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# Ni 基和 Co 基金属载氧体的持续循环能力研究

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**摘　要**: 化学链燃烧技术是一种新颖的二氧化碳分离技术, 其中金属载氧体持续循环反应能力的优劣直接关系到该技术的实际应用和推广。以 Ni 基和 Co 基金属载氧体为研究对象, 用热重分析仪( TGA) 、扫描电镜( SEM) 和 X 射线衍射仪( XRD) 等工具研究了二者的持续循环能力。结果表明, 添加惰性载体后载氧体的反应速率和持续循环能力均有大幅的提升, 且 Ni 基载氧体比 Co 基载氧体表现出更好的反应特性和持续循环能力。

**关　键　词**: 化学链燃烧; $CO_2$ 分离; 金属载氧体

**中图分类号**: TK16　　**文献标识码**: A

## 引　言

化学链燃烧( chemical looping combustion) 是一种 $CO_2$ 减排的新兴技术, 它既控制了 $CO_2$ 的排放, 又可以避免 $NO_x$ 的生成, 实现了燃料化学能的梯级利用[1]。其基本原理如图 1 所示, 是将传统的燃料与空气的直接反应, 通过载氧体的作用分解为两步气固反应, 燃料不直接与空气接触, 而是通过氧载体在两个串联的反应器之间来完成氧的转移, 两个反应器分别为空气反应器与燃料反应器。

在空气反应器侧发生金属颗粒( $Me_yO_{x-1}$) 的氧化反应:

$$Me_yO_{x-1} + \frac{1}{2}O_2 \rightarrow Me_yO_x \qquad (1)$$

被氧化后的金属颗粒( $Me_yO_{x-1}$) 粒经循环进入燃料反应器, 通过燃料气体对金属氧化物的还原反应来完成载氧体的再生, 发生的反应为:

$$(2n+m)\,Me_xO_y + C_nH_{2m} \longrightarrow (2n+m)\,Me_xO_{y-1} + mH_2O + nCO_2 \qquad (2)$$

现阶段的金属载氧体制备, 通常在纯金属氧化物的基础上通过不同的工艺添加惰性载体, 常见的制备工艺有: 机械混合法、浸渍法、冷冻成粒法和喷雾干燥法等, 评价载氧体特性的一个重要指标是其反应性。Ishida 等人首次制备了 NiO/YSZ( yttria-stabilized zirconia) 载氧体, 在氧化温度为 1,000 ℃的流化床下经循环测试发现其化学特性和机械强度都很好[2]。Lyngfelt 等人评估并比较了 $Fe_2O_3$ 和 NiO 携带氧的能力[3]。Adanez 等人用热重分析仪( TGA) 研究了 Fe 基载氧体的反应性, 对于该载氧体来说, 机械混合法比分散法制备的载氧体要好[4]。另外 Garacia 等[5] 经过循环测试之后没有观察到 $CuO/Al_2O_3$ 活性降低或烧结现象。Corbella 等人对 $NiO/TiO_2$ 进行了循环测试研究, 发现 $TiO_2$ 作为惰性载体的效果并不好[6]。

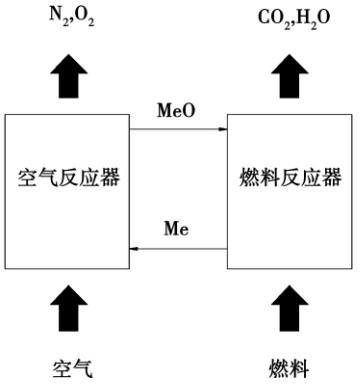


图 1　链式燃烧反应示意图

Fig. 1 Schematic drawing of a chain combustion reaction

结合上述情况, 对分析纯的载氧体, 以及经过机械混合法制备的 Ni 基和 Co 基载氧体的持续循环能力进行了对比实验研究。

## 1　实　验

### 1.1　金属载氧体的制备

选取市售的分析纯金属氧化物作为载氧体活性组分, 以 $Al_2O_3$ 为惰性载体, 按照比例混合, 并掺入

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淀粉作为粘结剂,然后加入适量水使其成为糊状物。成型后在 120 ℃左右的烘干箱内干燥,之后放入 900 ~ 1 200 ℃的马弗炉内高温焙烧 6 h,冷却后取出样品在玛瑙研钵中研磨,并用 200 目粒径筛进行筛分,得到制备的载氧体样品。

### 1.2　载氧体的物相结构和形貌表征

实验中载氧体的物相采用 RINT2000 型 XRD 衍射仪进行检测,实验条件为 CuK - α/40 kV/100 mA,扫描速率 4°/min( 度/分钟) 。循环实验后的样品表面形貌,用日本 JEOL JSM - 6360 LV 型扫描电镜进行观察。

### 1.3　热天平实验

热天平的实验工况如表 1 所示。

**表 1　实验工况**

Table 1 Test conditions

| 实验操作类别 | 实验工况 |
|---|---|
| 加热方式 | 升温到指定温度后恒温 |
| 反应温度/℃ | 还原反应 600、氧化反应 900 |
| 升温速率/℃ · $min^{-1}$ | 20 |
| 载气 | 高纯氮气( 99.999%) |
| 氧化气氛 | 压缩空气 |
| 还原气氛 | 高纯氢气( 99.999%) |
| 气体流量/mL · $min^{-1}$ | 40 |
| 参比物 | $Al_2O_3$ |
| 坩锅 | 铂金 |
| 样品重量/mg | 10 |

为了便于比较,规定转化率为:

$$X = \frac{m_0 - m_t}{\triangle m_{max}} \tag{3}$$

式中: $m_0$—试样初始质量; $m_t$—$t$ 时刻的试样质量; $\triangle m_{max}$—10 次循环中最大质量变化。

## 2　实验结果以及分析

### 2.1　制备前后两类载氧体的持续循环能力热失重分析

图 2 与图 3 分别是 Ni 基和 Co 基分析纯样品和制备后的载氧体样品循环反应的转化率曲线。

在图 2 与图 3 中,还原反应和氧化反应过程中转化率随时间变化的曲线,反映出样品的持续循环能力。由图可以看出,在第一次循环时,两类载氧体无论是还原阶段还是氧化阶段,均表现出比较好的再生能力。但此后随反应循环次数的增加,两种分析纯载氧体的再生能力迅速下降,如图 2( a) 和图 3( a) 所示,到第五次循环之后已基本上失去对氧的承载能力,同时反应衰减程度逐渐趋于稳定。

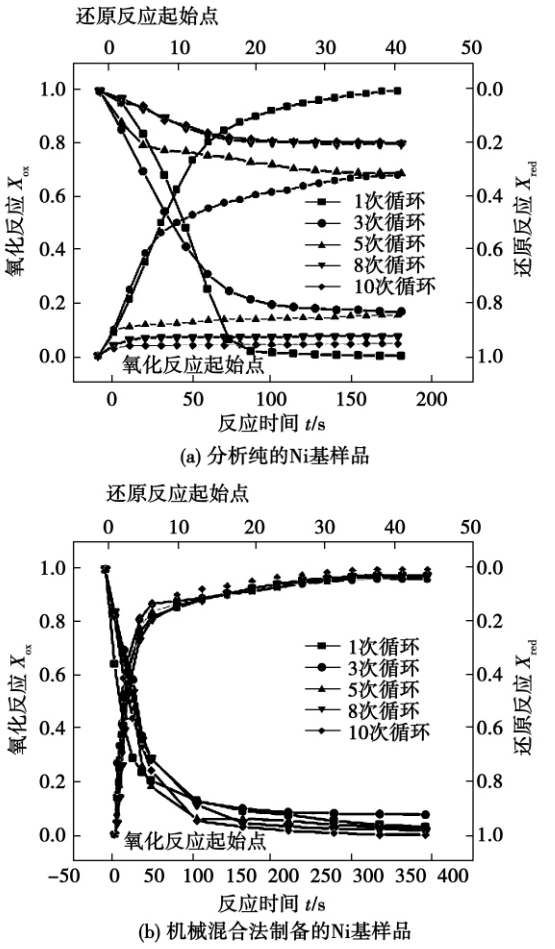


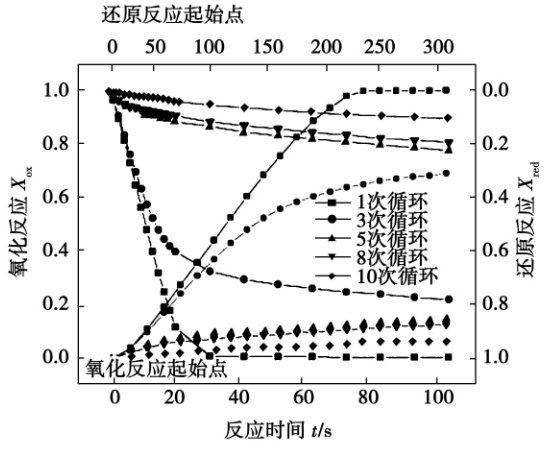

图 2　Ni 基载氧体的循环反应转化率曲线

Fig. 2 Curves showing the conversion rate of the circulating reactions of the Ni-base oxygen carrier

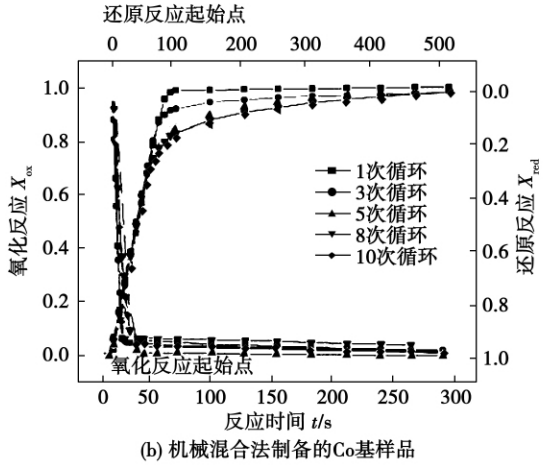
对于机械混合法制备的 Ni 基和 Co 基两种样品,由图 2( b) 和图 3( b) 可以看出,其反应持续循环能力得到了很大的改善,而且反应时间也大幅度缩短,但两者表现仍有所不同。制备后的 Ni 基载氧体在与氢气反应的过程中,第三次循环的反应速率和转化率比第一次有了小幅降低,但是直到第十次循环结束,其转化率又有了不同程度的提升,第十次循环的转化率甚至超过了第一次循环。制备后的 Ni 基载氧体在与空气反应的过程中,其反应速率没有发生很大的变化,但是转化率却也呈现出先降低后上升的态势。

对于 Co 基载氧体样品,其反应速率和转化率随着循环次数的增加基本上呈现递减趋势,尤其表

现在与空气发生氧化反应的过程中,其反应速率下降很明显。虽然也能到达第一次循环时的转化率,但是反应时间却大大增加。




(a) 分析纯的Co基样品




(b) 机械混合法制备的Co基样品

图 3　Co 基载氧体的循环反应转化率曲线

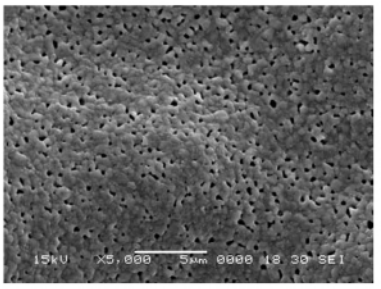
Fig. 3 Curves showing the conversion rate of the circulating reactions of the Co-base oxygen carrier

总体而言,机械混合法制备的 Ni 基和 Co 基两种载氧体在 10 次循环之内,随循环反应次数的增加,均保持着较高的转化率,表明仍有较强的持续循环能力;但 Co 基载氧体在与空气进行氧化反应时,其反应时间有所延长。

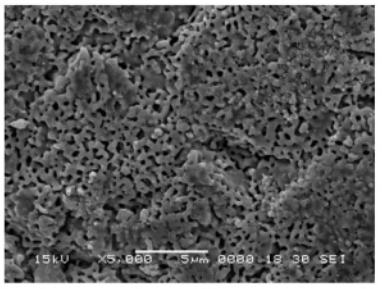
### 2.2　两类载氧体循环反应后的 SEM 分析

4 种金属载氧体经过 10 次循环后的样品表面 SEM 形貌,分别如图 4 和图 5 所示,放大倍率为5 000 倍。

从图中可以看出,在经过 10 次循环反应之后,分析纯的 Ni 基和 Co 基载氧体样品的颗粒相互烧结在一起,表面变得非常致密,仅剩下细小的孔洞,这可能是由于在反应过程中气体进出颗粒内部所致。由此可以看出,这两种样品在循环反应过程中转化率衰减程度非常快的原因,主要是因为载氧体在烧结后气固反应接触面积有了明显的减少所导致。



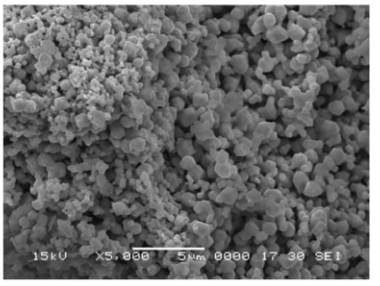
(a) 分析纯Ni基载氧体循环10次后样品表面



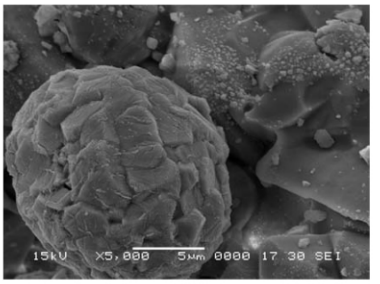
(b) 分析纯Co基载氧体循环10次后样品表面

图 4　分析纯金属载氧体样品循环反应后 SEM 照片

Fig 4 SEM photo of the circulating reaction of an analytic pure metallic oxygen carrier sample



(a) 制备后的Ni基载氧体循环10次后样品表面



(b) 制备后Co基载氧体循环10次后样品表面

图 5　制备后的金属载氧体样品循环反应后 SEM 照片

Fig. 5 SEM photo of the circulating reaction of a metallic oxygen carrier sample after preparation

观察扫描电镜拍摄的微观形貌图，制备后的 Ni 基载氧体在经过 10 次循环之后，样品空隙结构变大，小颗粒增多，颗粒粒径普遍在 5 μm 以下，样品表面变得蓬松，增大了气固反应的反应面积，因此经过 10 次循环反应后仍然表现出优良的活性。对于制备后的 Co 基载氧体，在循环反应后，其样品的颗粒粒径变大，表面还出现了局部烧结，从而导致该载氧体在 10 次循环后反应速率有所下降。

### 2.3 制备的载氧体样品循环反应后的 XRD 分析

图 6 是机械混合法制备的 Ni 基和 Co 基载氧体未经循环和经 10 次循环反应后的 XRD 分析图谱。

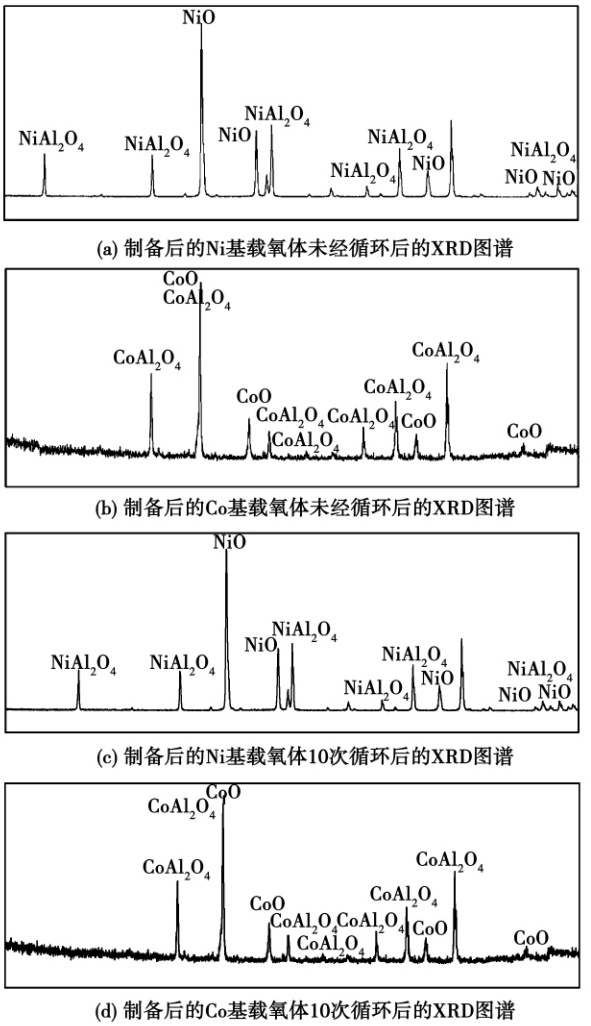



图 6 制备后的载氧体循环反应后的 XRD 图谱

Fig. 6 XRD atlas of the circulating reaction of a metallic oxygen carrier after preparation

图 6(a)、(c) 表明，机械混合法制备的 Ni 基载氧体循反应前后的成分仍然还是 NiO 和铝酸镍，说明它们在化学反应中得失氧的能力是比较强的，反应并没有对载氧体的组成产生影响，这也从另一个角度证明制备后的 Ni 基载氧体在持续循环能力方面表现出较高的优势。而制备后的 Co 基载氧体在多次循环后其样品组分发生了改变，循环后的 Co 基载氧体中已经不存在 $Co_3O_4$，而是变成 CoO 和 $CoAl_2O_4$ 的混合物。这些混合物已经难以恢复到最初的活性物质，因此进一步证明了 Co 基载氧体的持续循环能力比 Ni 基载氧体的持续循环能力要差。

## 3 结 论

(1) 根据热天平测定的循环反应转化率曲线，可以看出分析纯的金属载氧体在经过多次循环后其反应性能大幅度下降；而添加惰性载体 $Al_2O_3$ 制备后的两种载氧体，其可持续循环能力得到显著提高的同时，反应速度也有很大提高。

(2) 10 次循环后的扫描电镜形貌观察表明，未添加惰性载体的样品表面处于烧结状态，难以进行载氧体的再生。机械混合法制备的载氧体，均有良好的持续循环能力；其中 Ni 基载氧体仍然保持良好的活性组分，因此 Ni 基载氧体的循环能力明显优于 Co 基载氧体。

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of a gas-engine-driven heat pump system and the tactics for controlling the superheating degree of the evaporator when the set value of the superheating degree is being changed. The gain dispatchment control tactics were used to realize a control of the superheating degree of the evaporator. The test results show that when the rotating speed of the gas engine is being changed, the control of the superheating degree is relatively precise with its fluctuation varying in a range of ±0.5 ℃. When the set value of the superheating degree is being changed, the maximal overshoot of the superheating degree is less than 2 ℃ and the superheating degree response is quick. The system displays very good dynamic response characteristics with its time for attaining a steady state being not longer than 200 s. **Key words**: gas-engine-driven heat pump, superheating degree, electronic expansion valve, gain dispatchment control

再热 Brayton 循环效率特性分析 = **Analysis of the Efficiency Characteristics of the Brayton Reheat Cycle**

[刊,汉] WANG Jun-hua, CHEN Lin-gen, SUN Feng-rui (Postgraduate School, Naval Engineering University, Wuhan, China, Post Code: 430033) // Journal of Engineering for Thermal Energy & Power. - 2011, 26(6). - 660 ~ 664

In a gas turbine cycle, the working medium temperatue varies in a wide range and its specific heat also changes. By utilizing a numerical analytic method, studied were the efficiency characteristics of the Brayton reheat cycle under the condition of the specific heat of the working medium being changed. It has been found that there exist an optimum total efficiency of the device and its corresponding optimum pressure ratio. The influence of the temperature ratio of the cycle and the efficiency of the compressor and turbine on the optimal pressure ratio of the cycle and the optimal total efficiency of the device was also investigated. On this basis, the influencing extents on the efficiency of the compressor and turbine were compared and the mistakes existing in the currently available literatures were pointed out. The foregoing can offer certain guide for optimized design and selection of operating parameters of a gas turbine. **Key words**: Brayton reheat cycle, efficiency characteristics, power characteristics, numerical analysis

Ni 基和 Co 基金属载氧体的持续循环能力研究 = **Study of the Sustainable Circulating Capacity of Ni-base and Co-base Metallic Oxygen-carriers**

[刊,汉] CHEN Lei, JIN Jing, DUAN Hui-wei, et al (College of Power Engineering, Shanghai University of Science and Technology, Shanghai, China, Post Code: 200093) //Journal of Engineering for Thermal Energy & Power. -2011, 26(6). -665 ~ 668

Chemical chain combustion represents a relatively novel carbon dioxide separation technology, among which the sustainable circulating reaction capacity of the metalic oxygen carriers directly affects the actual application and popularization of the technology in question. With Ni-base and Co-base metallic oxygen carriers serving as objects of study, by using a TGA (thermogravimetric analyzer), SEM (scanning electron microscope) and XRD (X-ray diffractometer) etc. analytic tools, the sustainable circulating capacities of both metallic oxygen carriers were compared and studied. The research results show that the reaction rate and the sustainable circulating capacities of the oxygen carriers increase by a large margin after added with an inert carrier and the Ni-base oxygen carrier exhibits

better reaction characteristics and sustainable circulating capacity than the Co-base oxygen carrier. **Key words**: chemical chain combustion, $CO_2$ separation, metallic oxygen carrier

湍流射流冲击移动平板的流动和传热分析 = **Analysis of the Flow and Heat Transfer on a Moving Flat Plate Impinged by a Turbulent Jet Flow** [刊,汉] YE Chun-jie, PAN Hong-liang (College of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai, China, Post Code: 200237) // Journal of Engineering for Thermal Energy & Power. - 2011, 26(6). -669~674

By using the Reynaulds stress turbulent flow model, numerically analyzed was a moving flat plate impinged by a semi-closed turbulent jet flow with the configuration of its flow and temperature field under various speeds of the plate as well as the near-wall-surface turbulent flow intensity and the curves showing the Nusselt number distribution on partial plate surface being obtained. The analytic results show that to increase the speed of the moving plate will invariably result in an asymmetry of both flow and temperature field relative to the jet flow center and form a secondary vortex zone at a side of the flow field. The value of the turbulent flow intensity on the plate surface will increase while the peak value of the local Nusselt number in the zone under impingement will decrease with an increase of the speed of the plate in motion. When the speed of the plate is higher than the inlet jet flow speed, the plate surface average Nusselt number will gradually increase with an increase of the speed of the plate. When the speed of the plate increases to a value two times higher than the inlet jet flow speed, the plate surface turbulent flow intensity at the impingement point will increase by about 40% and the peak value of the Nusselt number will decrease about 60% but the plate surface average Nusselt number will increase by above 30%. The research findings can offer important guidance for the intensified heat and mass transfer during a continuous operation. **Key words**: jet flow, moving flat plate, turbulent flow intensity, heat transfer

板式换热器单边流动与对角流动数值模拟 = **Numerical Simulation of the Single-side and Diagonal Flow of a Plate Type Heat Exchanger** [刊,汉] XU Zhi-ming, WANG Yue-ming, ZHANG Zhong-bin (College of Energy Source and Power Engineering, Northeast University of Electric Power, Jilin, China, Post Code: 132012) // Journal of Engineering for Thermal Energy & Power. - 2011, 26(6). -675~680

Based on the control equation in heat transfer and by using the numerical calculation method, analyzed were the flow and heat exchange characteristics of a plate type heat exchanger when a single-side and diagonal flow was adopted. In the process of the analysis, the structural parameters of the heat exchanger were kept unchanged, only the flow mode at the inlet and outlet was changed. It has been found that at a same flow speed, the total convection heat exchange coefficient of the single-side flow is higher than that of the diagonal flow while the total pressure drop of the single-side flow is lower than that of the diagonal flow. Under the condition of the flow speed u = 0.6 m/s, the Nusselt number of the single-side flow is 10.87% higher than that of the diagonal flow and the pressure drop of the diagonal flow is 5.13% higher than that of the single-side flow. With an increase of the inlet flow speed, the