

铜冶炼精炼炉用镁铬质耐火材料损毁机制

李君霞^{1,2}, 段 锋¹, 丁冬海¹, 靳恩东¹, 闫光辉³

(1. 西安建筑科技大学材料科学与工程学院, 西安 710055; 2. 濮阳濮耐高温材料(集团)股份有限公司, 河南 濮阳 457100;
3. 郑州海迈高温材料有限公司, 郑州 452370)

摘 要: 镁铬质耐火材料作为一种优异的抗熔渣侵蚀材料,在铜冶炼领域具有广泛的应用前景。国内外关于铜冶炼耐火材料损毁机理研究主要集中在铜精矿火法炼铜工艺的熔炼炉、转炉、阳极炉等炉型,再生铜精炼炉用耐火材料损毁机理却鲜有研究。瑞林固体块料精炼炉(NGL)对废杂铜再生利用有重要意义,能缓解铜精矿资源的不足。采用扫描电子显微镜、能谱仪、衍射仪探讨了铜冶炼 NGL 炉用后镁铬质耐火材料侵蚀损毁机理。结果表明: 镁铬砖受炉渣与铜熔体的双重作用,橄榄石相的形成与方镁石晶粒的溶解是炉衬材料化学损毁的主要原因。随着熔渣的渗透、方镁石晶粒的溶解,粗铜及铜的氧化物等熔体表现出更强的渗透能力,基质铬铁矿颗粒边缘及镁质骨料的晶界、气孔或裂纹处被大量的粗铜、铜的氧化物熔体填充,破坏了镁铬砂、铬铁矿尖晶石、方镁石的直接结合,这种金属熔体能够深入镁铬砖的内部结构,可达 260 mm 以上。含 $\text{SO}_2\text{--O}_2$ 的气体扩散到残砖冷面的类原砖层,由于晶界处的钙镁橄榄石的离解,气相介质中 SO_2/SO_3 与砖中 CaO 反应生成了 CaSO_4 , XRD 结果证实,残砖冷面反应层存在 CaSO_4 物相。 $\text{SO}_2\text{--O}_2$ 的气体扩散作用下的相关反应会引起体积膨胀,导致结构疏松,加剧了耐火材料的熔融侵蚀。

关键词: 铜冶炼; 镁铬砖; 显微结构; 损毁机理

中图分类号: TQ175.1 文献标志码: A 文章编号: 0454-5648(2024)12-3841-08

网络出版时间: 2024-11-15



铜是支持中国低碳转型和经济发展的战略资源^[1]。铜冶炼的主要原料来源是铜精矿和再生铜资源。为了满足日益增长的市场需求,中国进口大量铜精矿,同时很多企业也纷纷加大了对再生铜或废弃铜料等废杂铜的进口力度,以进一步补充市场供应并推动资源的循环利用,部分品位高的废杂铜经加工直接制成铜制品,其余进入废杂铜冶炼行业精炼成阴极铜。废杂铜精炼炉型包括 NGL 炉和倾动炉、卡尔多炉等。NGL 炉废杂铜火法精炼装备是结合倾动炉和回转式阳极炉优点研发的新型炉型^[2],用于处理含铜品味大于 90% 的废杂铜,将杂铜或块状粗铜熔化并精炼,精炼脱除杂质,产出合格的铜液直接供给铜加工设备加工成铜材,或送阳极浇铸机浇铸成阳极板,进入电解精炼工序。

近年来,国内外关于铜冶炼耐火材料损毁机理研究主要集中在铜精矿火法炼铜工艺的熔炼炉^[3-4]、

转炉^[5-8]、阳极炉^[9-11]等炉型。铜精矿经熔炼炉熔炼成铜锍(冰铜),铜锍(冰铜)经转炉/吹炼炉吹炼成粗铜,粗铜经阳极炉精炼成阳极铜,阳极铜经电解精炼成精炼铜。铜冶炼工艺具有化学反应剧烈、速度快、热强度高、炉内气氛(O_2 和 SO_2)复杂等特点^[12-13],致使炉衬耐火材料易被侵蚀^[14]。镁铬质耐火材料因其优异的抗熔渣侵蚀能力,在火法冶金中通常用作铜冶炼的内衬材料^[15-19]。到目前为止,铜冶炼用最适宜的耐火材料仍然被认为是镁铬质耐火材料^[20]。据文献^[21-22]报道,中国国产氧气底吹熔炼炉(SKS)用镁铬质耐火材料的损毁机制是铜渣对镁铬耐火材料的侵蚀,研究发现渣中的 $\text{Cu-Cu}_x\text{O}$ 主要沿主相晶界和贯通气孔渗透,方镁石-方镁石和方镁石-铬铁尖晶石直接结合的显著损失是铜冶炼底吹 SKS 炉衬的主要损毁机制。阳极炉精炼用镁铬质耐火材料内衬的蚀损主要是由高氧势下碱渣作用使得晶间相铬尖晶石的溶解

收稿日期: 2024-05-21。 修订日期: 2024-07-22。

基金项目: 陕西省科技厅项目(2023-YBGY-421)。

第一作者: 李君霞(1983—), 女, 硕士研究生, 工程师。

通信作者: 段 锋(1970—), 男, 副教授。

Received date: 2024-05-21. Revised date: 2024-07-22.

First author: LI Junxia (1983—), female, Master candidate, Engineer.

E-mail: ljx1115@126.com

Correspondent author: DUAN Feng (1970—), male, Associate Professor.

E-mail: xjddf@163.com

生成了铬酸钠及氧化亚铜的渗透^[23]。Veselin 等^[24]研究了阳极炉铜渣对镁铬砖与无铬砖的渗透性和耐腐蚀的影响,发现无铬砖在阳极炉衬难以达到镁铬砖的抗铜渣的侵蚀效果。Zhiqian 等^[25]研究了 Mg–Cr 和 Al–Cr 2 种不同材质的用后耐火材料侵蚀机理,并指出耐火材料组分溶解和新相的形成是主要的损毁原因。铜冶炼高铬耐火材料损毁遵循渗透–溶解/反应–剥落机制^[26]。NGL 精炼炉对废杂铜再生利用有重要意义,能缓解铜精矿资源的不足。然而 NGL 精炼炉废杂铜所含杂质过多(含 Pb、Zn、As、Ni、Fe 等金属元素)且需反复氧化和造渣^[2],致使炉衬耐火材料服役环境

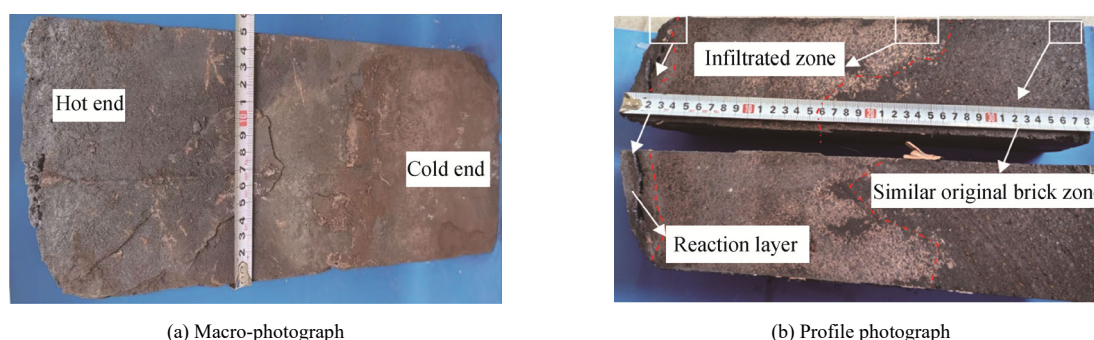
苛刻。

本工作通过分析 NGL 炉用后镁铬砖宏观形貌、物相组成及显微结构,以期揭示 NGL 废杂铜精炼炉用镁铬砖的损毁机理,为铜冶炼用耐火材料的发展和应用提供更多的科学依据。

1 实验

1.1 样品制备

试样选取江西某铜厂 NGL 炉用后镁铬砖,对其进行侵蚀行为及机理分析,残砖水平切面,按侵蚀程度分为不同区域,依次是挂渣反应层、渗透层、类原砖层(见图 1)。



(a) Macro-photograph

(b) Profile photograph

图 1 NGL 炉用后镁铬砖宏观照片

Fig. 1 Macro-photographs of used magnesia chrome brick in NGL furnace

1.2 样品表征

采用 S8 TIGER 型 X 射线荧光光谱仪(XRF)对服役前后镁铬砖不同区域成分进行分析,测试范围:元素 O~U。服役前镁铬砖(MGe–20)与服役后镁铬砖的化学组成与理化指标见表 1。利用帕纳科 X'Pert PRO 型 X 射线衍射仪(XRD)分析残砖的物相组成,

测试条件: Cu 靶,管电压 40 kV,管电流 40 mA。依据 Archimedes 原理,以水为浸渍液,测定了其体积密度和显气孔率。采用 IT510 型扫描电子显微镜(SEM)对样品进行侵蚀机理与显微结构分析,并通过所配备的 X 射线能谱仪(EDS)对未反应区和侵蚀区进行成分鉴定。

表 1 服役前后镁铬砖的化学组成与理化指标

Table 1 Chemical composition and properties of magnesia chrome brick before and after service

Brand No.	w/%							Bulk density/ (g·cm ⁻³)	Apparent porosity/%	Cold crushing strength/MPa
	MgO	Cr ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	Cu/Cu ₂ O			
MGe–20	57.62	21.16	5.63	1.19	1.01	12.73	0.00	3.30	14.50	52.6
Similar original brick	56.27	21.08	5.49	1.52	1.67	11.97	0.13	3.32	13.00	71.2
Infiltrated zone	49.33	18.49	4.97	2.94	2.00	12.13	8.32	3.94	4.80	184.6
Reaction layer	47.32	17.69	4.76	2.82	1.92	9.70	12.37	4.05	4.30	

w—Mass fraction.

2 结果与讨论

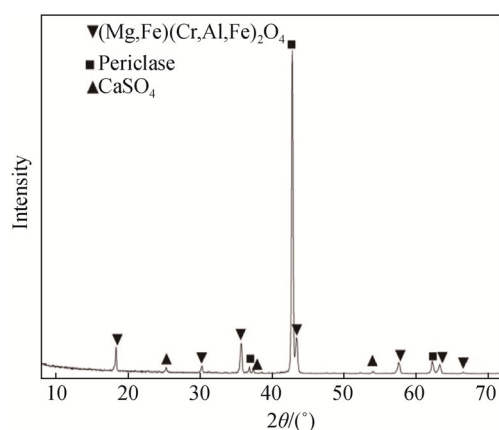
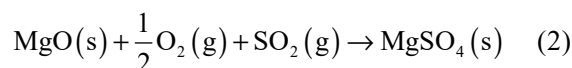
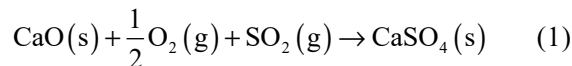
2.1 类原砖层的显微结构

图 2 为用后镁铬砖(类原砖层)的 XRD 物相与显微结构。由图 2 可见,骨料主要是由电熔镁铬熔块

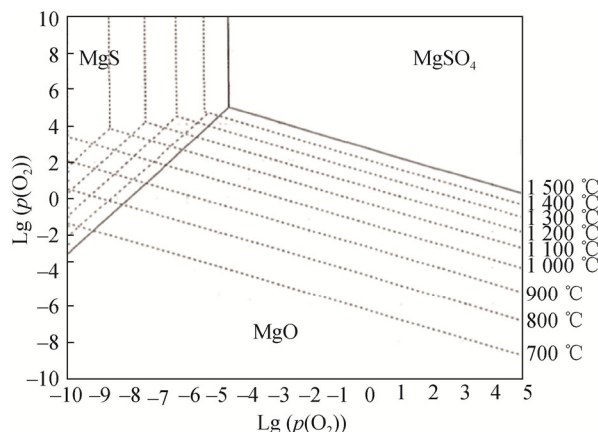
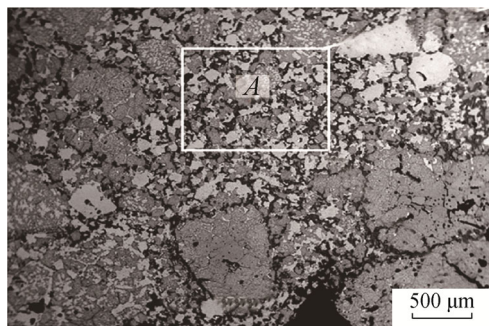
和镁砂颗粒组成,而基质主要由方镁石和铬铁矿尖晶石组成。基质中的孔隙明显,但相邻晶粒(方镁石–方镁石和方镁石–铬铁矿尖晶石)之间结合仍处于较高水平。残砖冷面 XRD 物相为方镁石和铬铁矿尖晶石(Mg, Fe)(Cr, Al, Fe)₂O₄,少量的 CaSO₄ 物相。

Malfliet 等^[27]提出铜冶炼中硫化物由于氧化形成气态 SO_2 , 并迁移到耐火砖中, 随着温度降低到 $1\ 050\ ^\circ\text{C}$ 以下, SO_2 转变为 SO_3 的硫氧化物会与镁铬砖中氧化物反应, 生成主要由 MgSO_4 和 CaSO_4 组成的低熔点碱土金属硫化物, 导致镁铬质耐火材料成分的变化。其次 $\text{SO}_2\text{--O}_2$ 的气体扩散到残砖冷面的类原砖层, 由于晶界处的钙镁橄榄石的离解, 气相介质中 SO_2/SO_3 与砖中 CaO 反应生成 CaSO_4 。XRD 分析证实, 残砖冷面反应层存在 CaSO_4 物相。当氧分压为 $10^{-9}\sim 10^{-5}$ MPa, SO_2 分压为 $0.01\sim 0.10$ MPa, 熔炼温度在 $1\ 200\ ^\circ\text{C}$ 条件下, 硫酸镁的形成温度为

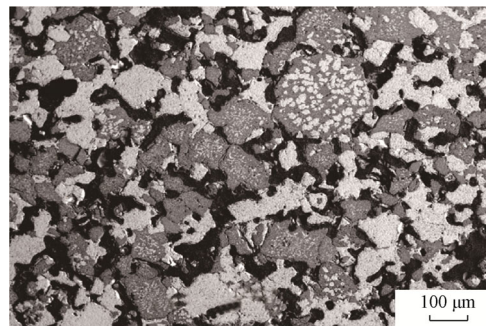
$700\sim 800\ ^\circ\text{C}$ ^[28-29]。 MgO 与气体中的 SO_2 反应生成 MgSO_4 , 式(1)和式(2)相关反应会引起体积膨胀, 当炉衬温度下降时, 耐火材料冷面形成的 MgSO_4 再分解成 MgO , MgSO_4 密度低, 仅为 $2.66\ \text{g}/\text{cm}^3$, 而 MgO 的密度为 $3.58\ \text{g}/\text{cm}^3$ 。因此, MgSO_4 分解所形成的 MgO 结构较为疏松^[29], 最后导致该处的镁铬耐火材料更易受到炉渣等介质的侵蚀。



(a) XRD pattern

(b) Thermodynamic stability diagram of MgSO_4 ^[28]

(c) SEM (similar original brick zone)



(d) SEM of local zone A in Fig.2(c)

图 2 用后镁铬砖(类原砖层)的 XRD 物相与显微结构

Fig. 2 XRD pattern and Microstructures of the used magnesite brick from the similar original brick zone

2.2 渗透层的显微结构

通过对 NGL 炉现场用后砖的宏观观察(图 1), $\text{Cu--Cu}_x\text{O}$ 等熔体对耐火材料的侵蚀以渗透为主, 这种熔体深入渗透到镁铬砖结构, 可达 $260\ \text{mm}$ 以上。耐火材料的体积密度和气孔率随着熔体的渗透而发生变化, 表 1(理化指标)显示残砖渗透层的气孔率较类原砖层有大幅下降, 体积密度相应的增加, 反映了材料内部结构和性质的显著变化。

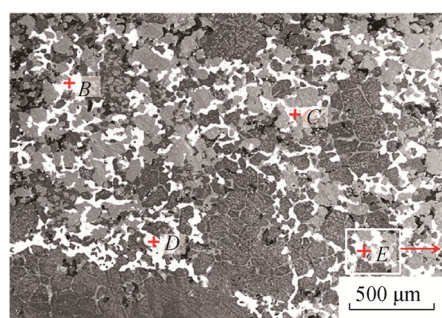
图 3 为镁铬砖(渗透层)各元素的面分布与

Cu_2O 的能谱特征峰。由图 3 可见, $\text{Cu--Cu}_x\text{O}$ 等金属熔体渗透形貌清晰可辨, 电熔镁铬砂、镁砂与基质铬铁尖晶石结合界面的渗透(亮白色区域)主要由 Cu 、 O 元素组成。表 2 为图 3a 中各点 EDS 能谱成分(渗透层)。由表 2 可知, 方镁石晶粒与基质铬铁尖晶石结合界面以金属熔体氧化亚铜(Cu_2O)渗透为主。

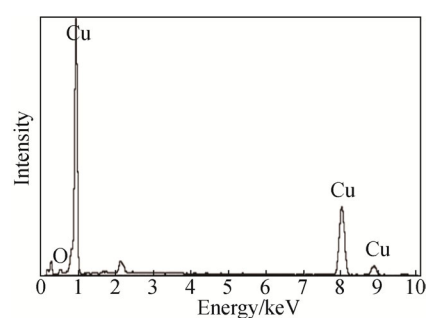
图 4 为用后镁铬砖(渗透层)显微结构。由图 4 可知, $\text{Cu--Cu}_x\text{O}$ 等熔体主要沿着颗粒及基质的开口

气孔、晶界裂纹处渗透,铜金属与周围矿相的热膨胀系数不同^[30],引起结构的改变,致使镁砂、镁铬砂颗粒被铜的熔体破坏,甚至形成穿晶裂纹,延伸至镁铬砖的内部结构。文献[31]研究表明:铜铈可以在较低的温度下被空气氧化形成CuO,转化路径:铜铈–Cu–Cu₂O(温度高于1 020 ℃)–CuO(温度低于1 020 ℃)。基质的气孔及镁质骨料的晶界或裂纹处被大量的粗铜、铜的氧化物等熔体填充,熔体包裹

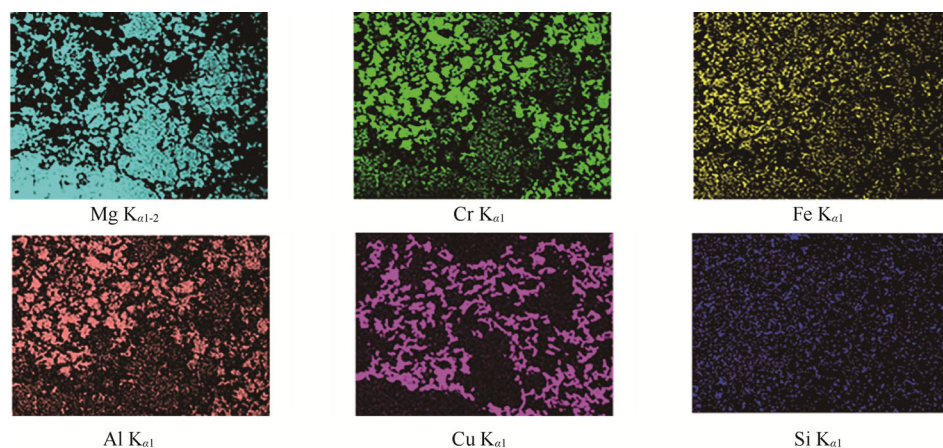
在镁砂、镁铬砂和铬铁矿颗粒周围,破坏了镁铬砂、铬铁尖晶石、方镁石的直接结合,镁砂颗粒的溶解与直接结合的显著损失是镁铬质炉衬的主要损毁机制。图4b中电熔镁铬砂(颗粒F)以镁铬尖晶石和方镁石混晶的均匀微观结构能较好的抵抗铜熔体的渗透。残砖渗透层XRD主要物相为方镁石和铬铁矿尖晶石(Mg,Fe)(Cr,Al,Fe)₂O₄,少量钙镁橄榄石(CaMgSiO₄)物相。



(a) SEM (overview)



(b) EDS of point E in Fig. 3(a)



(c) EDS surface scanning distribution maps in Fig.3 (a)

图3 用后镁铬砖(渗透层)EDS面扫描分布图

Fig. 3 EDS surface scanning distribution maps of used magnesia chrome brick from the infiltrated zone

表2 图3a中各点EDS能谱成分(渗透层)

Table 2 EDS of the points in Fig. 3(a) (infiltrated zone)

Element	w/%				x/%			
	Point B	Point C	Point D	Point E	Point B	Point C	Point D	Point E
Cu	97.82	95.87	92.71	91.23	91.86	87.15	77.92	75.38
O	2.18	2.97	5.45	5.76	8.14	10.72	18.10	18.92
Mg		0.70	1.12	1.50		1.67	2.16	3.26
Cr				0.45				0.45
Si			0.72	1.06		0.46	1.82	1.99
Fe		0.46						

x—Mole fraction.

2.3 反应层的显微结构

NGL 火法精炼工序的废杂铜一般杂质含量在

4%~20%,废杂铜杂质含量明显高于铜精矿熔融粗铜的杂质质量(0.5%~2.0%),废杂铜中含有Pb、Zn、

As、Sb、Bi、Ni、Fe 等金属元素, NGL 炉精炼废杂铜所含杂质过多需反复氧化和造渣, 致使炉衬耐火材料易被侵蚀。

图 5 为用后镁铬砖(反应层)的 XRD 物相与显微结构。由图 5 可知, 镁铬砖热面(反应层)受 NGL 炉渣与金属铜熔体的双重作用, 熔渣与 MgO 颗粒反应生成镁橄榄石(含铁)和(Mg,Fe,Ni)O 固溶体, 与铬铁矿尖晶石形成(Mg,Fe,Ni)(Cr,Al,Fe)₂O₄ 的复相尖晶石。残砖反应层 XRD 物相为方镁石和铬铁矿尖晶石, 少量橄榄石(含铁)物相。镁砂颗粒易受熔渣的侵蚀^[32], 部分方镁石晶粒被溶渣侵蚀, 在基质或颗粒与基质结合处溶解成孔及裂痕。铬铁矿颗粒没有被深入侵蚀现象, 铬铁矿颗粒中心 EDS 成分见表 3(点 M), 中心(点 M)Cr₂O₃ 质量分数是 52.67%, FeO 质量分数是 12.89%。铬铁矿颗粒边缘 EDS 成分见表 3(点 N)。边缘(点 N)FeO 质量分数上升到 51.37%, Cr₂O₃ 质量分数下降到 13.31%。由图 5f 还可以看出, 铬铁矿颗粒边缘形成了高铁尖晶石环带, 呈现颗粒中心深、边缘浅的显微结构特征。在

1 700 °C 条件下, FeO 和 Cr₂O₃ 在 MgO 的固溶度为 14%, 反映了镁铬质耐火材料具有良好的抗渣渗透能力^[33]。

由于 NGL 炉渣中铁、镍、锌等金属元素的扩散, 特别是铁、镍元素在炉渣中的含量较高, 铬铁矿尖晶石中, 三价 Fe³⁺ 易扩散, 趋向置换 Cr³⁺/Al³⁺ 形成新型高铁尖晶石^[34]。基质中的铬铁矿尖晶石在镁砂颗粒周围与渣反应形成高铁尖晶石致密层(图 5b), EDS 能谱成分见表 3(点 H、点 I、点 J)。Fe²⁺、Ni²⁺、Zn²⁺ 趋向于置换镁砂或镁铬砂颗粒的 Mg²⁺, 形成 (Mg,Fe,Ni)O 固溶体。能谱成分见表 3(点 K、点 L)。尖晶石致密层很好的保护了耐火材料颗粒, 减弱了侵蚀作用, 但严重的渣渗透的最终结果是导致靠近热面镁铬砖的致密化。理化指标(表 1)显示此反应层气孔率最低, 体积密度最大。镁铬砖挂渣反应层与渗透层界面附近应力聚集, 致使裂纹的形成与扩展。对其 NGL 炉现场用后砖进行宏观观察(图 1), 发现残砖挂渣反应层存在明显的深裂纹, 裂纹扩展最终可能导致结构剥落。

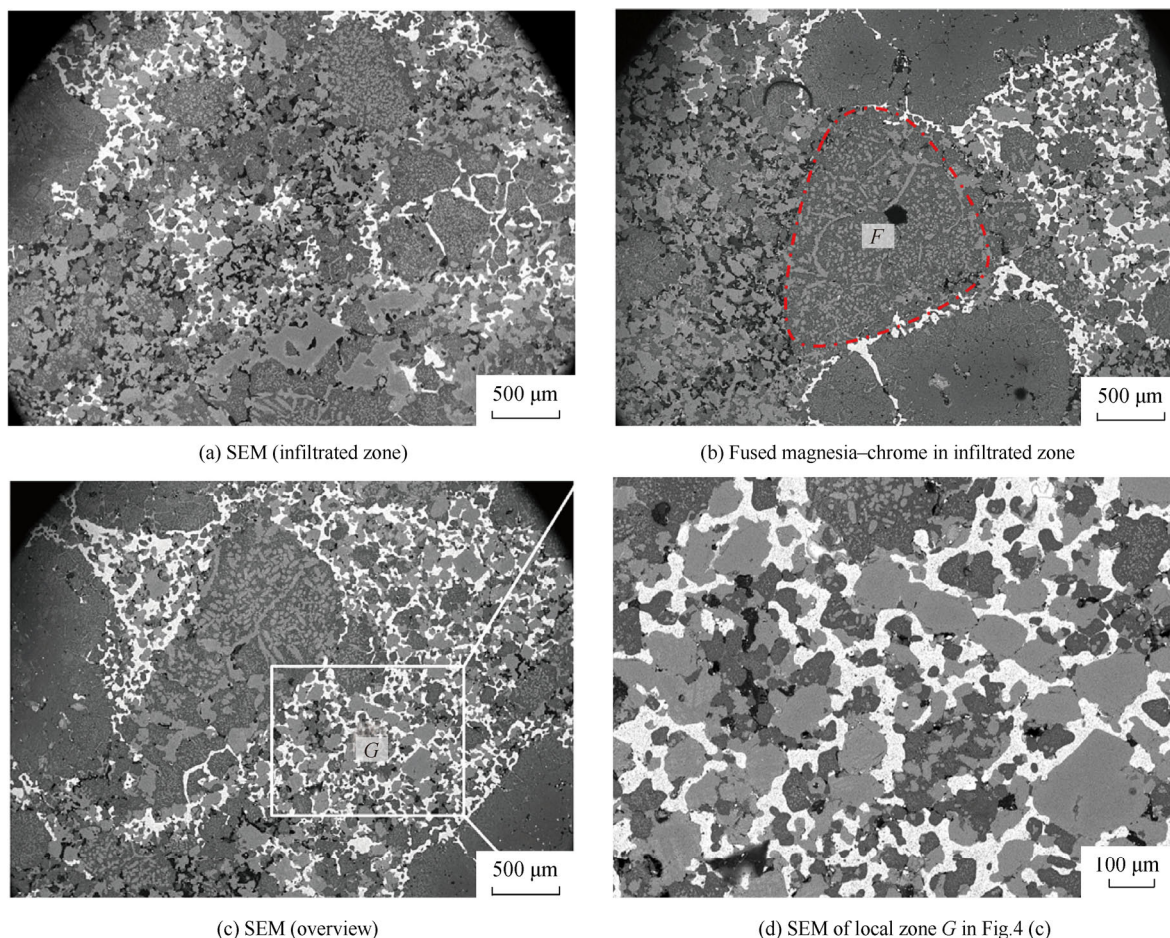


图 4 用后镁铬砖(渗透层)显微结构 SEM 照片

Fig. 4 SEM photographs of the used magnesia chrome brick from the infiltrated zone

表 3 图 5 中各点 EDS 能谱成分(反应层)
Table 3 EDS of each point in Fig.5 (reaction layer)

Points	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	NiO	MnO	CuO	ZnO	SnO ₂
H	8.41	3.54	11.35	53.68	17.76		3.02	2.25	
I	5.83	2.45	9.94	56.11	18.56	0.42		2.23	4.46
J	5.17	3.87	10.73	56.71	20.68			2.84	
K	41.09	2.32	8.42	27.36	18.38	0.39		2.05	
L	52.32	2.16	5.80	21.37	18.34				
M	18.55	14.34	52.67	12.89	0.76		0.78		
N	6.81	3.85	13.31	51.37	17.87	0.52	3.81	2.46	

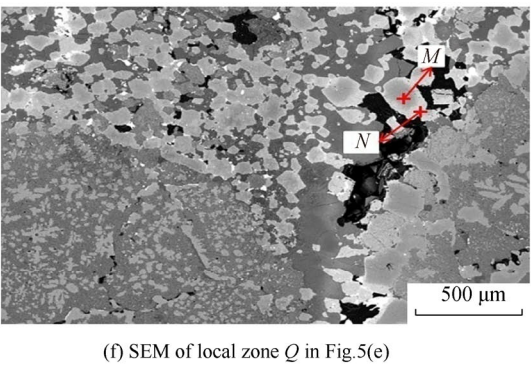
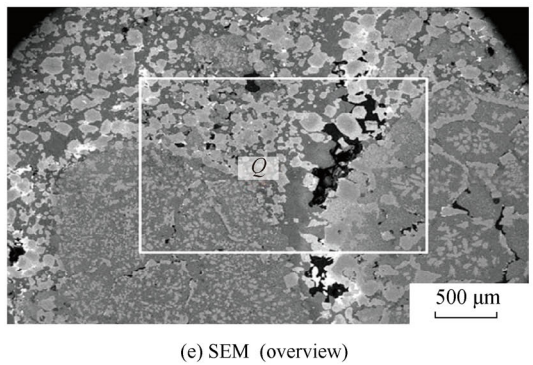
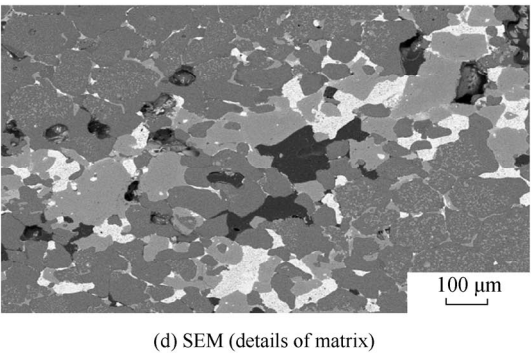
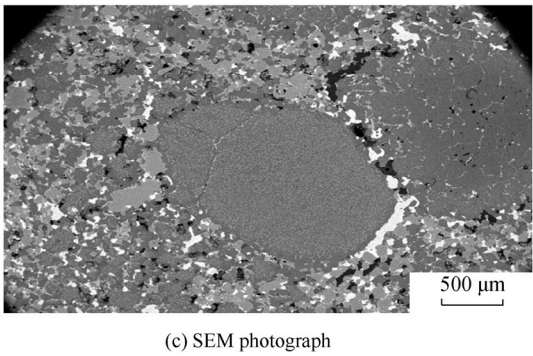
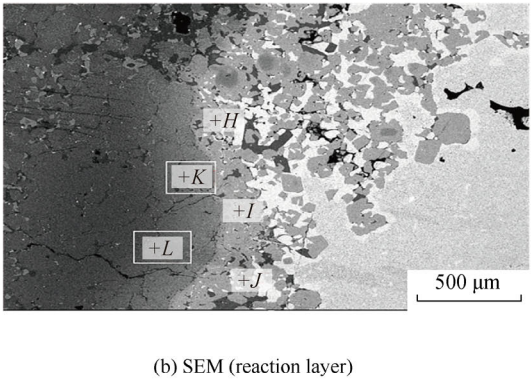
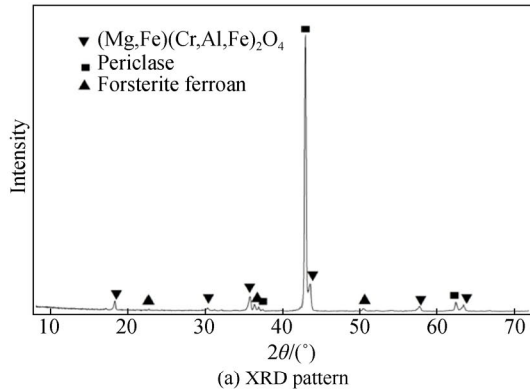


图 5 用后镁铬砖(反应层)的 XRD 物相与显微结构
Fig. 5 XRD pattern and SEM photographs of used magnesia chrome brick from the reaction layer

3 结论

1) NGL 精炼炉渣中铁、镍、锌等金属元素的扩散, 熔渣与方镁石晶粒相互作用生成橄榄石(含铁)和(Mg,Fe,Ni)O 固溶体, 与铬铁尖晶石形成(Mg,

Fe,Ni)(Cr,Al,Fe)₂O₄ 的复相尖晶石。橄榄石相的形成与方镁石晶粒的溶解是镁铬质耐火材料化学损毁的主要原因。

2) Cu–Cu_xO 等金属熔体对耐火材料的侵蚀以渗透为主, 含 SO₂–O₂ 的气体扩散到残砖冷面的类原

砖层,生成主要由 MgSO_4 和 CaSO_4 组成的低熔点碱土金属硫化物, $\text{SO}_2\text{--O}_2$ 气体作用下的相关反应会引起体积膨胀,导致镁铬质耐火材料结构疏松,加剧了耐火材料的熔融侵蚀。

3) 炉衬材料中电熔镁铬砂以镁铬尖晶石和方镁石混晶的均匀微观结构能较好的抵抗铜熔体的渗透,铬铁矿尖晶石颗粒边缘形成的高铁尖晶石环带,增强了抗熔渣侵蚀能力。

参考文献:

- [1] ZHANG J M, TIAN X, CHEN W, et al. Measuring environmental impacts from primary and secondary copper production under the upgraded technologies in key Chinese enterprises[J]. *Environ Impact Asses*, 2022(9): 106855.1–106855.9.
- [2] 姚素平. NGL 炉精炼废杂铜工艺及其应用[J]. *有色金属(冶炼部分)*, 2010(6): 13–15.
YAO Suping. *Nonferrous Met Extr Metall*, 2010(6): 13–15.
- [3] GREGUREK D, MAJCENOVIC C, SPANRING A, et al. Forsterite bursting in magnesia chromite bricks—two case studies from lead and copper smelting furnaces[J]. *Mater Sci*, 2011(2): 49–53.
- [4] 陈肇友. 奥斯特特铜熔炼炉用耐火材料与保护层形成问题[J]. *中国有色冶金*, 2005(1): 27–44.
CHEN Zhaoyou. *China Nonferrous Metall*, 2005(1): 27–44.
- [5] PÉREZ I, MORENO-VENTAS I, RÍOS G. Post-mortem study of magnesia-chromite refractory used in Peirce-Smith Converter for copper-making process, supported by thermochemical calculations[J]. *Ceram Int*, 2018, 44(12): 13476–13486.
- [6] 张原. 炼铜转炉用镁铬质耐火材料侵蚀机理的研究[D]. 郑州: 郑州大学, 2014.
ZHANG Yuan. Study on erosion mechanism of magnesia-chrome refractories for copper smelting converter[D]. Zhengzhou: Zhengzhou University, 2014.
- [7] 许名湘, 杨辉, 董跃, 等. 铜冶炼 PS 转炉风口区镁铬砖侵蚀机理的探究[J]. *铜业工程*, 2023(1): 167–171.
XU Mingxiang, YANG Hui, DONG Yue, et al. *Copp Eng*, 2023(1): 167–171.
- [8] 李真真, 徐义彪, 王庆虎, 等. 氧化钛对镁砂抗热震性能及抗渣渗透性能的影响[J]. *硅酸盐学报*, 2023, 51(3): 602–609.
LI Zhenzhen, XU Yibiao, WANG Qinghu, et al. *J Chin Ceram Soc*, 2023, 51(3): 602–609.
- [9] GREGUREK D, SCHMIDL J, REINHARTER K, et al. Copper anode furnace: Chemical, mineralogical and thermo-chemical considerations of refractory wear mechanisms[J]. *JOM*, 2018, 70(11): 2428–2434.
- [10] PÉREZ I, MORENO-VENTAS I, RÍOS G. Fundamentals of the refractory wear in an industrial anode furnace used in the copper-making process[J]. *Ceram Int*, 2019, 45(8): 9788–9798.
- [11] PÉREZ I, MORENO-VENTAS I, RÍOS G. Study of the refractory used in a submerged arc furnace in the copper-making industry[J]. *Int J Appl Ceram Technol*, 2020, 17(2): 625–636.
- [12] JIN E D, DING D H, ZHANG N X, et al. Regulating the pore structure of periclase refractories by adding Y_2O_3 to enhance corrosion resistance for copper slag[J]. *J Am Ceram Soc*, 2024, 107(5): 3146–3158.
- [13] 李勇. 铜冶金用镁铬耐火材料[M]. 北京: 冶金工业出版社, 2014.
- [14] 马三宝, 鄢文, 林小丽, 等. 钢包渣对轻质方镁石-镁铝尖晶石耐火材料的侵蚀机理[J]. *硅酸盐学报*, 2018, 46(3): 443–448.
MA Sanbao, YAN Wen, LIN Xiaoli, et al. *J Chin Ceram Soc*, 2018, 46(3): 443–448.
- [15] LIU G F, LI Y W, ZHU T B, et al. Influence of the atmosphere on the mechanical properties and slag resistance of magnesia-chrome bricks[J]. *Ceram Int*, 2020, 46(8): 11225–11231.
- [16] 李亚格, 刘雪枫, 李杭, 等. 熔渣与耐火材料高温润湿研究进展[J]. *硅酸盐学报*, 2023, 51(3): 677–686.
LI Yage, LIU Xuefeng, LI Hang, et al. *J Chin Ceram Soc*, 2023, 51(3): 677–686.
- [17] HOU X, DING D H, XIAO G Q, et al. Corrosion mechanism of magnesia-chrome refractory bricks with $\text{Fe}_2\text{O}_3\text{--SiO}_2\text{--Cr}_2\text{O}_3$ copper converter slag [J]. *Ceram Int*, 2023, 49(10): 15395–15401.
- [18] 李亚伟, 李勇. 耐火材料—高温工业的铠甲[J]. *硅酸盐学报*, 2023, 51(3): 561.
LI Yawei, LI Yong. *J Chin Ceram Soc*, 2023, 51(3): 561.
- [19] PÉREZ I, MORENO-VENTAS I, PARRA R, et al. Post-mortem study of magnesia-chromite refractory used in the gas area of a Submerged Arc Furnace for the copper-making process[J]. *Boletín De La Soc Española De Cerámica Y Vidrio*, 2019, 58(4): 178–188.
- [20] 罗旭东. 铜冶炼工艺用耐火材料内衬的使用及损毁机理回顾(1)[J]. *耐火与石灰*, 2015, 40(3): 21–33.
LUO Xudong. *Refract Lime*, 2015, 40(3): 21–33.
- [21] XU L, CHEN M, WANG N, et al. Chemical wear mechanism of magnesia-chromite refractory for an oxygen bottom-blown copper-smelting furnace: A post-mortem analysis[J]. *Ceram Int*, 2021, 47(2): 2908–2915.
- [22] 王光阳, 桑绍柏, 王庆虎, 等. Ni^{2+} 掺杂对 MgCr_2O_4 材料红外辐射性能的影响[J]. *硅酸盐学报*, 2023, 51(3): 562–570.
WANG Guangyang, SANG Shaobai, WANG Qinghu, et al. *J Chin Ceram Soc*, 2023, 51(3): 562–570.
- [23] 张宁轩, 肖国庆, 段锋, 等. 铜冶炼阳极炉镁铬质耐火材料损毁机理[J]. *硅酸盐学报*, 2021, 49(9): 2025–2035.
ZHANG Ningxuan, XIAO Guoqing, DUAN Feng, et al. *J Chin Ceram Soc*, 2021, 49(9): 2025–2035.
- [24] PETKOV V, JONES P T, JONES, E et al. Chemical corrosion mechanisms of magnesia-chromite and chrome-free refractory bricks by copper metal and anode slag[J]. *J Eur Ceram Soc*, 2007: 2433–2444.
- [25] YU Z Q, LIU Z H, YE F C, et al. Corrosion mechanism of magnesia-chrome and alumina-chrome refractories in E-scrap smelting[J]. *Ceram Inter*, 2022, 48(2): 2693–2703.
- [26] GAO J H, SU W G, WANG X, et al. Corrosion and degradation mechanisms of high chromia refractory bricks in an entrained-flow gasifier: Experimental and numerical analysis[J]. *J Mater Res Technol*, 2023.
- [27] MALFLIET A, LOTFIAN S, SCHEUNIS L, et al. Degradation mechanisms and use of refractory linings in copper production processes: A critical review[J]. *J Eur Ceram Soc*, 2014, 34(3): 849–876.
- [28] LIOW J L, TSIRIKIS P, GRAYNB. Study of Refractory Wear in the Tuyere Region of a Peirce-Smith Nickel Converter[J]. *Can Metall Quart*, 1998: 99–117.
- [29] 于仁红, 蒋明学, 李勇. SO_2/SO_3 气氛对镁铬耐火材料侵蚀机理的研究[J]. *耐火材料*, 2002, 36(增刊): 27–29.
YU Renhong, JIANG Mingxue, LI Yong. *J Refractories*, 2002, 36(suppl): 27–29.
- [30] 付琪琪, 钟立桦, 白文献, 等. 铜冶炼侧吹炉用镁铬质耐火材料损毁机制[J]. *耐火材料*, 2024, 58(2): 148–154.
FU Qiqi, ZHONG Lihua, BAI Wenxian, et al. *Refractories*, 2024, 58(2): 148–154.
- [31] CHEN M, CUI Z X, WEI C D, et al. Degradation mechanisms of refractories in a bottom blown copper smelting furnace[M]//*The Minerals, Metals & Materials Series*. Cham: Springer International Publishing, 2018: 149–157.
- [32] 陈欣雨, 黄奥, 李昇昊, 等. 电熔镁砂在 $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ 熔渣中的

溶解行为[J]. 硅酸盐学报, 2023, 51(3): 610–618.
CHEN Xinyu, HUANG Ao, LI Shenghao, et al. J Chin Ceram Soc, 2023, 51(3): 610–618.
[33] 钱凡, 段雪珂, 杨文刚, 等. 镁铬耐火材料及高温装备绿色化应用研究进展[J]. 材料导报, 2019, 33(23): 3882–3891.

QIAN Fan, DUAN Xueke, YANG Wengang, et al. Mater Rep, 2019, 33(23): 3882–3891.
[34] LIU W, WANG L, MA B Z, et al. Reactions between magnesia–chrome refractories and copper converter slags: Corrosion behavior and prevention by Fe-rich layer formation[J]. Ceram Int, 2022, 48(10): 14813–14824.

Degradation Mechanism of Magnesia–Chrome Refractory for Nerin–Gutai–Lu Copper Refining Furnace

LI Junxia^{1,2}, DUAN Feng¹, DING Donghai¹, JIN Endong¹, YAN Guanghui³

(1. College of Materials Science and Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China; 2. Puyang Refractories Group Co., Ltd., Puyang 457100, Henan, China; 3. Zhengzhou Haimai High Temperature Materials Co., Ltd., Zhengzhou 452370, China)

Extended Abstract

Introduction Copper is a kind of strategic resource to support low carbon transition and economic development. The main sources of raw materials for copper smelting are copper concentrate and recycled copper resources. The existing researches on the damage mechanism of refractories that are used in copper smelting mainly focus on the smelting furnace, converter, anode furnace and other furnace types for copper concentrate pyrometallurgical copper refining process. However, there is little research on the damage mechanism of refractory, used in recycled copper refining furnace. Nerin–Gutai–Lu (NGL) has a great significance for the recycled of waste copper and alleviates the shortage of copper concentrate resources. The copper smelting process is characterized by intense chemical reactions, fast speed, high heat intensity and complex furnace atmosphere (*i.e.*, O₂ and SO₂) in the furnace, which can easily damage the furnace lining refractories. The magnesia–chrome refractories have extensive applications in coppers smelting because of its excellent slag corrosion resistance. In this study, the damage mechanism of magnesia–chrome brick used in NGL recycled copper refining furnace was investigated. The macroscopic morphology, phase composition, and microstructure of the used magnesia–chrome brick were analyzed.

Methods The sample was selected from magnesia–chrome brick used in the NGL furnace of a copper plant in Jiangxi Province, China, and their corrosion behavior and mechanism were analyzed. The residual brick was horizontally cut and divided into different areas according to the degree of corrosion, which were the reaction layer, infiltrated zone and the similar original brick zone. The chemical and phase composition of different areas of the residual brick were characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD), and the bulk density and apparent porosity were measured based on the Archimedes principle using water as a medium. The degradation on mechanism and microstructure of the sample were analyzed by scanning electron microscopy (SEM), and the composition of the sample was identified by attached energy dispersive spectrometry (EDS).

Results and discussion The magnesia–chrome brick is destroyed through chemical damage by NGL slag and copper melt due to the forsterite phase and the dissolution of periclase grains. The crude copper and copper oxides exhibit an intense permeability due to the penetration of slag (containing gas) and dissolution of periclase particles. With a large number of crude copper and copper oxides melting, the direct combination of fused magnesia–chrome, and periclase is destroyed. This metal melt can penetrate into the internal structure of magnesia–chrome brick and reach over 260 mm, which distributes in the matrix around the chromite particles and the grain boundaries, and pores or cracks of magnesia aggregate. Subsequently, SO₂ and O₂ are diffused to the similar original brick layer on the cold face of the residual brick due to the dissociation of monticellite at the grain boundary. SO₂/SO₃ in gas-phase medium reacts with CaO in brick to form CaSO₄. The XRD patterns indicate that the main component of the reaction layer on the cold face of the residual brick is CaSO₄ phase. The related reaction under the gas diffusion of SO₂–O₂ can cause a volume expansion, leading to the structural looseness and exacerbating the melting corrosion of refractories.

Conclusions The diffusion of metal elements in NGL refining slag, *i.e.*, ferrum, nickel and zinc, led to the interaction between slag and periclase grains, resulting in the formation of forsterite (containing Fe) and (Mg, Fe, Ni)O solid solutions, which reacted with chromite to form (Mg, Fe, Ni)(Cr, Al, Fe)₂O₄ multiphase spinel. The reasons of chemical damage in magnesia–chrome refractories included the formation of forsterite phase and the dissolution of periclase grains. The corrosion of refractories by metal melts, such as Cu–Cu₂O, was mainly infiltrated. The gases containing SO₂–O₂ diffused into the similar original brick layer of the residual brick cold surface, generating low melting point alkaline earth metal sulfides mainly composed of MgSO₄ and CaSO₄. The relevant reactions under the action of SO₂–O₂ could cause a volume expansion, resulted in a loose structure of magnesia–chrome refractories and exacerbating the melting corrosion of refractories. The uniform microstructure of the fused magnesia–chrome block in the furnace lining was a mixture of magnesia–chrome spinel and periclase, which could effectively resist the infiltration of copper melt. In addition, the high-Fe spinel ring formed at the edge of chromite particles also enhanced the slag corrosion resistance.

Keywords copper smelting; magnesia chrome brick; microstructure; damage mechanism