Thesis name: Research on manufacturing zinc sacrificial anodes for corrosion protection of steel structures and constructions.

Major: Materials forming technology

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Abstract:

Thesis covers a research and application of zinc sacrificial anodes developed by the controllable crystallization through semi-solid casting technology for improving electrochemical capacity and depassivation ability without environmentally hazardous substances, and for increasing protective efficiency. Indoor and outdoor exposure tests have been carried out for quality evaluation of newly developed zinc sacrificial anode products.

Major results of the Thesis:

- Zinc sacrificial anode production by the controllable crystallization technology as an effective approach for improving anode quality without adding hazardous substances like cadmium for zinc anode depassivation has been successfully implemented and processed.

- The combined semi-solid and pressurized casting technology can form a zinc alloy with β phase and (α+β) easily melted phase with β solid solution as alluminium in
zinc, enhancing an uniform microstructure, spherical crystals of more fine sizes than those dendrites deposited from fully solid condition.

- The electrode potentials analysis shows a high polarization potentials and corrosion currents as required by technical specifications for zinc anodes. The electrode potentials in seawater reached -1.018 ÷ -1.029 (mV;Ag/AgCl); the electrochemical capacity of zinc anodes reached 795÷801 A.h/kg. Both a.m. electrochemical criteria of the zinc based anodes produced by semi-solid technology are considerably higher than values required by TCVN 6024-1995.

- The controllable technology of materials crystalization for zinc sacrificial anodes, including mechanical mixing with counterclockwise multi-propeller two-axial systems (discontinuous screw) has been proposed and selected. Rotating speed up to 89 rpm. Mixing temperature 412-397°C. The designed and manufacture zinc sacrificial anodes has 6.3 – 6.5 kg of mass.

- An outdoor exposure test for comparative evaluation of protective efficiency of the developed zinc anodes in sea water and coastal soil environments has been processed.

- Zinc anodes produced by semi-solid technology showed very high protective efficiency for CT51 steel in sea water conditions. The highest value of corrosion rate is only 0.1890 g/m²/day, compared with 0.5187 g/m²/day in the case of protected by traditionally produced zinc anodes and with 4.7960 g/m²/day for unprotected CT51 steel. Protective efficiency reached 96% in comparison with unprotected samples.

- Similar results have been obtained for zinc anodes produced by semi-solid technology, tested in soil conditions. The highest value of corrosion rate is only 0.1524 g/m²/day, compared with 0.2317 g/m²/day in the case of protected by traditionally produced zinc anodes and with 3.0889 g/m²/day for unprotected CT51 steel. Protective efficiency reached 95% in comparison with unprotected samples.
Analysis of corrosion products appeared during protection by zinc anodes show effective functioning of the system without passivation due to formed hard adhesive oxide layers preventing any electrochemical processes. The corrosion products comprise of zinc hydroxycarbonate hydrate $\text{Zn}_4\text{CO}_3(\text{OH})_6.\text{H}_2\text{O}/4\text{ZnO}.(\text{CO})_2.4\text{H}_2\text{O}$, specifically for sea water with high Cl⁻ concentration with porous surface preventing formation of biofouling on anodes. No sign of biofouling after one year of exposure for zinc anodes produced by semi-solid technology, meanwhile, 100% surface of traditionally produced anodes were covered by biofouling only after 3 months of testing.

Zinc anode products of semi-solid technology have been purchased and installed for marine ships by Nhatrang Ship Industry Co. Products show good operation after 12 months of functioning.

Regarding economic efficiency: Production of anodes by semi-solid technology requires higher cost and more complicated procedures. However, the products yield better electrochemical properties, safer environmental performances, higher protective efficiencies for steel structures and constructions. Generally, the new technology promises a substantial techno-economical benefits at industrial scales of application.

The scientific outputs of the Thesis:

A depassivation method by controllable crystallization without cadmium alloying has been proposed: formation of an uniform spherical microstructure, enhancing products with high electrochemical capacity, more durable products in comparison with the traditional manufactured methods.

The controllable crystallization method has been applied and to the technological parameters have been selected for manufacturing zinc sacrificial anodes. The main electrochemical characteristics of the anodes manufactured by the controllable crystallization method were determined.
- The additional data for corrosion rates of steels in the tropical sea water specific for Vietnam conditions and soil environments at different cases of protection were provided.

- An scheme for anodes installation on marine ship has been designed. Equation for calculation of required anode numbers has also been proposed.

**Future developments:**

- Production of zinc sacrificial anodes by the controled crystalization method bring first promising results and opens new direction for application of the technology. More thoroughly research on technological regimes, equipment lines for improving production yield, lowering cost and furthermore, to expand research on other kinds of anodes such as Al, Mg...

- It is possible a research on application of rare earth elements for modification during casting.

- It is neccessary to apply technology for production of other similar machinery parts.

The results are considered useful for new research direction on the controllable crystalization technology in manufacturing anodes for corrosion protection of steel structures and constructions in sea conditions.

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