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电化学动电位再活化法(EPR法)的应用研究

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摘要: 应用电化学动电位再活化法(EPR法)评价不锈钢复合板和低铬铁素体不锈钢的晶间腐蚀敏感性. 结果表明,以电化学动电位再活化法测得的反向扫描与正向扫描电流密度最大值之比(i_r/i_a)评价堆焊不锈钢复合板 00Cr17Ni14Mo2/20R 复层晶间敏感性与传统 H_2SO_4 - $CuSO_4$ - Cu 法测定的结果吻合甚好;评价爆炸复合板复层 06Cr13R 低铬铁素体不锈钢晶间腐蚀敏感性与草酸浸蚀法测定的也一致. 说明该法可以成功用于定性、定量地评价不锈钢复合板和低铬铁素体不锈钢的晶间腐蚀敏感性.

关键词: 电化学动电位再活化法(EPR法); 晶间腐蚀; 不锈钢复合板; 低铬铁素体不锈钢

中图分类号: TG173.3+3

文献标识码: A

电化学动电位再活化法(Electrochemical Potentiokinetic Reactivation,简称EPR)是一种以电化学加速腐蚀的试验方法,具有快速、无损、定量的特点^[1].自Duffault首次应用^[2]以来,至今已被广泛应用于Cr-Ni奥氏体不锈钢晶间腐蚀敏感性评价^[3-4].但是否适用于其它类型不锈钢(如:不锈钢焊接件和铁素体不锈钢)的晶间腐蚀敏感性评价,未见报道.本文针对实际工作中遇到的问题:①堆焊不锈钢复合板由于复层较薄,从复层上取样往往伴随有低合金钢(或碳钢)基体,如用化学浸泡方法评价难免导致复合板本身产生严重的电偶腐蚀;②低铬铁素体不锈钢由于铬含量低,采用化学浸泡法进行晶间腐蚀,则过程中又容易发生均匀腐蚀.为此,本文使用电化学动电位再活化法(EPR),研究这一方法是否能够适用堆焊不锈钢复合板和低铬铁素体不锈钢的晶间腐蚀敏感性的评价.

1 实 验

堆焊不锈钢复合板 00Cr17Ni14Mo2/20R,厚度 $\delta=3/10$ mm,从复层上取样,编号分别为 00Cr17Ni14Mo2 和 00Cr17Ni14Mo2-An.其中,00Cr17Ni14Mo2 直接由复层加工成试样;00Cr17Ni14Mo2-An 则先将该复层取样经过 610 ± 10 °C,1 h 消应力处理后,再精加工成试样.按

GB4334-2008 E 法和 JIS0580-86 的 EPR 法作晶间腐蚀敏感性试验. EPR 试验条件为:介质 0.5 mol/L H_2SO_4 + 0.01 mol/L KSCN,温度 25 °C,扫描速率 100 mV/min.

低铬铁素体不锈钢是复层 06Cr13R(厚度 $\delta=3$ mm) + 基层 Q345(厚度 $\delta=16$ mm)的爆炸复合板的复层.编号 06Cr13R-1 样品试验前先经 910 °C,0.5 h,强制吹风冷却的正火处理,而编号为 06Cr13R-2 的样品则于试验前在 800 °C,1 h 条件下作空冷的退火处理.按 GB4334-2008 A 法和 JIS0580-86 的 EPR 法作晶间腐蚀敏感性试验.

腐蚀后的微观组织分别由 OLYMPUS GX71 金相显微镜和 Philips CM200 透射电镜观察.

2 结果与讨论

图1分别给出 00Cr17Ni14Mo2 堆焊不锈钢复层(A)和 06Cr13R 低铬铁素体不锈钢(B)的 EPR 试验结果.可见,在回扫时 00Cr17Ni14Mo2 试样的再活化峰很小,其最大活化电流密度为 $i_r=0.0098$ mA·cm⁻²,与正扫最大活化电流密度 $i_a=0.1036$ mA·cm⁻²相比,得再活化率 $R_a=9.4\%$;00Cr17Ni14Mo2-An 试样回扫的再活化电流密度 $i_r=0.0389$ mA·cm⁻²,与正扫最大活化电流密度 $i_a=0.10357$ mA·cm⁻²相比,再活化率 $R_a=37.5\%$,远远大于前一试样.对 06Cr13R-1

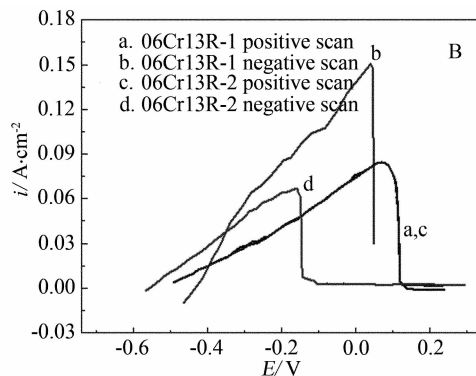
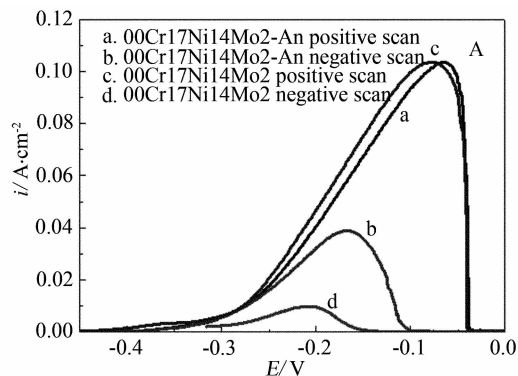


图1 00Cr17Ni14Mo2(A)和06Cr13R(B)的EPR扫描曲线

Fig. 1 EPR testing curves of the 00Cr17Ni14Mo2(A) and 06Cr13R(B)

和06Cr13R-2试样,二者的正扫曲线几乎重合,最大活化电流密度均为 $i_a = 0.0846 \text{ mA} \cdot \text{cm}^{-2}$,但回扫曲线06Cr13R-1的再活化峰大大超过06Cr13R-2,最大再活化电流密度分别为 $i_{r1} = 0.1501$ 、 $i_{r2} = 0.0671 \text{ mA} \cdot \text{cm}^{-2}$,算得其再活化率依次为 $R_{a1} = i_{r1}/i_a = 177\%$ 、 $R_{a2} = i_{r2}/i_a = 79\%$.显然,06Cr13R-1的再活化率远大于06Cr13R-2.

资料表明,对18Cr-8Ni型奥氏体不锈钢,只有当 R_a 值大于15%时,才具有晶间腐蚀现象^[3].参照这一评价指标,可以认为,00Cr17Ni14Mo2试样不发生晶间腐蚀现象,而00Cr17Ni14Mo2-An、06Cr13R-1、06Cr13R-2试样则表现出明显的晶间腐蚀敏感性.

图2为堆焊不锈钢复层试样经16 h沸腾 H_2SO_4 - CuSO_4 -Cu晶间腐蚀试验后弯曲外表面的形貌照片.可见,00Cr17Ni14Mo2-An的弯曲外表面出现了因晶间腐蚀产生的交叉细裂纹(A),而00Cr17Ni14Mo2的弯曲外表面则无此裂纹(B).图3进一步示出00Cr17Ni14Mo2-An试样晶间腐蚀后表面裂纹的透射电镜照片及其析出物衍射图谱和能谱.如图,沿着晶界有大量析出物析出(A),根据

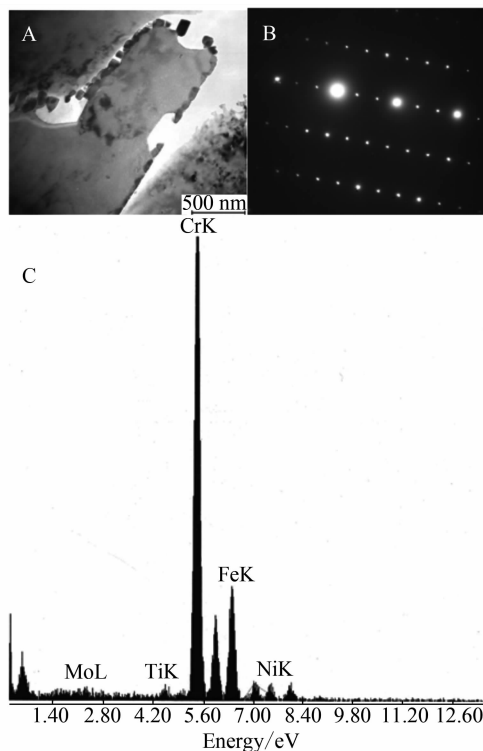


图3 00Cr17Ni14Mo2-An试样的透射电镜照片(A)及其衍射花样(B)和能谱分析(C)

Fig. 3 TEM image of the 00Cr17Ni14Mo2-An (A), selected area electron diffraction pattern (B) and EDS spectrum (C) of 00Cr17Ni14Mo2-An

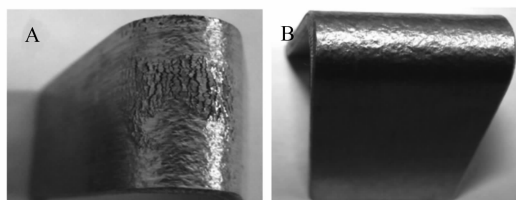


图2 00Cr17Ni14Mo2-An(A)和00Cr17Ni14Mo2(B)试样晶间腐蚀后弯曲面的金相显微照片

Fig. 2 Macroscopic photos of external bending surface for 00Cr17Ni14Mo2-An(A) and 00Cr17Ni14Mo2(B)

衍射图谱(B)和能谱(C)分析,可判断其主要成分为 Cr_{23}C_6 .由于析出物周边在晶间腐蚀过程中被优先溶解(图中析出物周边的亮区)使得样品于晶间腐蚀后力学性能下降,并于弯曲时沿弯曲外表面产生许多裂纹.

图4为06Cr13R-1、06Cr13R-2试样经草酸浸蚀后的金相组织形貌.可见,06Cr13R-1形貌呈沟状组织(三类),其晶界有腐蚀沟,晶界间已明显加

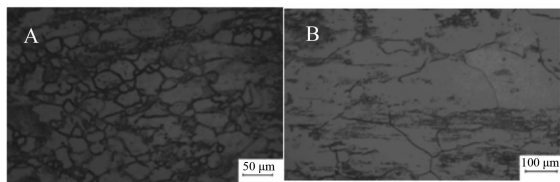


图4 06Cr13R-1(A)和06Cr13R-2(B)试样草酸浸蚀后的金相组织形貌

Fig. 4 Etch structures of the 06Cr13R-1(A) and 06Cr13R-2(B) after oxalic acid etch testing

粗,并连成网状;06Cr13R-2为混合组织形貌(二类),虽晶界也有腐蚀沟,但晶粒没有被腐蚀沟完全包围。由此可见,两试样均存在晶间腐蚀倾向,但经910℃正火处理的06Cr13R-1,其晶间腐蚀倾向大于800℃退火处理的06Cr13R-2。这与EPR法试验结果对应甚好。

EPR法是利用不锈钢的钝化再活化关联钝化膜中主体合金元素的含量及其特性这一特点,研究钢的敏化行为。在钝化状态下,钝化膜的形态、结构在很大程度上依赖于固溶体中Cr、Mo的含量。在一定电介质和外加电位作用下,钢的表面将形成一层完整、致密的钝化膜,而经敏化的试样因晶界贫Cr,形成的钝化膜则是不完整的。当在外加电位回扫到再活化区时,不完整的钝化膜将优先受到腐蚀,这在极化曲线上表现为一个大的活化峰;而在富Cr区或经固溶处理的试样则几乎不腐蚀,对应的极化曲线上不出现再活化峰或仅有一很小的峰。利用这一性质可判断钢的敏化程度^[5]。由透射电镜分析可见,00Cr17Ni14Mo2-An在晶界附近有Cr的富集,导致晶界周边贫Cr,故在电化学动电位再活化扫描中,出现的再活化峰较大。06Cr13R-1、06Cr13R-2经草酸浸蚀后,其晶界粗化当与晶界优先腐蚀有关,故在化学动电位再活化扫描时,也出现较大再活化峰。由此可见,EPR法可较好地评价不锈钢复合板和低铬铁素体不锈钢

的晶间腐蚀敏感性。

3 结 论

电化学动电位再活化法(EPR法)可用于定性、定量评价堆焊不锈钢复合板和低铬铁素体不锈钢的晶间腐蚀敏感性,所得结果与传统的 H_2SO_4 - $CuSO_4$ -Cu法和草酸浸蚀法吻合甚好。

本文试验直接套用奥氏体不锈钢的晶间敏感性评价指标,是否完全适用,尚需进一步深入研究。

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Applied Study of Electrochemical Potentiokinetic Reactivation Method

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Abstract: The susceptibility to intergranular corrosion of overlay welding stainless steel composite plate (00Cr17Ni14Mo2) and low-Cr ferritic stainless steel (06Cr13R) was studied by electrochemical potentiokinetic reactivation (EPR) method. The results indicated that the ratio of the maximum current i_r/i_a generated by the reactivation EPR scan to that of the anodic scan is appropriate for evaluating the intergranular corrosion of 00Cr17Ni14Mo2, which is consistent with the H_2SO_4 -CuSO₄-Cu method, and also appropriate for evaluating the intergranular corrosion of 06Cr13R, which is consistent with the oxalic acid test method. It shows that the EPR method can be applied to qualitatively and quantitatively evaluate the susceptibility to intergranular corrosion of stainless steel composite plate and low-Cr ferritic stainless steel.

Key words: EPR method; intergranular corrosion; stainless steel composite plate; low-Cr ferritic stainless steel