

中国激光

基于 LIBS 技术结合内标法的烧结矿碱度测量研究

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摘要 对检测烧结矿的实验参数进行优化,使其光谱信号的相对标准偏差(RSD)维持在4%左右。再结合内标法,分别选择合适的Fe元素谱线作为Ca、Si元素的内标谱线,利用内标后的比值与碱度值进行拟合分析。相比于无内标方法,其校准模型的决定系数(R^2)从0.468提升至0.951,且预测值的相对误差最高为1.14%。结果表明,在实验条件优化下,内标法对烧结矿碱度的预测精确度高。

关键词 光谱学; 激光诱导击穿光谱; 内标法; 烧结矿碱度; 稳定性

中图分类号 O433.4

文献标志码 A

DOI: 10.3788/CJL230520

1 引言

烧结矿是我国高炉炼铁的主要原料。含铁原料约占高炉炼铁成本的70%,而在高炉炉料中,烧结矿一般占70%(质量分数)以上,烧结工艺占钢铁企业能耗总量的6%~10%,烧结厂也是废弃物排放地之一^[1-3]。因此,无论是从成本,还是从节能与环保的角度考虑,烧结矿的生产对高炉炼铁都有着重要影响。碱度决定烧结矿的质量,它被定义为自身所含碱性氧化物与酸性氧化物的质量分数之比,在实际应用中一般采用二元碱度来表示,即CaO与SiO₂总含量的比值^[4-5]。烧结矿的碱度与高炉冶炼的质量、产量和能耗密切相关^[6]。

传统的烧结矿碱度分析方法一般有X射线荧光光谱法(XRF)、电感耦合等离子体原子发射光谱法(ICP-OES)、瞬发伽马射线中子活化分析(PGNAA)技术等^[7-9]。其中:XRF作为一种非破坏性的分析方法已在许多领域中得到应用,但是它不适用于分析原子序数小于20的轻量元素^[10];ICP-OES需要进行复杂的样品预处理,检测过程繁琐、成本高^[11];而PGNAA技术虽然分析灵敏度高,但其需要配备辐射源^[12],具有放射性,对操作者产生潜在危害。因此,发展一种实时、快速、安全的检测手段具有重要意义。

激光诱导击穿光谱(LIBS)技术是一种以激光为激发源进行元素成分分析的原子发射光谱(AES)技术。其基本原理是:待测样品在脉冲激光的激发下形成高温等离子体,等离子体在冷却过程中会辐射出不同频率的光,将其收集到光谱仪中进行识别,进而可以

对元素光谱信息进行处理分析。LIBS技术具有实时快速、原位检测、多元素同时分析、远程检测和无需复杂的样品预处理过程等优点^[13],被广泛地应用于诸多领域^[14-20]。

LIBS技术在铁矿石原料分析方面的应用取得了很大进展,但在烧结矿碱度定量分析方面的应用较少。Yang等^[21]使用随机森林回归(RFR)模型定量分析了烧结矿的碱度,二元碱度预测模型的决定系数(R^2)为0.869。但该研究没有优化实验条件,这会增加分析时间且预测准确度有待进一步提高。Ding等^[22]使用基于核极限学习机(K-ELM)的回归预测方法,定量分析了烧结矿中的全铁(TFe)与碱度,碱度预测模型的 R^2 为0.925,但K-ELM容易出现过拟合现象,无法获得稳定的操作结果。为减少实验参数与基体效应等因素对测量结果的影响,本文对烧结矿测量的实验参数进行优化,并结合内标法提高烧结矿碱度的测量准确性。

2 实验装置及样品

2.1 实验装置

本实验所使用的LIBS系统原理图如图1所示。实验使用一台调Q Nd:YAG脉冲激光器作为激发源,工作波长为1064 nm,激光能量最大可达100 mJ,重复频率最高为20 Hz,脉冲持续时间为5.82 ns。脉冲激光从激光器中发出,在反射镜的作用下,经过一个石英平凸透镜(焦距为100 mm)后聚焦在样品表面。收光装置(由两个焦距为60 mm的平凸透镜组成)从侧向45°方向收集样品激发辐射出的光信号。

收稿日期: 2023-02-13; 修回日期: 2023-03-10; 录用日期: 2023-03-15; 网络首发日期: 2023-03-25

基金项目: 国家自然科学基金(32171627, 62105050)、重庆市自然科学基金(cstc2020jcyj-msxmX0147)、重庆市教委科技研究项目(KJQN202000640, KJZD-M202200602)

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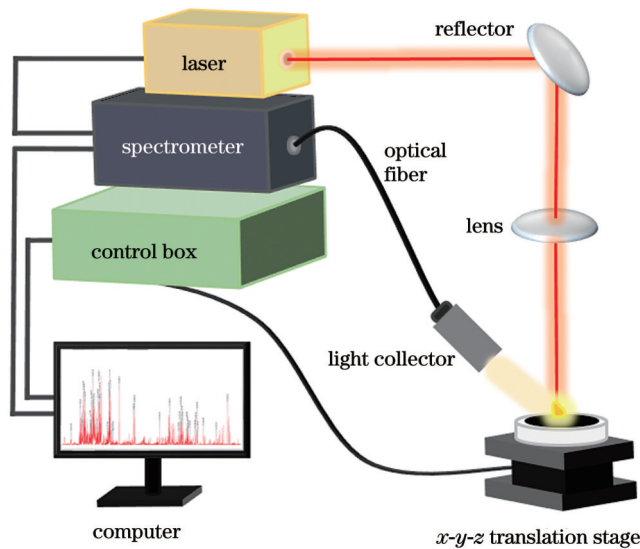


图1 LIBS实验原理图

Fig. 1 Experimental diagram of LIBS

收集到的光信号经光纤传输至多通道光谱仪,该光谱仪的波长范围为180~1100 nm,分辨率为0.07 nm。激光器采用外触发工作模式,由多通道光谱仪配套的软件进行控制,光谱仪的门宽度设置为1 ms。样品被放置在三轴移动平台上,使用步进电机控制箱控制样品台移动,以确保每次脉冲激光发射都会轰击在新的样品表面,便于光谱的连续采集并确保采集的稳定性。

2.2 样品制备

实验中所使用的样品是一批真实的烧结矿样品。由于烧结矿原样品的形状不规则,且表面与内部多孔,因此为了方便检测与分析,需要对烧结矿原样品进行简单的预处理。样品的处理过程如下:首先把烧结矿磨制成粉末并进行过筛处理,以便样品能有好的成型效果,保证实验测量的稳定性;由于原样品中SiO₂和CaO的含量基本相同,因此碱度基本无差异,为了使样品的碱度呈现出一定的变化梯度,因此需要进行加标处理,选择高纯度的SiO₂和CaO标准样品,将其掺入到过筛后的烧结矿粉末中,研磨并混合均匀;最后采用硼酸包边的方式,在粉末压片机的作用下,制作成直径为32 mm、厚度为5 mm的片状分析样品。采用上述样品制备方法,得到10个具有不同碱度值的烧结矿样品。样品的主要成分含量(通过XRF检测得到)与碱度值在表1中列出,其中样品编号含字母A的为加标样品,含字母B的为未加标样品。

在实验过程中,在每个烧结矿样品表面120个不同位置处进行连续光谱采集,为了获得更好的信号-背景比(SBR),每个光谱图均为连续10次脉冲激光烧蚀的平均光谱信号图,最终每个样品得到12个谱图。实验采用前6个烧结矿样品(A-1~A-5、B-1)建立碱度的校准模型,剩下4个样品(A-6、A-7、B-2、B-3)用

表1 10个烧结矿样品的主要成分与碱度值

Table 1 Main components and alkalinity values of 10 sintered ore samples

Sample No.	Mass fraction / %			Alkalinity
	TFe	CaO	SiO ₂	
A-1	53.56	10.32	7.37	1.40
A-2	54.11	10.27	6.22	1.65
B-1	54.62	10.47	5.52	1.90
A-3	53.32	12.27	5.70	2.15
A-4	52.81	13.06	5.44	2.40
A-5	52.45	13.97	5.37	2.60
A-6	53.89	10.31	6.88	1.50
A-7	53.64	12.12	5.77	2.10
B-2	54.69	10.52	5.96	1.76
B-3	55.04	10.52	5.46	1.93

作误差分析。

3 分析与讨论

3.1 烧结矿样品光谱

烧结矿是由多种含铁的原料混合炼制而成,发射光谱谱线较为丰富。根据相关文献及美国标准与技术研究院(NIST)的原子光谱数据库,结合测试所得到的真实光谱图,识别出Fe、Si、Ca等主要元素。烧结矿样品的LIBS图如图2所示。通过分析对比,选出干扰较少且无明显自吸收效应的三条特征谱线,分别为Fe II 248.266 nm、Si I 288.158 nm、Ca I 647.166 nm,将其作为后续实验条件优化的三条参考谱线。

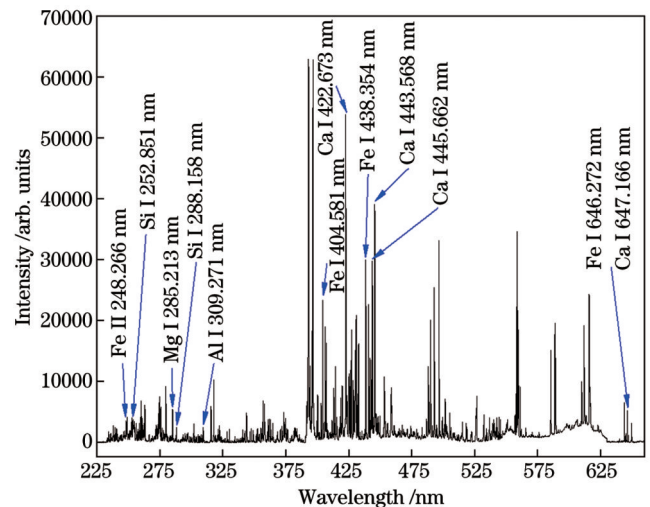


图2 烧结矿的LIBS

Fig. 2 LIBS of sinter

3.2 压片压强对光谱信号的影响

烧结矿粉末压片所需要的压力没有统一的标准。压力不同,成型后的样品压缩比、铺平度与单位面积内烧结矿粉末的密度都会有所不同,进一步会导致光谱强度与光谱稳定性不同。因此,为了获得较好的光谱信号,有必要探究压片压强对烧结矿样品光谱信号的影响。实验压片压强范围选取为 5~45 MPa,压片持续时间为 30 s,其他实验条件保持一致。图 3 展示了不同压强下光谱信号稳定性与光谱强度的相应变化。从图 3(a)可以看出,当压强为 30 MPa 左右时,Fe、Si、Ca 三种元素谱线(分别为 Fe II 248.266 nm、Si I 288.158 nm、Ca I 647.166 nm,下同)强度的相对标准偏差(RSD)较低,此时的光谱信号稳定性较好。在较小压强下,压片样品的硬度低且表面较粗糙,

脉冲激光轰击时样品表面容易开裂或散落;在较大压强下,硼酸和烧结矿粉末的回弹力差异较大,造成样品变形或开裂,进而可能导致样品局部分布不均匀的情况。因此,较小或较大压强都会导致光谱信号稳定性变差。图 3(b)为光谱信号的强度与压强之间的关系。可以看出,在压片压强较小时,获取的光谱信号强度较低,因为此时样品不够紧密,单位面积内烧结矿粉末的含量较低,所以脉冲激光轰击样品时烧蚀量较少。随着压强的增大,单位面积内烧结矿粉末的含量增多,脉冲激光可以烧蚀的烧蚀量增多,因此光谱信号强度增强,当压强大于 20 MPa 时,光谱强度变化减缓并趋于稳定,此时单次脉冲激光的烧蚀量已达到饱和状态。结合以上两种情况,选择 30 MPa 作为烧结矿粉末的压片压强。

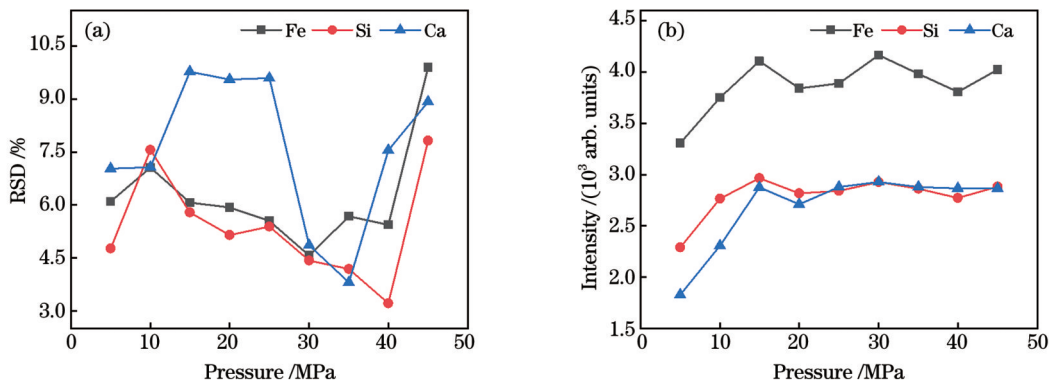


图 3 压强对 Fe、Si、Ca 三种元素光谱信号的影响。(a)信号稳定性;(b)信号强度

Fig. 3 Effects of pressures on spectral signals of Fe, Si, and Ca. (a) Signal stability; (b) signal intensity

3.3 脉冲激光能量对光谱信号的影响

由于 LIBS 系统的激发源为激光器,因此等离子体的形成和光谱强度与激光的能量密切相关。低激光能量无法诱导形成等离子体,激光能量较高时光谱背景噪声也会随信号强度的增大而增大,且信号波动也变大,影响测量准确性。因此,对于不同的待测样品,选择合适的激光能量进行 LIBS 分析是有必要的。

实验中选取的能量范围为 35~75 mJ,每隔 5 mJ 调整脉冲激光能量,多通道光谱仪采集延时设置为 1.5 μs。Fe、Si、Ca 三种元素谱线对应的信号强度以及 SBR 随脉冲激光能量变化的趋势如图 4 所示。可以

看出,三种元素谱线的信号强度和 SBR 的变化规律基本相同,都表现为谱线强度随着脉冲激光能量的不断增加而增加,而 SBR 则随着脉冲激光能量的不断增大而减小。其原因如下:随着激光能量的不断增大,样品烧蚀量逐渐增大,所以光谱信号强度不断增大;与此同时,背景信号的强度也不断增加,且背景信号强度的增大速度相对较快,因此 SBR 随着脉冲激光能量的增大而不断减小。从图 4 可以看出,在 50~60 mJ 的能量范围内,三种元素谱线有较高的信号强度与 SBR。综合考虑,选择 55 mJ 作为本次实验的脉冲激光能量值。

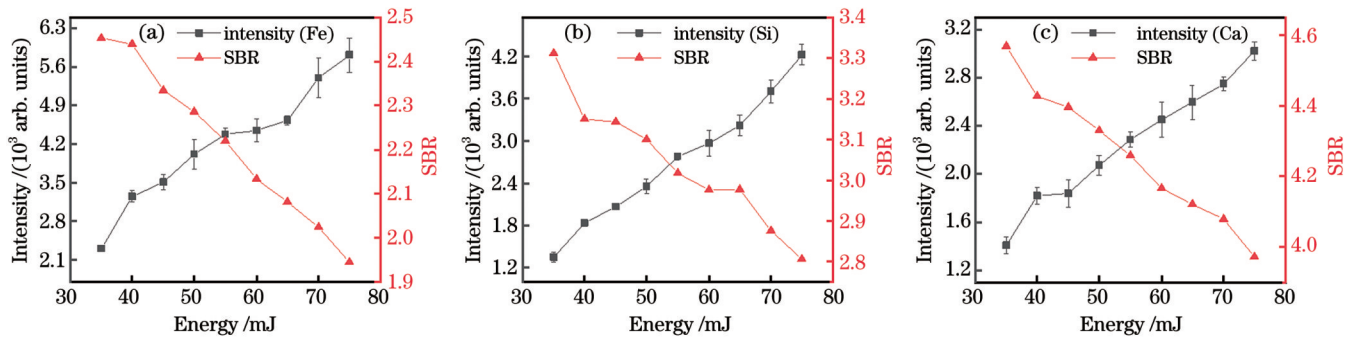


图 4 激光能量对光谱信号的影响。(a) Fe II 248.266 nm;(b) Si I 288.158 nm;(c) Ca I 647.166 nm

Fig. 4 Effects of laser energy on spectral signals. (a) Fe II 248.266 nm; (b) Si I 288.158 nm; (c) Ca I 647.166 nm

3.4 探测延迟时间对光谱信号的影响

由于激光诱导的等离子体是瞬态等离子体,其辐射强度随时间时刻变化,因此选择合适的光谱信号探测延迟时间也是非常重要的。在激光诱导产生等离子体初期,光谱信号辐射以连续的韧致辐射和复合辐射为主,此时有效信号较小,背景噪声信号较大,因此光谱信号强度较高,SBR却比较低。随着延迟时间的增加,连续背景辐射不断减弱,同时原子谱线辐射的强度也逐渐减弱,但是连续背景辐射信号的衰减速率远大于原子谱线辐射,所以光谱信号的强度随着延时的增加而降低,而SBR随着延时的增加而逐渐增大。

图 5 给出了探测延迟时间(0~4 μs)对激光诱导烧结矿样品光谱信号的影响规律。可以看出,当探测延时为零时,光谱信号的强度最大,但此时的连续背景辐射信号较大,故SBR较低。随着延迟时间的增加,背景噪声信号的强度快速降低,SBR不断增大。然而,等离子体寿命短暂,若延迟时间过久,则采集不到有效的光谱信号,因此探测延迟时间的选择比较重要。从图 5 所示的信号变化规律可以看出,当延迟时间为 1 μs 左右时,三种元素谱线有较好的信号强度与信背比。因此,选择 1 μs 作为本次实验的最佳探测延迟时间。

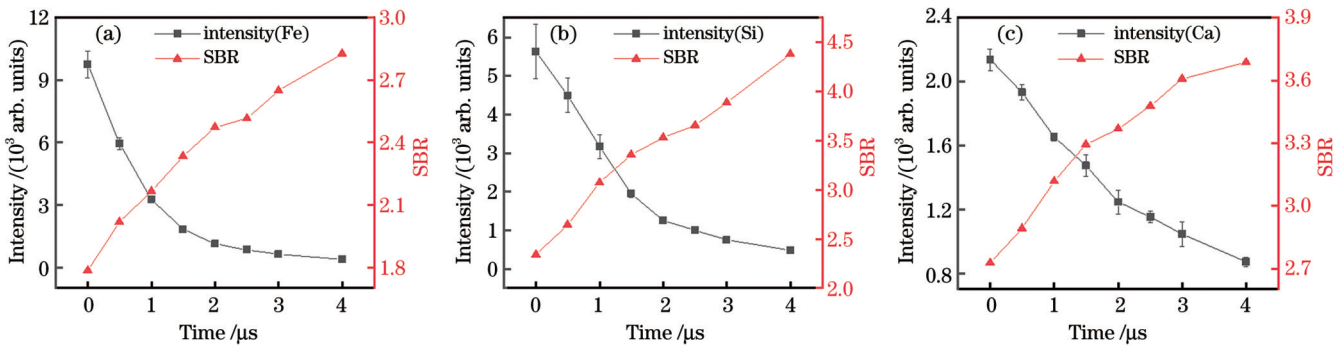


图 5 延迟时间对激光诱导烧结矿样品光谱信号的影响。(a) Fe II 248.266 nm; (b) Si I 288.158 nm; (c) Ca I 647.166 nm
 Fig. 5 Effects of delay time on spectral signals of laser-induced sinter samples. (a) Fe II 248.266 nm; (b) Si I 288.158 nm; (c) Ca I 647.166 nm

3.5 实际样品的稳定性测试

为了验证采集光谱信号的稳定性,利用优化后的实验条件,采集前 6 个烧结矿样品(表 1)的 LIBS 信号,分别选取多条 Fe、Si 和 Ca 元素的特征谱线,计算其光谱强度的 RSD。根据测试所得到的光谱图,并结合 NIST 原子光谱数据库,选取铁的谱线为 Fe II 248.266 nm、Fe II 259.94 nm、Fe I 438.354 nm 和 Fe I 646.272 nm,硅的谱线为 Si I 250.69 nm、Si I 251.611 nm、Si I 252.851 nm 和 Si I 288.158 nm,钙的谱线为 Ca I 422.673 nm、Ca I 443.568 nm、Ca I 445.662 nm 和 Ca I 647.166 nm。每个元素各选取 4 条谱线,一共 12 条参考谱线,其光谱强度的相

对标准偏差结果如图 6 所示。可以看出,同一特征谱线的信号波动程度在不同样品中表现不同,这与基体效应和实验参数波动(样品高度差异和激光能量波动等)有关。此外,可以看到,这 6 个样品的光谱信号稳定性整体表现较好,Fe、Si、Ca 的四条参考谱线强度的 RSD 基本都在 6% 以下,大多分布在 4% 左右。其中:Fe 元素的光谱强度 RSD 在 2.5% 左右,最低为 1.23%;Si 元素的光谱强度 RSD 集中在 4.5% 左右;Ca 元素的光谱强度 RSD 集中在 3% 左右。由此可以看出,在优化后的实验条件下,烧结矿 LIBS 信号的波动性较小,有利于 LIBS 技术的定量分析。

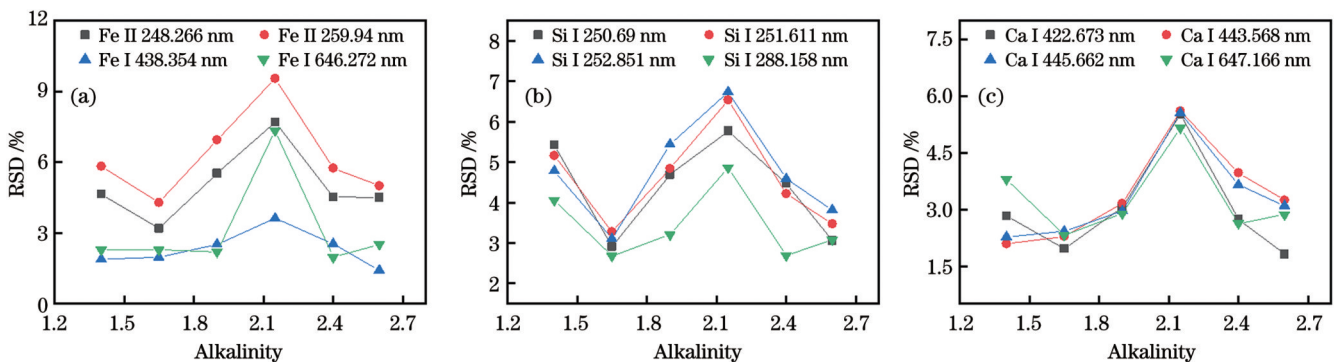


图 6 不同元素的光谱信号稳定性测试结果。(a)Fe 元素;(b)Si 元素;(c)Ca 元素
 Fig. 6 Test results of spectral signal stability of different elements. (a) Fe element; (b) Si element; (c) Ca element

3.6 烧结矿样品碱度的定量分析

由于基体效应、实验设备等因素的影响,即使在激光能量、光谱采集延时等参数相同的条件下,等离子体的激发辐射状态还是很难维持一定的稳定性。对于元素相同但含量不同的样品,在同一条件激发下,LIBS信号也会出现无规律波动的情况。因此,用光谱信号的强度直接定标分析,其效果往往很差。LIBS技术常用的定量分析方法主要为定标法,定标法包括自由定标法、外标法和内标法。其中自由定标法需要复杂的计算,且只对含量高的元素分析效果好。而相对于外标法,内标法能够减小激光能量不稳定以及样品高度偏差等实验参数波动导致的测量误差。由于烧结矿的碱度主要取决于其自身所含的CaO与SiO₂的浓度比值,这就意味着需要对两种不同的元素进行分析和处理,此时采用单一的内标谱线不能取得很好的分析效果,因此采用内标法对样品碱度进行定量分析时,选择合适的分析谱线是十分重要的。

本文选取Ca I 422.673 nm、Ca I 647.166 nm和Si I 288.158 nm作为碱度定量分析的谱线,它们都有较好的光谱强度且干扰小、稳定性好。由于烧结矿中含量最多的元素为Fe元素,且Fe元素的原子发射谱线比较丰富,因此选取Fe元素的发射谱线作为内标谱线。对比分析可知,Fe II 248.266 nm、Fe I 438.354 nm与Fe I 646.272 nm的光谱信号稳定性较好,且它们的能级差分别与Ca I 422.673 nm、Ca I 647.166 nm和Si I 288.158 nm的能级差接近,这在一定程度上保证了它们具有相似的激发状态。选取谱线的具体能级信息如表2所示,其中 E 与 E' 是该波段粒子激发跃迁的

上能级和下能级。因此,选择Fe II 248.266 nm作为Si I 288.158 nm的内标谱线、Fe I 438.354 nm作为Ca I 422.673 nm的内标谱线、Fe I 646.272 nm作为Ca I 647.166 nm的内标谱线,然后计算Ca、Si谱线与其对应的Fe谱线的光谱强度内标值的比值,并基于最终比值结果建立碱度的校准模型。

表2 分析谱线的能级值

Emission line	E / cm^{-1}	E' / cm^{-1}
Si I 288.158 nm	6298.850	40991.884
Ca I 422.673 nm	0	23652.304
Ca I 647.166 nm	20371.000	35818.713
Fe II 248.266 nm	0	40257.314
Fe I 438.354 nm	11976.239	34782.421
Fe I 646.272 nm	19788.251	35257.324

为了突显内标法定量分析的优势,实验首先采用Ca I 647.166 nm与Si I 288.158 nm、Ca I 422.673 nm与Si I 288.158 nm的光谱信号强度的比值,与实际的碱度值进行拟合。图7为无内标处理的拟合结果。从图7(a)、(b)可以看出,没有经过内标方法处理的校准曲线的相关性很差,其决定系数(R^2)分别为0.681和0.468。主要原因是样品的基体效应与实验参数波动引发的测量误差,导致光谱信号强度与实际碱度值之间无明显的线性相关性,此校准模型无法对烧结矿碱度进行准确分析。

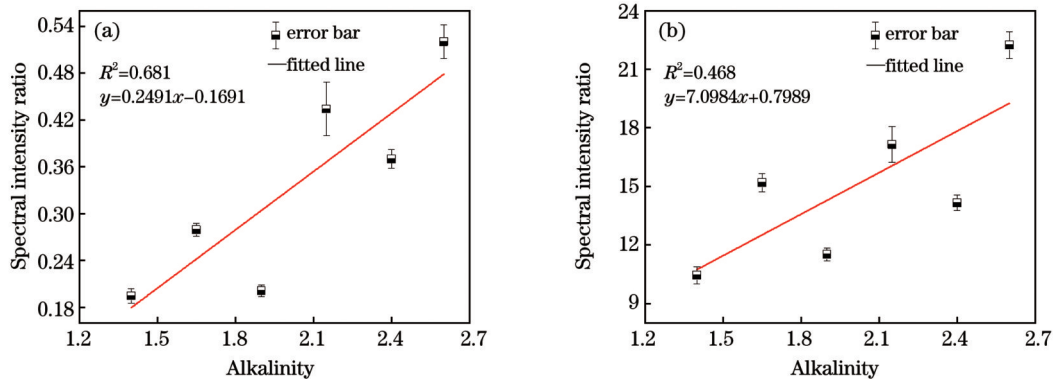
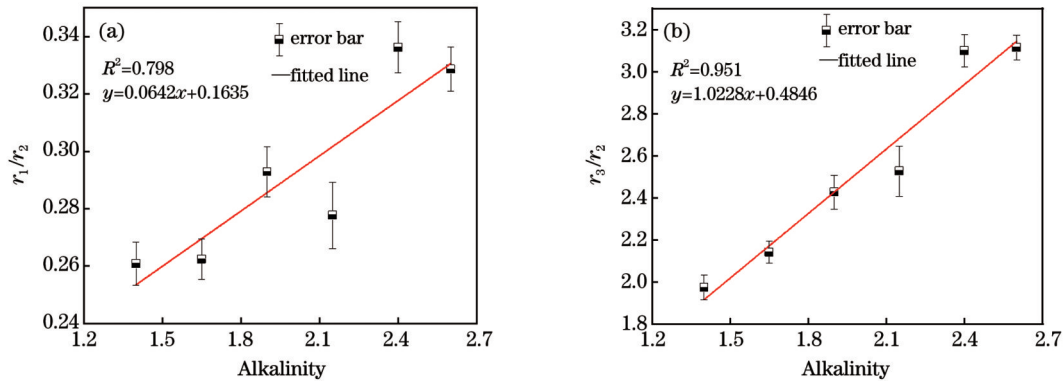


图7 没有经过内标法处理的校准曲线。(a) Ca I 647.166 nm和Si I 288.158 nm的强度比值;(b) Ca I 422.673 nm和Si I 288.158 nm的强度比值

Fig. 7 Calibration curves before processing by internal standard method. (a) Intensity ratio of Ca I 647.166 nm and Si I 288.158 nm; (b) intensity ratio of Ca I 422.673 nm and Si I 288.158 nm

采用经内标法处理得到的比值,建立校准曲线,结果如图8所示,其中 r_1 为Ca I 647.166 nm和Fe I 646.272 nm的强度比值, r_2 为Si I 288.158 nm和Fe II 248.266 nm的强度比值, r_3 为Ca I 422.673 nm和Fe I 438.354 nm的强度比值。以Ca I 647.166 nm和Si I 288.158 nm作为分析谱线,分别以Fe I

646.272 nm、Fe II 248.266 nm作为内标谱线建立校准曲线,如图8(a)所示,其 R^2 为0.798。由此可以看出,与图7(a)相比,其线性相关性得到明显的提高,这表明采用内标法进行数据处理,能明显提升校准模型的拟合优度。采用稳定性较好的分析谱线与内标谱线,模型的拟合优度还能得到进一步提升。以Ca I

图 8 经内标法处理得到的校准曲线。(a) r_1/r_2 ; (b) r_3/r_2 Fig. 8 Calibration curves after processing by internal standard method. (a) r_1/r_2 ; (b) r_3/r_2

422.673 nm 与 Si I 288.158 nm 作为分析谱线, 分别以 Fe I 438.354 nm、Fe II 248.266 nm 作为内标谱线建立校准模型, 如图 8(b) 所示, R^2 达到了 0.951, 相比其他三种情况都有显著的提升。

采取同样的实验方法, 对 A-5、A-6、B-2、B-3 四个样品进行测量, 并对碱度进行定量分析, 结果如表 3 所

示。可以看出, 经内标法处理后建立的校准模型的预测值与实际碱度值的偏差较小, 预测结果的相对误差低于 1.14%, 效果远远好于无内标处理模型的预测结果。由此可见, 采用内标法对烧结矿的碱度进行分析, 可以降低基体效应与实验参数波动导致的测量误差, 从而实现烧结矿碱度的准确测量。

表 3 碱度预测结果的对比分析

Table 3 Comparison and analysis of alkalinity prediction results

Sample No.	XRF	Alkalinity		Relative error / %	
		Before processing by internal standard method	After processing by internal standard method	Before processing by internal standard method	After processing by internal standard method
A-6	1.50	1.22	1.51	-18.67	0.67
A-7	2.10	2.22	2.11	5.71	0.48
B-2	1.76	3.14	1.78	78.41	1.14
B-3	1.93	1.27	1.92	-34.20	-0.52

4 结 论

利用激光诱导击穿光谱技术对烧结矿样品进行检测分析时, 受基体效应、噪声信号与实验参数的影响, 光谱信号波动较大, 进而 LIBS 测量结果与实际偏差较大。为了减小光谱信号的波动并确保碱度测量的准确性, 首先对实验条件进行优化并测试了光谱信号的稳定性, 然后选择合适的分析谱线进行内标处理, 再对烧结矿碱度进行定量分析。实验结果表明, 在优化样品制备条件与实验参数后, 烧结矿样品的 LIBS 信号波动性小, 稳定性较好, 有利于碱度的定量分析。对比无内标方法, 经内标法处理后得到的碱度校准模型的拟合优度更高, 且测量结果更加精准, Ca、Si 元素的光谱强度比与碱度之间的线性相关性得到显著提升。研究结果对烧结矿碱度的 LIBS 检测分析具有一定的参考意义。

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Study on Alkalinity Measurement of Sinter Based on LIBS Technology Combined with Internal Standard Method

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Abstract

Objective Sinter is made from a variety of iron-containing raw materials and is the main raw material for blast-furnace ironmaking in China. Iron-containing raw materials account for nearly 70% of the blast-furnace ironmaking cost, sinter for more than 70% (mass fraction) of the blast-furnace ironmaking materials, and the sintering process for 6%–10% of the total energy consumption of iron and steel enterprises. Therefore, sinter production has a significant impact on blast-furnace ironmaking from the perspectives of cost, burden proportion, and energy savings. Alkalinity is an important parameter of sinter, which is closely related to the quality, output, and energy consumption of blast-furnace smelting. Conventional sinter alkalinity analysis methods have some limitations; therefore, it is necessary to find novel technical methods to measure sinter alkalinity. Laser-induced breakdown spectroscopy (LIBS) is used in many fields, especially in raw material screening and product analysis in the metallurgical industry, owing to its advantages of real-time, rapid, and *in-situ* detection, simultaneous multi-element analysis without complex sample pretreatment, and remote detection. LIBS is known as the “future chemical analysis superstar” and has attracted the attention of numerous researchers recently.

Methods Ten sinter samples with different alkalinity values are obtained by spiking SiO₂ and CaO standard samples. The experiment is conducted under atmospheric conditions. Continuous spectrum acquisition is performed at 120 different positions on the surface of each sinter sample. To obtain a better signal-to-background ratio (RSD), each spectrum is averaged from 10 consecutive pulsed laser ablation signals, and 12 spectra are obtained for each sample. Six sinter samples are used to establish the calibration model for alkalinity, and the remaining four are used as error analysis samples. The spectral lines of Fe, Si, and Ca with low interference and good stability are selected as reference spectral lines for the experimental parameter study. The effects of pressure,

pulse laser energy, and spectrum acquisition delay time on the spectrum signal are studied, and the best experimental parameters are selected. Employing the optimized experimental parameters, the spectral signal stability of the sinter samples is tested. Si and Ca spectral lines with good signal strength and stability are selected as the spectral lines for quantitative analysis of alkalinity. The Fe spectral line, which has a similar spectral line energy level to those of Si and Ca, is selected as the internal standard spectral line. The ratio of the internal standard values of the spectral intensities of Ca, Si, and their corresponding Fe is calculated and used to establish the calibration model of the alkalinity value.

Results and Discussions To verify the stability of LIBS-collected spectral signals, 4 spectral lines are selected for each element, totaling 12 reference spectral lines, and the RSD of their spectral intensities is calculated. The results indicate that the RSDs of the four reference spectral lines of Fe, Si, and Ca are below 6% and mostly distributed around 4% (Fig. 6). The RSD of Fe I 438.354 nm is 2.5%–1.23% [Fig. 6(a)], and the spectral stabilities of Si and Ca are approximately 4.5% [Fig. 6(b)] and 3% [Fig. 6(c)], respectively. After optimizing the experimental conditions, the fluctuation of the sinter LIBS spectral signal is small, which is conducive to the quantitative analysis of LIBS technology. Fe II 248.266 nm and Fe I 438.354 nm are selected as the internal standard spectral lines of Si I 288.158 nm and Ca I 422.673 nm, respectively. The calibration model for alkalinity is determined based on the ratio of their internal standard ratios, and the determination coefficient (R^2) approaches 0.951 (Fig. 8). Using the same experimental method to conduct quantitative analysis on the remaining four samples, the deviation between the predicted value and the actual alkalinity value is small, and the relative error of the prediction result is lower than 1.14% (Table 3). The influence of the measurement error caused by the matrix effect and fluctuation of experimental parameters can be reduced by analyzing the sinter alkalinity via the internal standard method to achieve accurate measurement of the sinter alkalinity.

Conclusions When utilizing LIBS to detect and analyze a sample, the spectral signal fluctuates significantly, owing to the influence of the matrix effect, noise signal, and experimental parameters, which further makes the LIBS measurement result deviate substantially from the actual. To reduce the fluctuation of the spectral signal and ensure the accuracy of alkalinity measurement, first the experimental conditions are optimized, the stability of spectral signal is tested, appropriate analytical spectral lines for internal standard processing are selected, and then a quantitative analysis of alkalinity is conducted. The results demonstrate that after optimizing the sample preparation conditions and experimental parameters, the LIBS spectral signal of the sinter sample fluctuates less and is maintained at approximately 4%, which is conducive to the quantitative analysis of alkalinity. Compared with the non-internal standard method, the R^2 of the calibration model treated by the internal standard method is increased from 0.468 to 0.951, and the maximum relative error is 1.14%, significantly improving the correlation between the spectral intensity ratios of Ca and Si and alkalinity. This results in the accurate measurement of sinter alkalinity, which has certain reference significance for LIBS detection and analysis of sinter alkalinity.

Key words spectroscopy; laser induced breakdown spectroscopy; internal standard method; sinter alkalinity; stability