMC is stronger between Ni and Sn than that between Cu and Sn [24]. The retardation of the growth of the Cu<sub>3</sub>Sn occurs because the (Cu, Ni)–Sn IMC layer is more stable than the Cu<sub>6</sub>Sn<sub>5</sub> IMC layer.

Figure 8 shows the EDS and elemental analyses, taken from the regions 'P', 'Q', and 'R' marked in Fig. 7a, b, c. According to the EDX analysis, the formation of the IMC layer between the Sn–Ag–Cu based solders on Ag/Ni-metallized Cu substrates comprised 63.2 wt% Sn, 10.7 wt% Ni, and 26.1 wt% Cu. Rod-like IMC particles appeared at the interface marked 'Q' in Fig. 7b—and comprised 24.6 wt% Ag and 75.4 wt% Sn, and the fine needle-shaped IMC particles consisted of 86.0 wt% Sn and 14 wt% Cu elements.

Figure 9 shows backscattered SEM micrographs of, in Fig. 9a, b plain Sn–Ag–Cu solder and (c, d) Sn–Ag–Cu–1CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu, depending on the reaction time; i.e., (a, c) 5 min and (b, d)

**Fig. 7** SEM micrographs of (**a**, **b**) Sn–Ag–Cu solder and (**c**, **d**) Sn–Ag–Cu-1 wt%CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu pads depending on the reaction time (**a**, **c**) 5 min and (**b**, **d**) 30 min at 230 °C



Ag<sub>3</sub>Sn Ag<sub>3</sub>Sn (Cu, Ni)-Sn Acc.V Spot Magn 15.0 kV 4.0 2000x Det WD E BSE 13.7 0 (C) (**d**) Ag.S Ag<sub>3</sub>Sn (Cu, Ni)-Sn 15 0 k 'P' region 'Q' region (a) (b) Ag Sn Element Wt% At % SnL 63.2 47.33 Element Wt % At% NiK 10.7 16.13 AgL 24.6 26.4 CuK 26.1 36.54 SnL 75.4 73.6 Total 100 100 100 100 Total 18.88 12.88 14.88 6.88 4.88 6.88 12.00 14.00 2.88 4.88 8.88 2.88 8.88 18.88 'R' region (c) Element Wt % At % 76.6 SnL 86.0 CuL 14.0 23.4 100 100 Total Cu 4.88 6.88 8.88 10.00 12.88 14.86 2.88

30 min at 270 °C. From SEM observations, it was found that the (Cu, Ni)–Sn IMC layer was clearly observed in the both solder joints as the same as Fig. 7. Fine, needle-

shaped  $Cu_6Sn_5$  IMC and rod-like  $Ag_3Sn$  IMC particles adhered to the top surface of the (Cu, Ni)-Sn IMC layer, as shown in Fig. 9a, c, d. However, after a long reaction time,

**Fig. 9** SEM micrographs of (**a**, **b**) Sn–Ag–Cu solder and (**c**, **d**) Sn–Ag–Cu-1 wt%CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu pads depending on the reaction time (**a**, **c**) 5 min and (**b**, **d**) 30 min at 270 °C



the fine needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC of the plain Sn-Ag-Cu solder detached from the top surface of the (Cu, Ni)-Sn IMC layer, as shown in Fig. 9b. The needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC grew much faster in the plain Sn-Ag-Cu solder systems, and with a coarse microstructure, which explains this detachment. The Sn-Ag-Cu solder joint containing 1 wt% CeO<sub>2</sub>, the (Cu, Ni)-Sn IMC layer, and the fine needleshaped Cu<sub>6</sub>Sn<sub>5</sub> and rod-shaped Ag<sub>3</sub>Sn IMC particles had a thinner layer and finer microstructure than those of the plain Sn-Ag-Cu solder joints. The finer microstructure in composite solder systems is due to the second phase CeO<sub>2</sub> nanoparticle inhibiting grain growth. It was noted that the fine microstructure of the composite solder system and the dispersed second phase reinforcing CeO<sub>2</sub> nanoparticle can significantly affect the mechanical reliability of solder joints.

Figure 10 shows the backscattered SEM micrographs of (a, b) plain Sn–Ag–Cu solder and (c, d) Sn–Ag–Cu–1CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu substrates taken from solder ball regions, depending on the reaction time; i.e., (a, c) 5 min and (b, d) 30 min at 270 °C. The SEM micrographs clearly show fine Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> IMC particles in the  $\beta$ -Sn solder matrix of both types of solder joints. The IMC particles and the  $\beta$ -Sn grain sizes slightly increased with the reaction time. After non-coarsening, non-reacting ceramic nanoparticles were added, a fine microstructure appeared. The formation of the rod-like Ag<sub>3</sub>Sn IMC particles, as shown in Fig. 10, was more obvious.

3.6 IMC thickness measurement of Sn-Ag-Cu based solders on Ag surface finished Cu substrates

The thickness of the IMC layer was calculated by measuring the total area with image analysis software. The average thickness was obtained by dividing the phase areas by the interface length. The IMC layer thicknesses were a function of the reaction time of, in Fig. 11a, c, plain Sn-Ag-Cu and, in Fig. 11b, d, Sn-Ag-Cu-1CeO<sub>2</sub> composite solders, as a function of the surface finish of the substrates, in Figs. 11a, b, immersion Ag-plated and, in Figs. 11c, d, Ag/Ni-metallized Cu substrates, at various temperatures. It is clear that the IMC layer thicknesses increased with the reaction time, at various temperatures, in both types of solder system. The value of the IMC layer thickness of the plain Sn-Ag-Cu solder-on immersion in Ag-plated Cu substrates and after 5 min of reaction at 270 °C-was 4.73 µm, reaching 7.89 µm after 30 min. However, after the addition of  $CeO_2$  nano-particles, the values were 3.76 and 6.15 µm, respectively. The (Cu, Ni)-Sn IMC thickness values of the plain Sn-Ag-Cu solder-Ag/Ni metallized Cu substrates after 5 and 30 min of reaction at 270 °C were 4.01 and 6.12 µm, respectively, and after the addition of CeO<sub>2</sub> nano-particles, 3.78 and 5.56 µm. This confirmed that the CeO<sub>2</sub> nanoparticles inhibited the growth of the IMC layers. The plausible explanation here is that the noncoarsening, non-reacting CeO<sub>2</sub> nanoparticles are effective surface active materials, and accumulated at the grain boundary or in the IMC layers. Surface adsorption theory

Fig. 10 SEM micrographs of (a, b) Sn-Ag-Cu solder and (c, d) Sn-Ag-Cu-1 wt% CeO<sub>2</sub> composite solder joints on Ag/Ni metallized Cu pads depending on the reaction time (a, c) 5 min and (b, d) 30 min at 270 °C



can be used to explain the retardation of the IMC growth mechanism of solder joints during reflow and aging by nanoparticles. According to this theory, [27] for a surfaceactive material, the surface free energy of a whole crystal is:

$$\sum_{K} \gamma_{c}^{K} A_{K} = \sum_{K} \left( \gamma_{0}^{K} - RT \int_{0}^{c} \frac{\Gamma^{K}}{c} dc \right) A_{K}$$
(1)

where  $A_K$  is the area of the crystal plane K;  $\gamma_c^k$  is the surface tension of K with the adsorption of active materials;  $\gamma_0^k$  is the surface tension of K without the adsorption of active materials; R is the ideal gas constant;  $\Gamma^K$  is the adsorption surface-active material at the crystal plane K; T is the absolute temperature and c is the concentration of the surface-active material.

Given that the volume of a crystal is constant, the surface energy of the crystal planes must be kept to a minimum in the equilibrium state; that is:

$$\sum_{K} \gamma_{c}^{K} A_{K} = \sum_{K} \left( \gamma_{0}^{K} - RT \int_{0}^{c} \frac{\Gamma^{K}}{c} dc \right) A_{K} \to \min$$
(2)

Here,  $\sum_{K} \gamma_0^K A_K$  is assumed to be constant because it is independent of the concentration of surface active materials. Thus,  $\sum_{K} A_K \int_0^c \frac{\Gamma^K}{c} dc$  should be maximized, and demonstrates that the effect of the crystal plane with the maximum amount of adsorption  $\Gamma^K$  is most active. Therefore, an increase in the amount of absorbed particles results in a decrease in the surface energy of the crystal plane, and consequently decreases its growth velocity. Hence, the non-reacting, non-coarsening second phase reinforcement  $CeO_2$  nanoparticles were crucial as they minimized the surface energy, which retarded the formation of the IMC layers.

## 3.7 Hardness test of Sn-Ag-Cu based solders on Ag surface finished Cu substrates

Measurement of micro-hardness determines the mechanical properties of bulk solid-state surfaces. The micro-hardness of a solder alloy depends on the motion of dislocations and the growth and configuration of the grains. The processes involved are more sensitive to the microstructure of the solder than to its chemical composition. Micro-hardness, a mechanical property, is particularly dependent on factors such as microstructure, processing temperature, and the alloy composition [28]. Figure 12 shows the micro-hardness values of the plain Sn-Ag-Cu and the Sn-Ag-Cu-1CeO<sub>2</sub> composite solder joints on: (a) immersion Ag plated-and (b) Ag/Ni metallized Cu substrates, as a function of the reaction time at 250 °C. The test results showed that the micro-hardness values of composite solders doped with CeO<sub>2</sub> nanoparticles were consistently higher than those of the plain Sn-Ag-Cu solder joints, in both types of substrates. The hardness of the composite solder was improved because the ceramic nanoparticles inhibited the grain

Fig. 11 IMC layer thicknesses as a function of reaction time of (a, c) plain Sn-Ag-Cu and (b, d) Sn-Ag-Cu-1CeO<sub>2</sub> composite solders depending surface finished substrates; (a, b) immersion Ag plated and (c, d) Ag/Ni metallized Cu substrates at various temperatures



**Fig. 12** Hardness of plain Sn–Ag–Cu and Sn–Ag–Cu–1CeO<sub>2</sub> composite solder joints on (**a**) immersion Ag plated and (**b**) Ag/Ni metallized Cu substrates as a function of reaction time at 250 °C

growth and were homogenously distributed throughout the solder matrix. This was due to: (1) the pinning of the grain boundaries, (2) obstacles to the movement of dislocations and the increasing dislocation densities—and (3) the strengthening of the matrix, i.e., the finely dispersed IMC particles and ceramic CeO<sub>2</sub> nanoparticles [29]. The microhardness values of the plain Sn–Ag–Cu solder joints and the composite solder joints containing CeO<sub>2</sub> nanoparticles on immersion Ag plated Cu substrates after 5 min of reaction were approximately 16.6 and 18.6 Hv, respectively, and approximately 14.4 and 16.6 Hv after 30 min of reaction time. For the plain Sn–Ag–Cu solder joint and

composite solder joints on Ag/Ni metallized Cu substrates, after 5 min of reaction at 250 °C, the values were approximately 15.9 and 17.4 Hv, respectively, while, after 30 min, the values were approximately 14.4 and 15.5 Hv.

#### 4 Conclusions

The interfacial microstructure of plain Sn-Ag-Cu solder joints and those containing 1 wt%  $CeO_2$  nanoparticles on Ag surface-finished Cu substrates were investigated as a function of reaction time at various temperatures. The thin

top surface Ag layer of the immersion Ag plated Cu substrate was observed to dissolve into the molten solders as a result of the reactions. An island-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMC layer was observed at the interfaces of the Sn-Ag-Cu solder joints and the Sn-Ag-Cu-1 wt% CeO2 composite solder joints of the immersion Ag-plated Cu substrates. After a long reaction time, a very thin Cu<sub>3</sub>Sn IMC layer was found, adhering to the Cu<sub>6</sub>Sn<sub>5</sub> IMC layer and the immersion Ag plated Cu substrates. A scallop-shaped (Cu, Ni)-Sn IMC layer was formed at the interfaces of both types of solder joints on the Ag/Ni metallized Cu systems. Very fine (submicron sized) needle-shaped Cu<sub>6</sub>Sn<sub>5</sub> with dark contrast and rod-shaped Ag<sub>3</sub>Sn IMC particles with bright contrast were clearly observed on the upper surface of the (Cu, Ni)-Sn IMC layer. The thickness of the IMC layers increased with reaction time and temperature. In the solder ball region, Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> IMC particles were clearly observed in the  $\beta$ -Sn matrix in both types of solder joints. However, the formation of IMC layers and the Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> IMC particles in the solder matrix of composite solder doped with CeO<sub>2</sub> nanoparticles exhibited a fine microstructure, due to an accumulation of surface active CeO<sub>2</sub> nanoparticles at the grain boundary or in the IMC layers.

The Sn–Ag–Cu composite solder joints doped with 1 wt% CeO<sub>2</sub> nanoparticles consistently displayed higher hardness values than the plain Sn–Ag–Cu solder joints on both substrates. From the results that we have obtained, it is reasonable to suggest that the micro-hardness of the bulk solder was improved by the addition of the non-coarsening, non-reacting CeO<sub>2</sub> nanoparticles, as the dispersion of the nanoparticles strengthened the solder and refined the IMC particles in the solder matrix.

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袁志清先生 T: +852 2343 3671 E: hkoffice@wingchun.com.cn

業務範圍:電鍍

### Wing Yee (Hong Kong) International Trading Ltd. 永怡(香港)國際貿易有限公司

郭傳方先生 郭傳方先生 T: +852 6201 5708 E: gcf608@163.com 業務範圍:原料供應商,經營 電鍍添加劑,甲基磺酸,苯酚磺 酸,電子磷酸。

## Winstar Chemicals Co. Ltd.

永星化工有限公司

張志恒先生

T : +852 2499 9363 E : winchem@winstarchem.com.hk

業務範圍:研發、生產及銷售表 面處理化學藥品、新材料、電子 及半導體材料、防腐材料及塗 料,以及相關設備。

### 深圳市海韵翔超聲波 有限公司

楊永武先生 T:+8675527509006 E:643977520@qq.com 業務範圍:超聲波清洗設備、 純水、冷凍、烘乾設備等



## 香港表面處理學會翻

## Hong Kong Surface Finishing Society Ltd.

## 會員申請表 Member Application Form

申 公司名稱(中文) Company № 請	ame(Chinese):	公司名稱(英文)Company Name(English):			
│ 入 資 申請人姓名 Chinese & English 料	Name :	職位 Position:			
業務範圍、性質(如:貴金屬電鍍加) and services e.g. electroplating):	L ,原料供應商 ,請	簡述)Business Scope, Nature (Give details of your products			
地址(中文)Address(Chinese):		電話 Tel:			
		傳具 Fax:			
地址(英文)Address(English):		手機 Mobile:			
		電郵 Email:			
		網址 Website:			
國內地址:		國內電話:			
		國內傳真:			
申請會員類別 Type Applied for (請	在合適方格內加上	✓ 號/please tick ✓ a box)			
公司會員 Company Membershi	р	● 公司會員年費為港幣壹仟伍佰元正			
□ 個人會員 Personal membership	o	<ul> <li>個人會員年費為港幣三百元正,人會費為壹百元正。</li> </ul>			
一 個人永久會員 Permanent Memb	pership	<ul> <li>申請個人永久會員只需一次性繳交會費叁千元正,不</li> </ul>			
		需入會費。			
如選擇公司會員,請填寫公司代表名	單 Company Rep	resentative List :			
(1)	_ 電郵 Email:				
(2)	電郵 Email:				
(3)	_ 電郵 Email:				
(4)	電郵 Email:				
(5)	電郵 Email:				
介紹人姓名 Name of Referee:		聯絡方式 Contact information:			
公司蓋章 Company Chop:		簽署 Signature:			
		日期 Date:			

支票抬頭:香港表面處理學會有限公司 或 Hong Kong Surface Finishing Society Limited 請郵寄:香港荃灣沙咀道 57 號荃運工業中心 2 期 21 樓 L 座,香港表面處理學會有限公司秘書處 Hong Kong Surface Finishing Society Ltd., Block L, 21/F, Superluck Industrial Centre Phase 2, 57 Sha Tsui Road, Tsuen Wan, Hong Kong 電話: (852) 8120 0323 傳真: (852) 8120 0325 電郵: <u>secretary@hksfs.org.hk</u> 網頁: <u>www.hksfs.org.hk</u>

## 香港表面處理學會通訊廣告收費表

刊登	價目(黑白)	價目(彩色)		尺寸
封面	-	\$6,500	233×210mm	(另4邊加出血位3mm)
第二封面	-	\$6,000	297×210mm	(另4邊加出血位3mm)
封面內頁	-	\$5,500	297×210mm	(另4邊加出血位3mm)
封底	—	\$5,500	297×210mm	(另4邊加出血位3mm)
封底內頁	—	\$4,500	297×210mm	(另4邊加出血位3mm)
內頁彩色	—	\$3,500	297×210mm	(另4邊加出血位3mm)
內頁彩色(半頁)	_	\$2,000	148×210mm	
其他內全頁(黑白)	\$2,000	_	297×210mm	
其他內半頁(黑白)	\$1,000	_	148×210mm	



隨著時代的進步及發展,刊登廣告請直接電郵AI檔/高解像PDF致秘書處(secretary@hksfs.org.hk),並與本會羅小姐聯絡。

為使各廣告達致統一的標準,故本會要求統一的AI格式,附參考資料如下: 檔案格式:一個附高解像圖及已轉換成曲線的AI檔案 參考檔案:JPG及PDF均可(只用作排位)

如蒙惠賜廣告,請與本會秘書處聯絡 電話:8120 0323 傳真:8120 0325

香港表面處理學會 2017-2019年度會刊資訊部

# 「香港表面處理」

## 是合資格申請中小企業市場推廣基金資助的貿易刊物

第70期(將於2019年7月出版)

第71期(將於2019年11月出版)

\*欲申請基金資助的中小企業須於刊物出版後的六十個曆日内遞交申請\*

請注意,申請基金資助的企業必須為香港的中小企業,並在本港有實 質業務運作,空殼公司或在香港境外從事主要業務運作的中小企業, 均不會被視為在本港有實質業務運作,故有關申請會遭拒絕。同時申 請企業必須以本港中小企業身份刊登廣告,因此申請企業必須在廣告 上展示其名稱,以及其香港的聯絡資料(包括地址、電話號碼及傳真 號碼等)。如有需要,申請企業會被要求提供足夠的營運證明(例如 業務上的報價單、合約、托運貨件紀錄、付款紀錄、僱員強積金供款 紀錄等),未能符合此要求的有關申請會被拒絕。請注意,貿易刊物須 與申請企業所經營的業務有直接關係。

有關基金的申請手續、資助金額及範圍的詳情可瀏覽 http://www.smefund.tid.gov.hk/。

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