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绿色锑冶金技术研究进展

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摘要: 我国是世界锑资源大国, 其储量、产量均居世界首位。传统锑冶金过程普遍存在能耗高、二氧化硫烟气排放量大、资源利用率低等问题, 难以满足绿色低碳发展的要求。本文系统梳理了锑产业链结构及消费结构变化趋势, 围绕金属锑、三氧化二锑、焦锑酸钠和高纯锑等主要锑系列产品, 综述了绿色锑冶金技术的研究进展, 指出锑冶金过程的短流程化、清洁化、高纯化及资源循环利用是未来的重要研究方向。

关键词: 绿色冶金; 三氧化二锑; 焦锑酸钠; 高纯锑; 资源循环利用

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锑是一种关键的战略性金属材料, 在半导体、光学材料、军工武器、核技术等方面具有重要应用[1-3]。同时作为重要的添加剂或者催化剂, 广泛用于生产各种阻燃剂、特种合金、陶瓷、玻璃、医药、化工等工业领域, 有着“工业味精”的美名[4]。

锑在地壳中的丰度低, 自然界中锑主要通过中低温热液成矿作用和构造活动, 发生迁移、富集形成以硫化锑矿为代表的高品位矿床[5-8]。世界锑资源主要分布在环太平洋沿岸、地中海地带以及中亚天山构造成矿带, 其中, 太平洋构造成矿带锑矿资源最为丰富, 约占锑资源总量的72%[9-10]。我国锑资源储量约占全球总储量的32%, 已探明的锑矿主要集中分布在湖南、广东和广西等地, 其中, 湖南冷水江市锡矿山拥有全球最大锑矿, 年产量占全国三分之一[11]。近十年来, 全球每年的矿锑产量维持在10万t左右, 其中, 中国产量几乎占50%[12-13]。

长期以来, 高品位硫化锑矿是锑冶金的主要原料基础, 也支撑了我国锑冶炼工业的发展[14]。随着高品位锑矿资源的持续消耗, 锑冶金原料逐步向低品位、多组分和复杂共伴生方向演变[15]; 而基于环保和对锑品质要求的不断提高, 传统火法冶炼逐渐向湿法分离、产品精制和清洁冶金不断推进[13,16-20]。国内冶金科技工作者围绕锑火法精炼、锑白制备、氯化—水解提锑、固硫还原熔炼等关键技术开展了大量系统研究, 为我国绿色锑冶金技术体系的形成和发展奠定了重要基础[13,21-32]。本文梳理了锑产业链及消费结构的变化趋势, 针对金属锑、氧化锑、焦锑酸钠和高纯锑等主要锑系列产品, 综述绿色锑冶金技术的进展, 探讨了低碳、清洁导向下锑冶金技术的发展方向。

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1　锑产业发展现状及产品结构升级

1.1　锑产业链结构

锑产业链主要由资源供给、冶金加工和终端应用三个环节构成(图 1)。资源供给端包括原生锑矿和二次含锑资源，其中，以辉锑矿为代表的硫化锑矿长期以来是锑冶金的主要原料[33-34]。近年来，资源结构中低品位、多金属共伴生资源及再生资源占比持续提高，原料组成日趋复杂化。冶金加工环节位于产业链中游，主要通过火法焙烧—还原熔炼、湿法浸出—分离等工艺实现锑的富集、提取和分离[25,35-38]，其高纯产品还需结合重结晶、选择性沉淀、真空蒸馏、电解精炼、区域熔炼等技术进一步制备[39-44]。终端应用环节随产品形态的不同呈现明显分化。金属锑主要用于合金材料，三氧化二锑主要用作阻燃协效剂、玻璃工业原料及高纯锑制备原料，焦锑酸钠主要用于光伏玻璃澄清，高纯锑则面向半导体、红外探测和高端光学等战略新兴领域[18,43,45]。

1.2　锑消费结构及发展趋势

长期以来，传统锑的消费主要集中于锑合金、阻燃剂及玻璃工业等传统领域[46-47]。其中，三氧化二锑作为卤系阻燃体系中的重要协效剂，在塑料、橡胶、纺织品和电子电器材料中应用广泛[48-49]。金属锑及锑合金则广泛用于铅酸蓄电池板栅、轴承合金、焊料和军工材料等领域[50-52]。

随着“双碳”目标推进和新能源产业快速发展，锑的消费结构正由传统大宗用途向功能化、高端化应用延伸。光伏玻璃是近年来锑消费增长的重要牵引领域，中国光伏玻璃的锑消费占比已由 2020 年的约 11% 提升至 2025 年的 30%，跃升为继阻燃剂之后的第二大消费领域[53-55](图 2)。焦锑酸钠作为高效玻璃澄清剂，可促进玻璃熔体中气泡排出，并改善铁杂质引起的着色问题，对制备高透光率光伏玻璃具有重要作用[56]。同时，半导体、红外探测及高端光学器件等战略性新兴产业对锑的需求也在不断增长。锑是硅基材料的 n 型掺杂元素，也是锑化铟、锑化镓等Ⅲ - Ⅴ族化合物半导体的重要原料[39]。这类应用虽然总量占比有限，但对纯度、杂质控制和缺陷水平要求极高，相关产品具有显著的经济附加值，已成为推动锑冶金向高端化、无污染精细化发展的方向[39,57]。

2　锑冶金技术研究进展

锑冶金技术的发展经历了由火法冶炼、湿法与

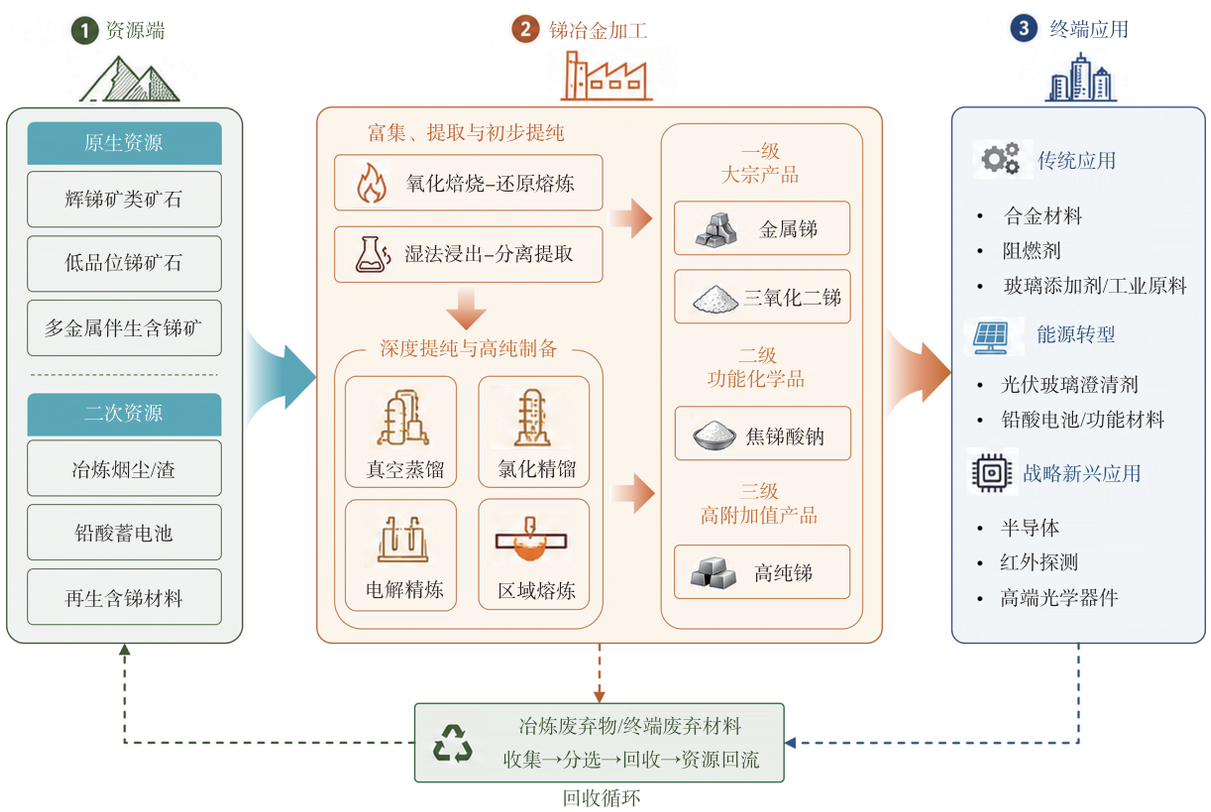


图 1　锑产业链及主要产品应用

Fig. 1　Antimony industrial chain and applications of major products

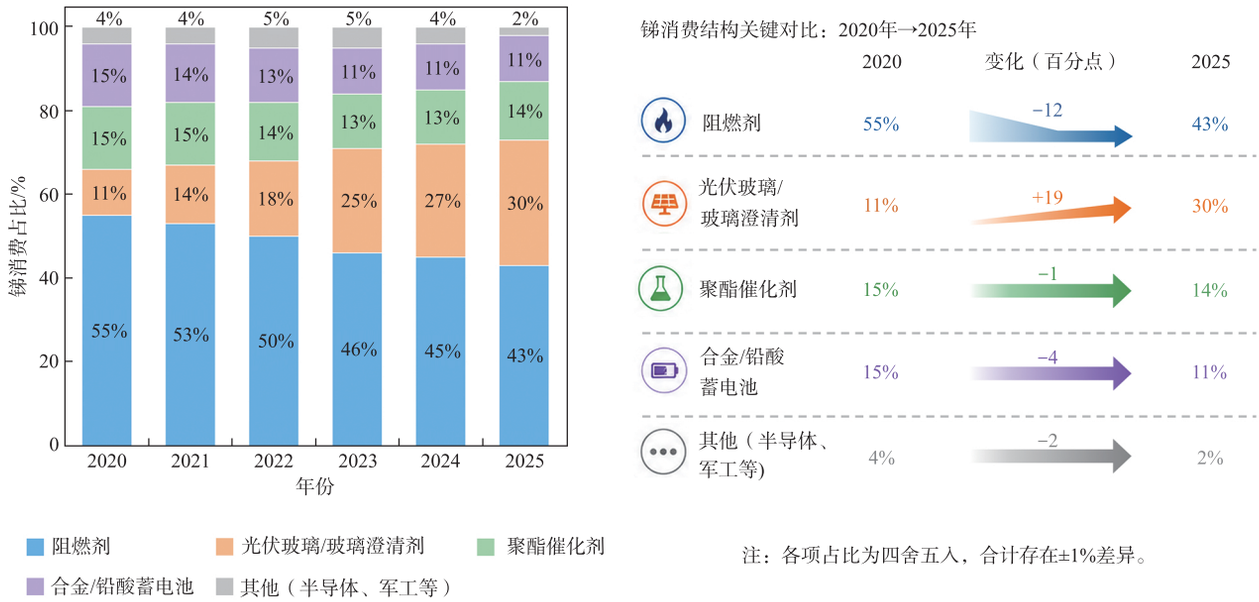


图2 锑消费结构及其变化趋势

Fig. 2 Antimony consumption structures and trends

电化学提取，到清洁化和高纯化制备的演进过程[4]。19世纪中叶，随着工业革命的推进，欧美国家逐步采用焙烧—还原法提取锑，标志着锑冶金正式进入工业化阶段，其应用领域扩展至合金、印刷和阻燃剂等多个方面。1884年，博比西雷、鲁尔兹和鲁等首次提出焙烧—还原法生产金属锑；1887年，锑盐溶液电解试验的出现，推动锑提取方式由单一火法向湿法和电化学方向延伸。20世纪初，随着湿法炼锑研究和电解技术的发展，锑冶金逐步形成火法、湿法和电冶金并行发展的技术格局。1942年，美国邦克·希尔沙利文公司建立世界第一条锑电解生产线，标志着湿法电冶金炼锑实现工业化应用[58]。

中国的锑冶金工业起步较晚，20世纪初，华昌公司在长沙设立中国第一个锑冶炼厂，开启了我国锑冶金工业化进程[4]。此后，在赵天从等学者的推动下，中国锑冶金技术体系逐步形成并不断完善，他提出和发展的吹碱氧化精炼法、间接法制取锑白技术以及氯化—水解法提锑技术对锑冶金现代化具有重要意义[28,59-60]。其中，20世纪80年代形成的氯化—水解法利用氯化浸出和水解沉淀实现锑的提取提纯与氧化物制备，为高品质三氧化二锑生产提供了重要技术路线。进入21世纪后，锑原料供给结构日趋复杂，环保压力增大，锑冶金技术进一步向高效化、清洁化和高值化方向发展。富氧熔池熔炼、矿浆电解、固硫还原熔炼、熔盐电解以及真空蒸馏、氯化精馏等技术不断发展，推动锑冶金由传统资源提取向清洁生产、污染源头控制和高纯锑制备转型。图3为近代以来锑冶金发展中具有代表性的技术变革事件。

2.1 锑火法冶金技术

2.1.1 鼓风炉挥发熔炼—反射炉还原熔炼

火法炼锑的典型工艺为鼓风炉挥发熔炼—反射炉还原熔炼与精炼，也是国内应用最广泛的炼锑流程[6,35]。其工艺原理主要是利用高温下硫化锑和三氧化二锑蒸气压较大且硫化锑易于氧化的特性，将精矿中锑富集于烟气烟尘进行处理[38]，如图4所示。硫化锑精矿、广西脆硫铅锑矿和锑金矿均采用该工艺[4,61-62]。

鼓风炉挥发熔炼—反射炉还原熔炼工艺的特点是在低料柱、薄料层、高焦率、热炉顶等条件下实现挥发熔炼，能有效处理硫化锑矿和硫氧混合型锑矿，原料包容度及金属回收率高，易于实现机械化生产[63]。该工艺的缺点在于产生大量的烟气，需要庞大的收尘系统配套，且热量流失严重。此外，烟气内低浓度的二氧化硫导致硫组分回收利用难度大，粗锑和锑锍等需返回鼓风炉再次熔炼，进一步增加能耗与生产负荷[64-65]。

2.1.2 富氧熔池熔炼技术

富氧熔池熔炼技术是一类强化火法熔炼工艺，将富氧气体鼓入高温熔池进行反应，与鼓风炉挥发焙烧相比，富氧空气或工业氧直接鼓入熔体后，可强化熔池搅拌和多相传质，加快硫化锑氧化挥发过程，从而提高烟气中二氧化硫浓度，为后续硫资源回收创造条件[13](图5)。根据供氧方式不同，富氧熔池熔炼可分

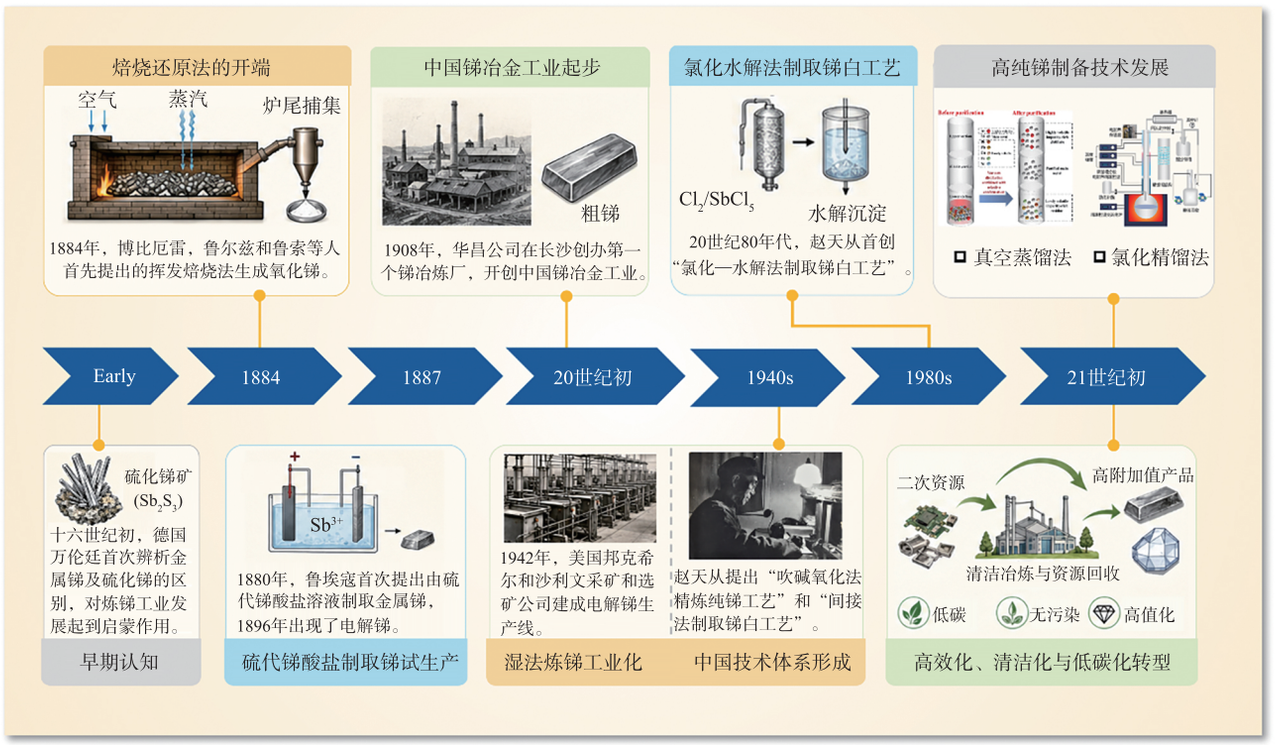


图3　锑冶金技术发展历程

Fig. 3　Development of antimony metallurgical technologies

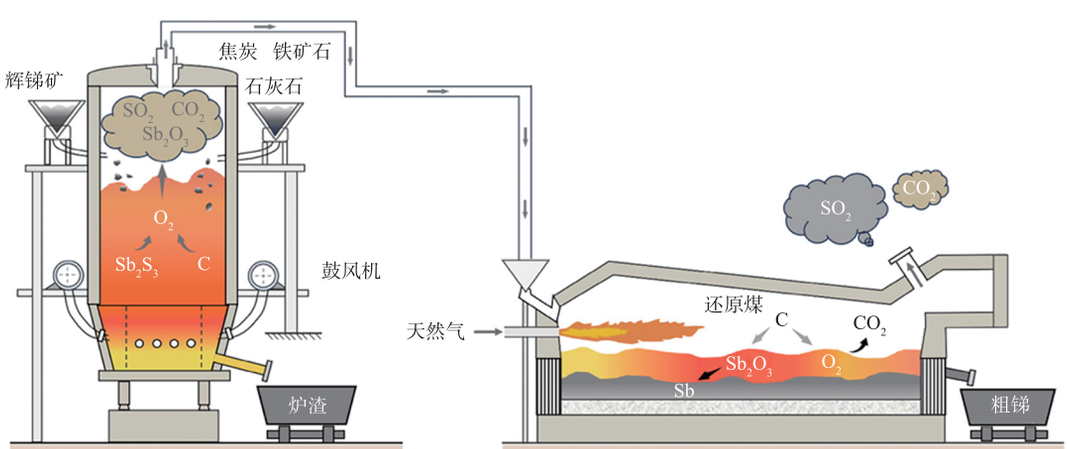


图4　“鼓风挥发—反射炉还原”炼锑工艺示意图[38]

Fig. 4　Schematic of antimony smelting by blast furnace volatilization and reverberatory furnace reduction[38]

为顶吹、底吹和侧吹等形式[35](图6)。我国科研工作者围绕顶吹、底吹、侧吹等炼锑工艺进行了深入研究，如木利锑矿、久通锑业和中国瑞林开发了顶吹熔池炼锑工艺，并配套研发专用熔炼炉装备[66-67]。豫光金铅及中南大学刘维开发了富氧底吹熔池熔炼技术[68-69]。闪星锑业联合长沙有色院等单位开发了富氧侧吹熔池熔炼技术[70]。

然而各强化熔炼技术在强化传质传热的同时，仍面临炉衬侵蚀、金属挥发及生产稳定控制等工程难题。相较而言，富氧侧吹熔池熔炼具有原料适应性广、预处理流程简便、单位炉床产能高、伴生有价金属回效率高等优势[14]。闪星锑业、广西万仕智以及南方有色等企业均已将富氧侧吹熔池熔炼作为锑冶炼技术升级的重要方向。

2.1.3　固硫还原熔炼技术

唐谟堂系统论证了用氧化铁作固硫剂消除二氧化硫污染的可行性，提出了固硫还原熔炼技术[71]。该技术基于不同元素与硫亲和力的差异，引入铁源或锌源等固硫剂，使硫优先生成硫化亚铁、硫化锌等热力学稳定的硫化物，而锑则经还原进入金属相(图7)。

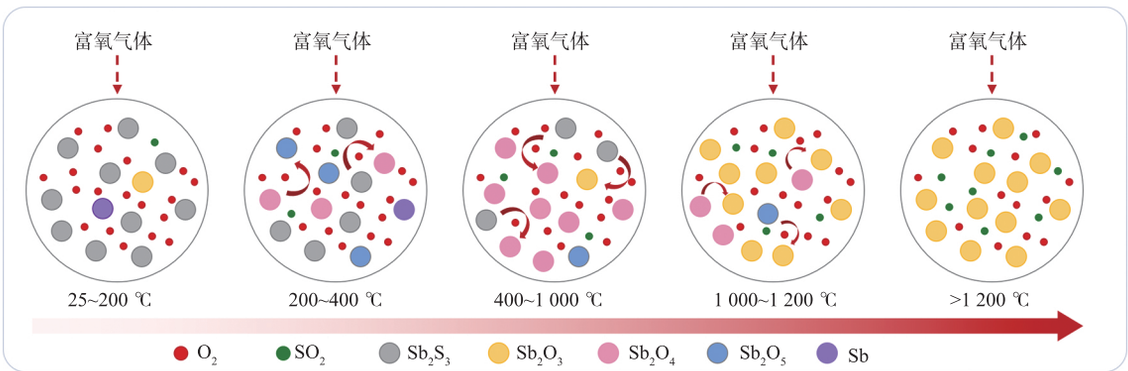


图5　富氧熔池熔炼氧化机理

Fig. 5　Oxidation mechanism of oxygen-enriched bath smelting

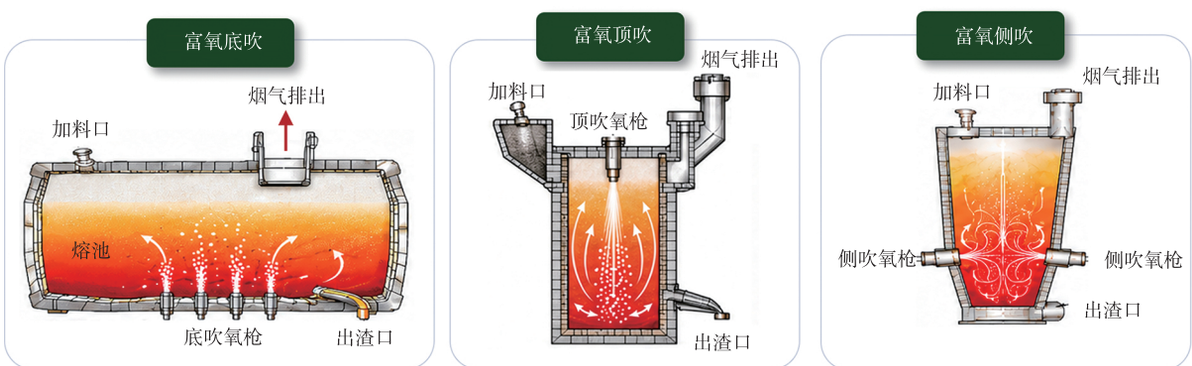


图6　底吹、顶吹和侧吹富氧熔炼反应器示意图

Fig. 6　Schematic diagrams of bottom blowing, top blowing and side blowing oxygen enriched smelting reactors

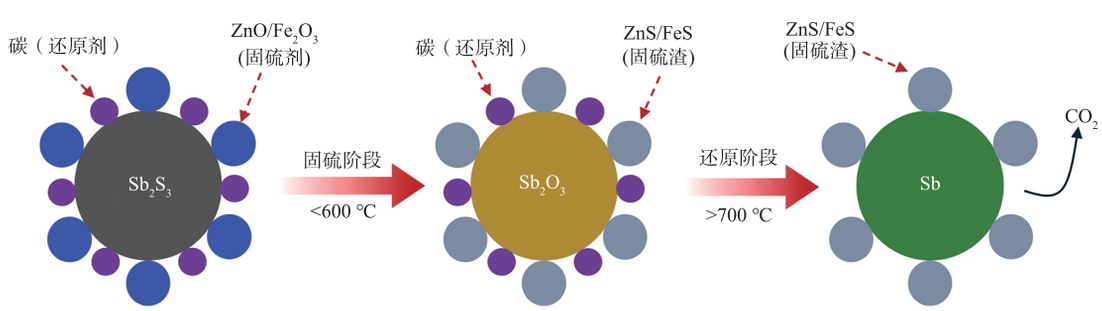


图7　固硫还原熔炼技术机理

Fig. 7　Mechanisms of sulfur-fixing reduction smelting

与传统氧化挥发流程相比，固硫还原熔炼重塑了硫的转化路径，实现了源头固硫。试验结果表明[23]，在850 °C条件下碳还原熔炼60 min，锑回收率可超过90%，所得粗锑品位高于94%；硫则主要以硫化亚铁或硫化锌等稳定硫化物形式被固定，因而可抑制二氧化硫的生成，大幅降低二氧化硫外排。为进一步改善固硫还原熔炼过程中熔盐消耗较大的问题，丁瑞泽等[72]采用二氧化碳顶吹手段强化反应过程，实现碳酸钠熔盐的再生。通过优化熔炼温度和二氧化碳通入量，可将体系固硫率提高至97.8%，提升了工艺的资源循环利用水平。因此，固硫还原熔炼技术有望成为硫化锑资源清洁、高效冶炼的重要技术方向，但其工业化应用仍需解决熔盐循环利用、硫化物渣资源化及工艺连续运行稳定性的问题。

2.2　锑湿法冶金技术

湿法炼锑路线无二氧化硫排放、整体能耗较低，是当前处理复杂锑资源清洁冶金的重要技术路线，现阶段国内外研究主要聚焦于浸出体系与电解工艺的开发和优化。

2.2.1　酸性浸出—电沉积

三氯化铁浸出体系的原理是利用酸性条件下Fe^{3+}的氧化性，对硫化锑矿物进行氧化，将矿中的硫

组分转化为单质硫进入渣相，锑元素则以氯盐形式进入液相。根据最终产品不同，该工艺可分为两条技术路线：三氯化铁浸出—电沉积制备金属锑，三氯化铁浸出—水解制备锑白[28]。

浸出—电沉积工艺在金属锑制备过程中不产生二氧化硫，且能耗低、产品纯度高，但高酸度工况下盐酸挥发问题突出，对生产设备的防腐等级要求高。另一方面，浸出液组分复杂，增加了净化除杂难度，尤其是铁离子不断累积，电沉积过程存在爆锑风险[73]，均不利于连续稳定生产和工业化推广，主要反应如式(1)~(4)所示。

$$Sb_2S_3+6FeCl_3=2SbCl_3+6FeCl_2+3S \quad (1)$$

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S\uparrow \quad (2)$$

$$阳极：Fe^{2+}-e=Fe^{3+} \quad (3)$$

$$阴极：Sb^{3+}+3e=Sb \quad (4)$$

针对传统三氯化铁浸出体系的铁离子累积问题，高亮等[22]采用五氯化锑或氯气作为氧化浸出剂代替三氯化铁，得到三氯化锑浸出液，再通过电沉积获得金属锑。该方法有效解决了铁杂质大量积累造成的产品质量问题。此外，工艺还配套隔膜电沉积装置，可在阳极室实现五氯化锑的氧化再生，从而建立浸出、电沉积、浸出剂再生的闭环工艺路线[74](图8)。由于酸性体系中各类杂质离子易累积，阴离子膜使用寿命短，以及电沉积稳定性调控等问题，导致该技术现阶段尚难以实现大规模产业化[13]。

2.2.2　碱性浸出—电沉积工艺

碱性体系处理硫化锑矿主要包含碱性浸出与电沉积还原两个核心工序[75-76]。在碱性浸出体系中，硫化锑矿物可与硫化钠发生配位溶解反应，生成水溶性硫代锑酸钠，实现锑组分从固相至液相的高效迁移，主要反应如式(5)~(6)所示；若硫化钠浓度不足，将发生式(7)所示副反应，生成亚锑酸。浸出液经固液分离、净化后采用隔膜电沉积技术可在阴极获得金属锑产物(图9)。采用该工艺锑综合回收率提升至98%以上，且避免了二氧化硫污染物释放，易于实现工业化应用[75]。但该碱性提锑处理过程中硫元素会在溶液中持续累积，并以硫化钠、硫酸钠、硫代硫酸钠、亚硫酸钠、硫代锑酸盐等多种复杂含硫组分共存，导致尾液成分复杂、后续处置流程繁琐[77]。同时，硫离子易在阳极发生氧化析出单质硫，造成电阻升高、能耗增大，同时阴极室伴随析氢副反应，因此，现有隔膜电解体系实际电流效率约为80%~85%。目前，陕西某冶炼厂已针对锑含量8%~10%的低品位硫化锑精矿，完成碱性浸出—隔膜电沉积提锑工艺的工业实践[13,78]。

$$Sb_2S_3+3Na_2S=2Na_3SbS_3 \quad (5)$$

$$Sb_2S_3+6Na_2S+6H_2O=2Na_3SbS_3+6NaOH+3S^0+3H_2\uparrow \quad (6)$$

$$Sb_2S_3+6NaOH=3Na_2S+2H_3SbO_3 \quad (7)$$

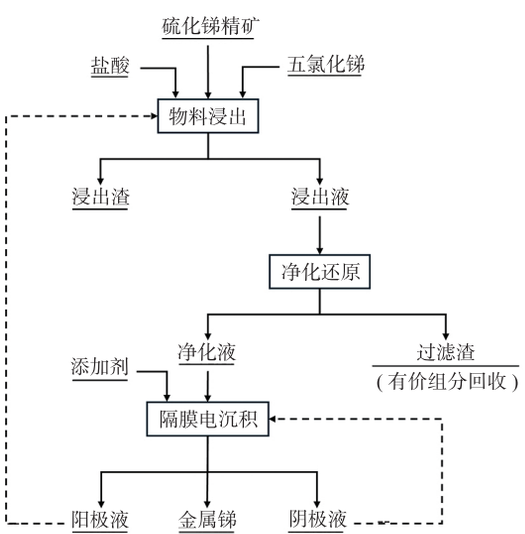


图8　新氯化浸出—隔膜电积提锑工艺流程

Fig. 8　Flow chart of novel chlorination leaching and diaphragm electrowinning

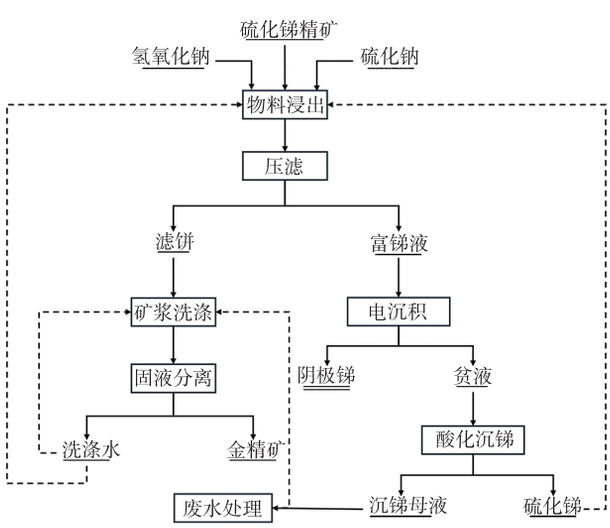


图9　碱性浸出—电沉积提锑工艺流程

Fig. 9　Flow chart of alkaline leaching and electro-deposition

2.2.3　矿浆电解技术

矿浆电解技术将浸出、净化和电沉积过程耦合于同一设备中，减少了传统湿法流程中固液分离、溶液转移和多级净化等环节，简化了工艺流程(图10)。邱定蕃院士团队自1998年开始了复杂锑铅矿矿浆电解的研究[79]。该工艺采用盐酸体系，在阳极区，硫化锑

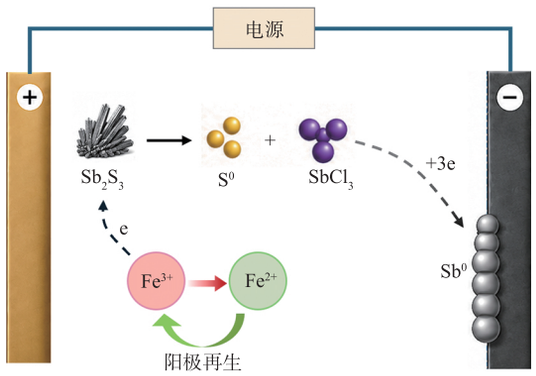


图 10 硫化锑矿浆电解机理示意图

Fig. 10 Mechanism of slurry electrolysis of antimony sulfide

发生氧化反应生成三氯化锑，铅转化为氯化铅进入渣中，硫则氧化成单质硫留在浸出渣中；在阴极区，锑离子被还原沉积为金属锑，实现了锑、铅的一步分离和金属锑的一步提取，实现了锑的清洁冶炼[37,80]。该工艺先后处理湖南高砷锑金精矿(2013 年)及缅甸锑矿(2016 年)，实现工业化应用[81]。

矿浆电解技术保留了传统湿法冶金优点的同时，还具有以下几个特点：

1)实现了金属锑的一步产出，金属回收率高。体系中锑浸出率高于 97%，砷、金基本不进入浸出液，二者浸出率低于 0.2%，所得阴极锑产品纯度大于 98%，杂质砷含量低于 0.3%，后续经碳酸钠熔铸脱砷处理，能够直接得到纯度高于 99.9% 的金属锑锭；

2)硫及有毒杂质砷等随铁及脉石矿物进入浸出渣中，过程简单，所产元素硫便于贮存和运输，消除了低浓度二氧化硫和烟尘的污染；

3)电解所需槽电压较低，试剂消耗少，吨锑加工成本与鼓风炉挥发熔炼基本持平。但含砷氯盐体系的电沉积过程存在砷化氢气体泄露的安全隐患[34]。

2.3 三氧化二锑制备技术

2.3.1 火法制备技术

传统三氧化二锑生产工艺为“高温氧化挥发—冷凝捕集”的技术路线，以硫化锑矿为原料通过氧化焙烧将硫化锑转化为次锑氧，并经烟气冷凝捕集得到粗制三氧化二锑；所得产物再经升华、冷凝或其他精制过程提高纯度。该路线流程成熟、生产效率高，是工业生产三氧化二锑的主流工艺[82]。然而，硫主要以二氧化硫形式进入烟气，需要配套制酸或烟气治理系统；同时，砷、铅等伴生杂质可能随次锑氧共挥发并富集于烟尘中，导致返尘循环过程中杂质积累，增加含锑粉尘和含砷固废处置压力[83-86]。此外，工业上也可采用金属锑为原料，在富氧气氛下于 500~600 ℃ 直接氧化制备三氧化二锑[87]。

2.3.2 氯化—水解技术

氯化—水解法是制备高品质三氧化二锑产品的重要技术路线[27]。通过氧化浸出将硫化锑转化为可溶性锑氯化物进入溶液，经溶液净化、水解沉淀、中和脱氯和洗涤干燥等步骤制备三氧化二锑[36,88]。早期以三氯化铁作为氧化剂，但铁盐在循环过程中不断累积，会干扰后续分离与提纯。20 世纪 80 年代，唐谟堂等提出采用氯气或五氯化锑作为可循环的氯系氧化剂，较好地缓解了铁盐累积问题[89]。

然而，氯化—水解法存在废水量大的问题。其一，三氯化锑水解过程需消耗大量纯水，并生成含盐酸和氯盐的酸性废水；其二，水解产物通常以氯氧锑等含氯中间体形式存在，需借助氨水等碱性试剂进行中和转化和洗涤脱氯，会产生含氯、含氨氮废水[90]。为减少中和剂消耗和洗涤废水排放，有学者[91-92]尝试采用热脱氯替代湿法转化。氯氧锑在升温过程中发生逐级歧化，最终转化为三氧化二锑，同时析出挥发性三氯化锑，反应如式(8)~(10)所示。虽然缩短了工艺流程和减少废水外排，但氯氧锑完全脱氯所需温度较高，伴生三氯化锑若不能有效冷凝回收，将造成锑挥发损失和含氯尾气污染，同时还可能引起设备腐蚀、产品烧结以及空气气氛下三氧化二锑进一步氧化等问题。

$$5SbOCl \xrightarrow{245\sim280\ ℃} Sb_4O_5Cl_2+SbCl_3\uparrow \quad (8)$$

$$4Sb_4O_5Cl_2 \xrightarrow{410\sim475\ ℃} 5Sb_3O_4Cl+SbCl_3\uparrow \quad (9)$$

$$3Sb_3O_4Cl \xrightarrow{475\sim565\ ℃} 4Sb_2O_3+SbCl_3\uparrow \quad (10)$$

2.4 焦锑酸钠制备技术

早期焦锑酸钠多采用高温硝酸钠氧化法制备，通常以三氧化二锑或金属锑为原料，在高温条件下借助硝酸钠等氧化剂将低价锑氧化为五价锑，并进一步转化为焦锑酸钠产品，工艺流程相对简单。由于硝酸盐在高温条件下易产生氮氧化物有害气体，不适用于工业生产，已被淘汰[93]。

目前，工业上常用氯化水解法和碱性氧化法制备焦锑酸钠[94]。氯化水解法以氯气将锑转化为五氯化锑，经氢氧化钠中和水解沉淀，原料适应性强、产品质量较好，但存在流程长，氯介质腐蚀性强，中和与洗涤过程产生大量含氯废水等问题。

碱性氧化法系在氢氧化钠或氢氧化钾体系中将

硫化锑或氧化锑溶解为可溶性的锑酸盐,再经氧化沉淀制得焦锑酸钠。该路线虽省去了氯化和多级水解环节,但转化效率受锑氧化速率影响。研究人员采用绿色催化空气氧化和加压氧化技术提高碱性体系中Sb(Ⅲ)的氧化效率。钱福军等[95]引入栲胶作为绿色生物质催化剂,利用栲胶分子中的多酚羟基活性官能团,促进氧气活化并加速Sb(Ⅲ)氧化反应速率,焦锑酸钠产品转化率可达到97.8%。刘伟锋等[93]通过提高氧分压改善气液传质,进而提高Sb(Ⅲ)氧化的推动力,缩短氧化时间并提高焦锑酸钠生产效率。然而碱性氧化法同样存在废水难处理的问题。

2.5　高纯锑制备技术

真空蒸馏法是4N高纯锑提纯的重要物理方法,其基本原理是利用锑与杂质元素在真空条件下蒸气压和挥发行为差异实现分离[96]。该路线流程短、介质引入少,适合规模化提纯,但受砷、锑挥发行为相近及共凝析影响,单一真空蒸馏难以实现难除杂质砷的有效脱除。Zheng等[97]通过理论计算预测真空蒸馏过程中砷的去除极限约为1~10×10^{-6}。由于真空蒸馏过程中砷极易与锑形成As_mSb_n簇,有学者[98-99]提出引入铝等合金化助剂促使砷形成As-Al金属间化合物,从而抑制As_mSb_n簇的共挥发行为,减少锑中砷的掺杂,但引入合金化剂也会影响锑纯度。

5N~6N高纯锑生产通常采用氯化精馏—还原工艺。金属锑经氯化转化为三氯化锑后,利用各组分氯化物挥发度的差异脱除砷、铅、铋和铁等杂质,再经氢还原获得高纯锑产品。传统工艺对进料纯度,尤其是前端除砷效果较为敏感,通常需通过增加塔板数、提高回流比来强化分离效果,导致产品直收率偏低、能耗显著增加[100]。Kong等[101]提出在精馏之前采用铜-锑电偶联选择性除砷策略,在三氯化锑溶液中将砷以铜砷合金形式固化去除,可将砷深度去除,简化了精馏过程。

7N以上超高纯锑通常以5N~6N锑为原料,通过多道次区域熔炼完成主体净化,并根据产品形态进一步结合单晶提拉[39,102]。区域熔炼技术利用杂质在固、液两相间分配行为的差异,使有效分配系数小于1的杂质随移动熔区向锑棒尾端富集,经多次区熔和尾料切除逐步提高纯度。由于砷在锑中的有效分配系数接近1,单纯增加区熔次数难以实现有效富集[42,53,103]。进入7N以上纯度后,提纯上限已不再完全取决于区熔次数,而更多受原料初始纯度、舟体和坩埚材料、保护气氛、装料环境以及取样分析过程中的二次污染制约[39,43]。

2.6　各技术特征与工业化现状对比

不同锑冶金技术的工业适用性受原料特性、目标产品及环境约束等因素共同影响,其技术成熟度与产业化条件存在明显差异。表1系统比较了主要锑冶金技术的适用范围、关键技术瓶颈、代表性技术指标及工业化应用现状,为不同原料和产品需求下的工艺选择提供参考。

表1　不同锑冶金技术的适用性及工业化水平比较

Table 1　Comparison of the applicability and industrialization status of different antimony metallurgical technologies

技术路线	适用原料	主要产品类型	技术特征	应用现状
鼓风炉挥发-还原熔炼	硫化锑矿和硫氧混合矿	金属锑	原料的适应性强,能耗高,存在SO_2烟气污染	工业应用
富氧熔池熔炼	硫化锑精矿及复杂含锑二次物料	金属锑、氧化锑	有利于硫资源回收	工程推广
固硫还原熔炼	硫化锑精矿	金属锑	有利于硫资源回收	试验研究
酸浸—电沉积	硫化锑精矿、含锑冶炼烟尘	金属锑	产品纯度高,但防腐要求高,工艺稳定性差	试验研究
碱浸—电沉积	低品位硫化锑精矿	金属锑	含硫废水处理困难	工业应用
矿浆电解	复杂锑铅矿、高砷锑金精矿、含锑冶炼渣	金属锑	流程短,锑回收率高	工业应用
氧化挥发—冷凝	硫化锑矿、金属锑	氧化锑	原料适应性强,生产效率高	工业应用
氯化—水解	硫化锑矿、氧化锑矿和含锑冶炼烟尘	氧化锑、焦锑酸钠	产品质量较好,但水耗及药剂消耗较大	工业应用
高温硝酸钠氧化	金属锑、三氧化二锑	焦锑酸钠	工艺简单,但存在NO_x生成及治理问题	已淘汰
碱性氧化	硫化锑、氧化锑	焦锑酸钠	氧化效率受反应动力学及传质影响	工业应用
生物质催化氧化	硫化锑	焦锑酸钠	催化转化率高	试验研究
加压氧化	硫化锑、氧化锑	焦锑酸钠	利用氧分压强化氧化反应,缩短反应时间	试验研究
真空蒸馏—区域熔炼	金属锑	高纯锑	流程短、工艺简单	工业应用
氯化精馏—区域熔炼	金属锑、氧化锑	高纯锑	产品纯度高	工业应用

3 结论与展望

当前金属锑、三氧化二锑、焦锑酸钠及高纯锑的生产过程普遍存在污染严重、能耗高以及伴生资源利用率低等问题。虽然富氧熔池熔炼、固硫还原熔炼、矿浆电解及熔盐电解等技术强化了硫资源回收与污染源头控制,为金属锑的清洁冶金和短流程生产提供了新的技术路径。但污染问题仍需进一步解决。同样地,真空蒸馏、氯化精馏及区域熔炼等技术促进了高纯锑制备水平提升,而砷与锑深度分离仍是制约高纯锑制备的重要瓶颈。因此,绿色锑冶金的攻关重点应聚焦于:

1)复杂含锑矿物及二次锑资源的高效预处理与砷-锑定向分离技术开发;

2)湿法冶金废液减量化、资源化循环利用技术;

3)面向光伏、半导体等新兴赛道的高纯锑与焦锑酸钠短流程制备技术;

4)开展多尺度模拟与工程放大研究,推动实验室新技术向工业化落地转化。随着低碳冶金理念不断落地,多工艺耦合、全流程污染协同控制将成为绿色锑冶金技术发展的重要方向。

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Research Progress on Green Antimony Metallurgy Technology

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Abstract: China plays a pivotal role in the global antimony (Sb) industry, ranking first worldwide in both antimony reserves and production. As an important strategic metal, antimony is widely used in flame retardants, alloys, photovoltaic glass, semiconductor materials, and other industrial applications. However, conventional antimony metallurgical processes are generally characterized by high energy consumption, substantial sulfur dioxide emissions, and relatively low resource utilization efficiency, posing considerable challenges to the sustainable development of the antimony industry. These challenges have become increasingly prominent with the growing exploitation of low-grade ores, complex polymetallic resources, and secondary antimony-bearing materials. Developing cleaner, more efficient, and environmentally sustainable metallurgical technologies has therefore become an important research priority. This review systematically examines the structure of the antimony industrial chain, covering resource supply, metallurgical processing, and downstream applications, and summarizes the evolving trends in antimony consumption. Particular attention is given to recent advances in green metallurgical technologies for the production of major antimony products, including metallic antimony, antimony trioxide, sodium pyroantimonate, and high-purity antimony. For metallic antimony production, conventional roasting and reduction smelting processes were reviewed alongside emerging technologies, such as oxygen-enriched smelting, sulfur-fixing reduction smelting, hydrometallurgical leaching, and electrochemical extraction. The technical characteristics of these processes were discussed, with an emphasis on reducing energy consumption and sulfur dioxide emissions while improving the recovery of antimony and associated valuable metals. For antimony trioxide production, conventional oxidative volatilization-condensation processes and alternative chlorination-hydrolysis routes were examined, focusing on production efficiency, impurity control, and the environmental challenges associated with off-gas treatment and wastewater management. For sodium pyroantimonate production, representative preparation processes and recent developments in alkaline oxidation, catalytic oxidation, and pressure-assisted oxidation were summarized, highlighting approaches to improving reaction efficiency and reducing reagent consumption. For high-purity antimony production, purification technologies, including vacuum distillation, chlorination-distillation-reduction, and zone refining, were reviewed, with particular emphasis on the separation of chemically similar impurities, deep arsenic removal, and the stringent purity requirements of advanced applications. Furthermore,

the technical advantages, practical limitations, and industrial applicability of different metallurgical routes were comparatively discussed from the perspectives of process complexity, energy consumption, environmental impact, resource recovery, and product quality. Although emerging metallurgical technologies offer considerable potential for cleaner production and improved resource utilization, their large-scale implementation still faces challenges associated with complex raw material compositions, reagent recycling, secondary waste management, equipment corrosion, and operational stability. Future research should focus on the development of shorter process flowsheets, cleaner production technologies, advanced purification methods, and more efficient recycling of primary and secondary antimony resources. The integration of process intensification, pollution control, impurity separation, and comprehensive resource utilization is expected to facilitate the transition of antimony metallurgy toward cleaner, more efficient, and higher-value production, thereby supporting the green and low-carbon development of the antimony industry.

Key words: clean metallurgy; antimony trioxide; sodium pyroantimonate; high-purity antimony; resource recycling

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