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气氛和压力对脱灰煤颗粒着火温度的影响

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摘 要:为实现高效低污染能源利用,提出煤基燃料氧水蒸气燃烧的近零排放发电技术.在一维沉降炉上研究伊敏脱灰煤、准东脱灰煤在不同氧浓度、水蒸气浓度下的着火温度,并利用快速升温水蒸气高压热重分析仪研究压力对着火温度的影响.结果表明:氧浓度对脱灰煤着火温度影响较大,随着氧体积浓度的增加,着火温度逐渐降低;随着水蒸气体积浓度的增加,脱灰煤着火温度逐渐升高,水蒸气体积分数从 10%~50%每增加 10%,着火温度升高约 30℃. 当压力小于 1.0 MPa 时,随着压力的增加,准东脱灰煤着火温度降低;当压力在 1.0~2.0 MPa 增大时,着火温度基本不变;在压力大于 2.0 MPa 时,着火温度逐渐升高.

关键词: 脱灰煤;氧燃烧;水蒸气;着火温度;热重分析

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Influence of atmosphere and pressure on the ignition temperature of demineralized coal particles

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Abstract: For energy conversion with high efficiency and low carbon emission, Oxy-Coal Combustion Steam System for power generation with near-zero emissions was proposed. The Ignition Temperature of Yimin demineralized coal and Zhundong demineralized coal were studied in a one-dimensional drop tube furnace at different oxygen concentration and steam concentration. The impact of pressure on the ignition temperature was investigated by High Pressure Steam TGA. The results show that the oxygen volume concentration is very important for the ignition temperature of demineralized coal. With the increasing of oxygen concentration, the ignition temperature is gradually reduced. With the increasing of the concentration of steam, the ignition temperature is gradually raised. When the steam volume concentration, range from 10% to 50%, increases 10%, the ignition temperature increases about 30 °C. When the pressure is less than 1.0 MPa, with the increasing of pressure, the ignition temperature of Zhundong demineralized coal decreases, when the pressure is in the range of 1.0–2.0 MPa, then no obvious change for the ignition temperature, but when the pressure is greater than 2.0 MPa, the ignition temperature increases.

Keywords: demineralized coal; Oxy-coal combustion; steam; ignition temperature; thermogravimetric analysis

近年来,环境污染和全球气候变化越来越受到各国的重视,研究和开发先进的洁净煤燃烧技术具有重要的意义. 富氧燃烧技术是一项非常有潜力的 CO₂ 减排技术. 加拿大 CANMET 能源技术中心 Salvador^[1]和美国的 Anderson 等^[2-3]都提出了采用水作为稀释剂的富氧燃烧技术,并进行了大量的研究. 基于中国以煤为主的能源结构,孙绍增等^[4-5]提出了煤基燃料氧水蒸气燃烧近零排放发电技术,原煤经过去矿物质预处理,得到超净煤,在纯氧条件下

燃烧,把逐级喷入燃烧室内的水直接加热成高温高压混合气体(水蒸气体积分数 90%左右,其余以 CO2为主),推动先进的透平做功,排气中的水蒸气冷凝后得到高浓度的 CO2,实现 CO2的低成本捕集. 煤中的矿物质制约着煤的清洁和高效利用,矿物质的组分和含量影响着煤着火、燃烧及气化特性^[6-7]. 矿物质能够通过化学方法洗去,HPC ^[8-9] (hyper-coal)和 UCC ^[10-11] (ultra clean coal)技术能获取灰分质量分数低于 0.1%的脱灰煤,它能够直接应用在燃气轮机、整体煤气化联合循环发电和先进的煤燃烧技术中,提高了燃烧效率并减少了污染物的排放^[12-13]. 已有研究表明^[14-16],脱灰煤的燃烧、气化和热解特性比原煤好很多,因此,原煤去矿物质处理

是洁净煤燃烧的重要处理过程.

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煤粉颗粒着火过程的研究对于煤高效稳定燃烧是非常重要的. 煤粉颗粒的着火特性不仅受颗粒自身特性的影响,而且受颗粒周围着火环境的影响^[17-21]. 煤粉颗粒的着火与煤种、颗粒大小、挥发分含量等有关,其着火模式能够从异相着火到均相着火变化^[22]. 初伟^[23]研究发现 O₂/CO₂气氛下,随着氧浓度的增加着火温度逐渐降低. 乔瑜等^[24-25]研究发现在 O₂/CO₂气氛下煤粉颗粒的着火较空气气氛下延迟,颗粒周围气氛的导热特性对颗粒的着火温度具有重要的影响. 邹春等^[26]对原煤在 O₂/H₂O 气氛下煤粉的着火较空气气氛下出现延迟,随着氧浓度的增加,煤粉的着火湿度降低.

煤基燃料氧水蒸气燃烧技术在燃烧条件和燃料上具有特殊性,整个燃烧过程具有高温、高压、高氧浓度和高水蒸气浓度的特点.燃料由于去除了灰,表现为纯煤的燃烧特性,其着火特性将发生很大变化.已有的研究主要集中在燃烧气氛对原煤的着火温度的影响,脱灰煤在 O_2/H_2O 气氛下的着火特性还未见相关研究,因此,高水蒸气浓度氧燃烧条件下脱灰煤的着火特性的研究具有重要的科学意义.

本文在一维沉降炉上研究伊敏脱灰煤(YMT) 和准东脱灰煤(ZDT)在不同氧浓度和不同水蒸气浓 度下的着火温度,分析氧浓度和水蒸气浓度对着火 温度的影响,并利用快速升温水蒸气高压热重分析 仪研究压力对脱灰煤着火温度的影响,获得脱灰煤 在高水蒸气浓度氧燃烧条件下着火特性的清晰 认识.

1 实验

对于煤粉着火温度的测量一般不能直接得到其着火温度的绝对值,而是通过一些间接的方法代表煤粉颗粒的着火温度^[27].考虑到沉降炉具有高升温速率(10³~10⁴℃/s)以及良好的动态性能等特点,煤粉颗粒处于气体携带状态,更贴合实际锅炉反应状况,所以采用沉降炉测量脱灰煤煤粉颗粒的着火温度.沉降炉的原理图如图 1 所示.本试验采用测量沉降炉烟气的温度作为着火温度的方法测量脱灰煤在常压下的着火温度.详细测量方法参考初伟^[23]和肖佳元等^[28]的实验方法,这里只对测量过程简单描述.待炉膛温度和给粉稳定后,在沉降炉出口用镜子观察是否着火;同时在炉膛出口采用烟气分析仪监测氧气含量,依次往复升高或降低沉降炉的温度,直到找到氧气含量基本不变,且恰能使给粉完全着火的温度;测量不给粉和给粉两种情况下炉膛轴

线上的烟气温度变化曲线;两曲线分离点说明温度 发生突变,即煤粉发生着火现象,此点即定义为煤粉 在该气氛下的着火温度.

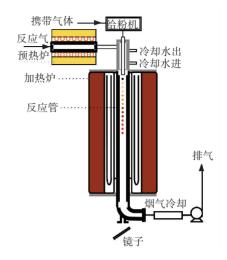


图 1 DTF 实验系统示意

Fig.1 Schematic of the DTF

压力对着火温度影响的实验在快速升温水蒸气高压热重分析仪^[29]上进行,升温速率为20 ℃/min,从室温升高至 700 ℃,根据实验样品的失重曲线,采用常用的 TG-DTG 曲线切线法^[23,30]定义着火温度,能够获得不同压力下的着火温度.

伊敏脱灰煤和准东脱灰煤均采用 $HCl-HF-HCl^{[31]}$ 的方法获得,煤质参数见表 1. 实验所有工况均以 N_2 作为平衡气体,给粉量为 0.5 g/min,反应气体为 O_2/H_2 O/N_2 的混合气体,总流量为 10 L/min,携带气体的总流量为 1 L/min. 在研究不同氧气体积分数(10%~50%)的影响时,水蒸气的体积分数保持 30%不变;研究水蒸气浓度影响时, O_2 体积分数保持在 30%;研究压力(O.1~3.0~MPa)影响时,保持 O_2 和水蒸气体积分数均为 30%.

表 1 准东脱灰煤及伊敏煤脱灰煤工业分析及元素分析(空 干基,质量分数)

Tab.1 Proximate analysis and element analysis of the Zhundong demineralized coal and Yimin demineralized coal (air dry basis, mass fraction) %

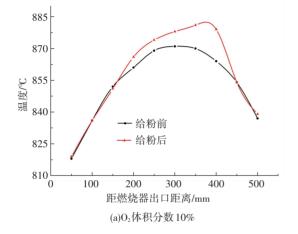
- 煤样 -	质量分数						
	工业分析				元素分析		
	水分	灰分	挥发分	固定碳	С	Н	N
准东脱灰煤	5.82	0.32	31.29	62.57	75.77	3.64	0.94
伊敏脱灰煤	6.26	0.17	42.34	51.23	67.84	4.52	0.91

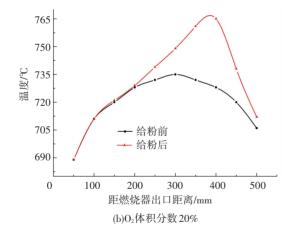
2 结果与讨论

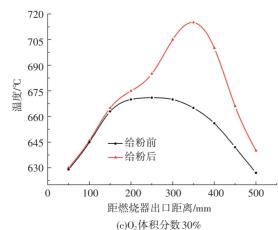
2.1 氧浓度对着火温度的影响

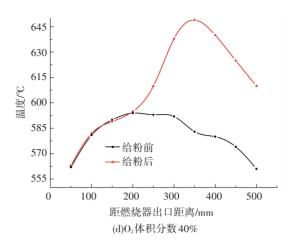
不同氧体积分数(10%~50%)下伊敏脱灰煤着火过程中炉膛烟气温度的变化如图 2 所示,水蒸气

体积分数全部为 30%. 由图 2 可以观察到,在给粉前与给粉后炉膛烟气温度曲线产生分离,给粉后的温度线开始高于给粉前温度值的点,即作为着火温度点. 对比不同氧浓度下炉膛中心烟气温度线可知,随着氧浓度的增加,给粉前后温度的差值逐渐增大. 随着氧气浓度的增大,会有更多的氧气扩散到挥发分火焰中^[32-33],脱灰煤粉周围气体混合物的活性增加,脱灰煤一旦着火,燃烧速率增大,热释放速度加快. 因此随着氧气浓度的增加,煤粉着火后火焰温度上升速率增大,导致给粉前后炉膛中心烟气的温度上升幅度逐渐增大.









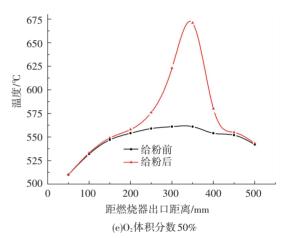


图 2 不同 O_2 体积分数下伊敏脱灰煤的温度分离曲线(水蒸气体积分数为 30%)

Fig.2 The temperature separation curves of Yimin demineralized coal in different O_2 volume fraction (water vapor volume fraction \cdot 30%)

伊敏脱灰煤和准东脱灰煤的着火温度随氧体积分数增加的变化规律如图 3 所示.

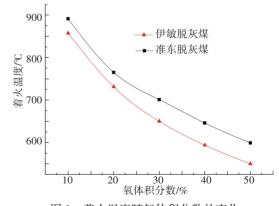


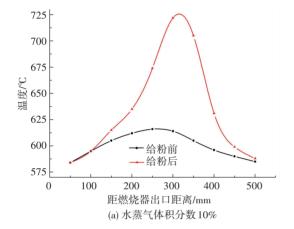
图 3 着火温度随氧体积分数的变化

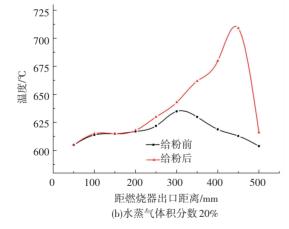
Fig.3 Variation of ignition temperature with O₂ volume fraction 两种脱灰煤的着火温度都随着氧体积分数的增加呈单调下降规律. 这是因为在常压下,随着氧浓度的增加,氧气的浓度梯度增大,而压力和扩散系数是恒定的,由菲克扩散定律可知,扩散通量等于浓度梯度与扩散系数之积. 随着氧浓度的提高,氧气获得了更强扩散

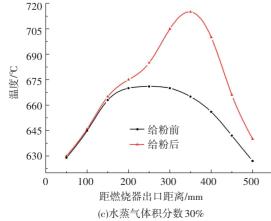
能力,这不仅促进了 O_2 与挥发分的扩散混合,也使氧分子可以占据更多的煤粉颗粒孔隙,为氧化反应的发生提供了有利条件,能够促进脱灰煤粉颗粒的着火,因此,着火温度随氧气浓度的增加而降低,与煤粉在 O_2/CO_2 和 O_2/N_2 气氛下 $^{[23-25]}$ 的研究结果一致.与伊敏脱灰煤相比,准东脱灰煤具有高碳且低挥发分的特点,准东煤脱灰煤进入炉膛后挥发分的析出较慢,颗粒周围的挥发分与氧气混合达到着火极限后才能发生着火,因此,准东脱灰煤相对伊敏脱灰煤较难着火,使得准东脱灰煤的着火温度高出伊敏脱灰煤约50 °C.

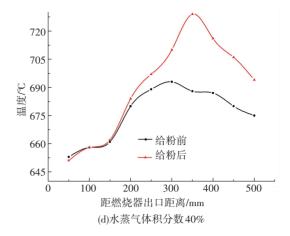
2.2 水蒸气浓度对着火温度的影响

伊敏脱灰煤在不同水蒸气浓度下的着火过程如 图 4 所示.









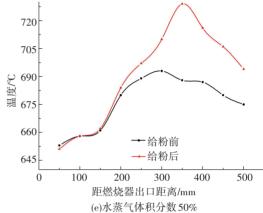


图 4 不同水蒸气体积分数下伊敏脱灰煤的温度分离曲线 (氧气体积分数:30%)

Fig.4 The temperature separation curves of Yimin demineralized coal in different water vapor volume fraction (oxygen volume fraction: 30%)

从图 4 中可以看出,随着水蒸气体积分数的增加,给粉前后炉膛中心烟气的温度差逐渐下降.分析原因,水蒸气的比热较 N_2 更高些,水蒸气浓度高时,混气的比热较大,脱灰煤粉燃烧所产生的热量对炉膛中心烟气加热作用变得不明显.

准东脱灰煤和伊敏脱灰煤的着火温度随水蒸气浓度的变化规律见图 5. 随着水蒸气体积分数的增加,两种脱灰煤的着火温度逐渐升高. 产生这种现象的原因是水蒸气比热值较高,在温度为 500 ℃~700 ℃的区间内,水蒸气的比热较同温下的氮气约高出 20%. 煤粉颗粒的着火可以解释为由于煤粉颗粒从外界吸收热量,自身温度提高,当散热量不足以补偿吸热量时,温度逐渐升高至着火温度后发生着火. 随着水蒸气体积分数的增加,混合气中水蒸气比重增加,导致混合气体平均比热整体增加. 煤粉颗粒在混合气体中沉降的过程即为混合气在颗粒表面绕流的过程,比热较高混合气在绕流过程中会携带煤粉颗粒周围的热量,增加了对煤粉吸热量的补偿,最终表现为煤粉颗粒的着火温度升高. 由理论计算可知,常压下水蒸气与焦炭的气化反应一般发

生在高温下,所以在温度为 500~700 ℃时水蒸气气 化反应可认为没有发生或极其微弱.

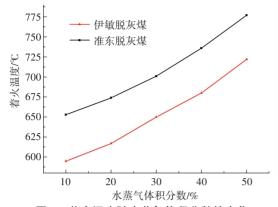


图 5 着火温度随水蒸气体积分数的变化

Fig.5 Variation of ignition temperature with water vapor volume fraction

2.3 压力对脱灰煤着火温度的影响

准东脱灰煤在不同压力下的着火温度如图 6 所示. 当压力从 0.1 MPa 增加到 1.0 MPa 时,着火温度快速下降,降低约 70 ℃;当压力超过 1.0 MPa 时,压力对着火温度的促进作用趋于平稳,1.0 MPa 与 2.0 MPa压力下的着火温度已无明显差距;在压力超过 2 MPa 时着火温度出现小幅度的增加.

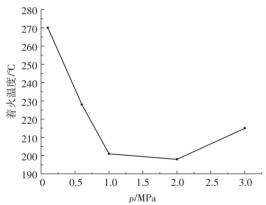


图 6 准东脱灰煤着火温度随压力的变化规律

Fig.6 Variation of ignition temperature of Zhundong demineralized coal with pressure

在环境气氛一定时(O₂体积分数 30%,水蒸气体积分数 30%),压力升高会提高颗粒附近的氧分压,进而提高碳氧反应速率,热量的释放和热传递过程得到增强,使煤粒温度上升,着火温度下降^[34-35]. 当压力继续增大超过 2.0 MPa 后,着火温度出现缓慢上升,总压力较高时,氧气扩散系数减小,削弱了氧分压提高的作用. 同时,总压升高,挥发分的扩散减慢,导致挥发分的释放速率减慢,使煤粉颗粒非均相着火的成分增大,挥发分在颗粒内氧化比在颗粒外氧化容易^[36],挥发分在析出颗粒前就与煤焦一起发生了着火,着火模式逐渐向非均相着火转变. 因此,压力逐渐增大时,由于氧气的扩散特性和挥发分

的释放特性的共同作用,导致准东脱灰煤的着火温度先下降后升高.

3 结 论

- 1)氧浓度对伊敏脱灰煤及准东脱灰煤着火温度的影响较大,随着氧体积分数的增加,着火温度近似呈现单调下降规律.与伊敏脱灰煤相比,准东脱灰煤具有高碳且低挥发分的特点,使得准东脱灰煤的着火温度高出伊敏脱灰煤约50℃.
- 2)水蒸气浓度对伊敏脱灰煤及准东脱灰煤具有相同的影响规律,即脱灰煤着火温度随着水蒸气体积分数的增加呈上升趋势,水蒸气体积分数每增加 10%,着火温度升高约 30 ℃.
- 3)当压力<1.0 MPa 时,随着压力的增加,准东脱灰煤着火温度呈降低趋势;当压力在 1.0 ~ 2.0 MPa增大时,着火温度基本不变;当压力超过 2.0 MPa 时,着火温度逐渐升高.

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