

Study of the anti-corrosion of metal key handles using cold-sprayed zinc coatings

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Abstract. We assessed the chemical corrosion resistance of zinc-modified metal key handles (MKHs) obtained by cold spraying and post-heat treatment. A programmable logic controller module for the nozzle was employed to satisfy the requirements of an auto-spraying system. The spraying time and sediment restriction were monitored to achieve film thicknesses of 100–140 μm. The anti-corrosion property and neutral salt-spray test results of cold-sprayed zinc were investigated. The corrosion degree of the modified MKH increased quickly during the inception phase, and its corrosion tendency gradually slowed during 90 h of salt-fog exposure. Lower surface erosion in salt-fog atmospheres and a limited number of frust stains on the MKH substrate both indicated their use as appropriate coating materials on steels. A parabolic relationship between the corrosion degree and time was further suggested. This work proposes an effective anti-corrosion method with practical prospects.

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I. Introduction

Galvanisation technology has been widely applied to hardware anti-corrosion, which presents higher requirements for the chemical corrosion protection of sheet metals [1–3]. Key handles become rusted in humid environments or as a result of surface scratches. If rust removal is employed, such as applications of ordinary anti-rust coatings to on-site repair of metal key handles (MKHs), the handles may rust again rapidly. Thus, the design of an effective galvanisation process with long-term corrosion resistance is necessary [4]. When metallic zinc is corroded, it generates ZnO (or ZnCO₃ in humid air), improving the compactness of the zinc film and isolating oxygen to prevent corrosion [5,6]. Considering the usage scenarios of locks, MKH rust problems can be solved by modifying zinc.

Cold-sprayed zinc, as a zinc-rich coating, is convenient for anti-corrosive engineering and anti-corrosion techniques [7–9]. Compared with other zinc coatings, the content of zinc in cold-sprayed zinc coatings is very high [10,11] and offers the following advantages: rapid construction at room temperature (similar to paint) and mechanical recoating with easy repairability. This technique has become increasingly popular because it provides efficient field maintenance and steel refurbishment [12]. In general, cold-sprayed zinc is regarded as a micron-thick film and exhibits excellent corrosion resistance compared with hot-galvanised zinc in polarisation curve tests [13]. Electron microscopy has revealed that the corrosion products of hot-galvanised zinc are relatively loose.

Herein we aim to develop a beneficial anti-corrosion method for MKHs. The morphologies of cold-sprayed zinc-modified MKHs and corroded surfaces are characterised using a digital camera and scanning electron microscopy (SEM). The anti-corrosion property, corrosion degree and neutral salt-spray test (NSST) results of the cold-sprayed zinc are evaluated. This study specifically investigates the feasibility of hydrophobic sprayed zinc over epoxy resin as a sealing agent for moisture-resistant films. In addition, we ensure that the normal service condition of keys is not affected. A cold-sprayed system equipped with nozzle is employed to generate zinc coatings. Through triplicate measurements, zinc modified on a sheet-metal substrate is optimised, and the chemical corrosion effects of the zinc coatings are investigated.

II. Experimental procedures

2.1 Materials

House key handles (made of steel, steel grade: 35) were purchased from XiaoL Hardware (China). Commercial zinc powder (total Zn \geq 98%, Fe $<$ 0.005%, Pb $<$ 0.01%, Cd $<$ 0.01% and ZnO $<$ 2%) for the coating preparation was purchased from Shenglan Zinc (China).

2.2 Coating preparation

The available zinc was used as the feedstock. Compressed air was used as the carrier gas, and zinc was injected into the nozzle. Cold spraying was applied to spray zinc onto the spoon-tooth end of the MKH surface. Then, epoxy resin was used as a sealing agent to form a hydrophobic sealing layer. The spraying time and sediment restriction were matched to achieve film thicknesses of 100–140 μ m. Finally, the MKH specimens were heated in a vacuum oven at 120 $^{\circ}$ C for 50 min. Post-heat treatment helped to form intermetallic compound layers at the MKH/coating interface through atom diffusion. The process parameters of the zinc coatings prepared by cold spraying are presented in Table 1. The stand-off distance (distance between the nozzle outlet and substrate) was maintained at approximately 16 mm to determine the optimal spraying.

Table 1. Parameters of cold-sprayed process.

Parameter	Value
Pressure	2.4 MPa
Gas temperature	280 $^{\circ}$ C
Flow velocity	5 m s $^{-1}$
Nozzle traverse rate	30 cm min $^{-1}$
Stand-off distance	16 mm
Feed rate	10 g min $^{-1}$

2.3 Coating characterisation

NSST was conducted to simulate a salt-fog environment in an atomised manner (corrosion behaviour in contrived atmospheres) [14]. Based on the salt-spray cycles specified in ISO 9227:2017 [15], the surface stains of the MKH specimens were removed before their placement in a salt-fog box. The keys were continuously sprayed with 45 g L $^{-1}$ NaCl (pH 7.0) at a fog deposition rate of 0.035 mL cm $^{-2}$ h $^{-1}$. Following the 90-h test, the keys were pinched out from the box and gently rinsed with pure water. The rust-spot size and corrosion degree were analysed after the specimens were dried at 75 $^{\circ}$ C for 0.5 h.

The morphologies of the cold-sprayed zinc-modified MKHs and corroded surfaces were observed microscopically using SEM at an accelerating voltage of 15 kV. The distribution of corrosion pits was determined by a white-light interferometer [16]. Each set of data from parallel experiments was collected in triplicate.

III. Results and discussion

Actual keys of different sizes, shapes and curved planes were prepared (Figure 1). The key handles were connected to a section of the spoon-tooth end. Apart from the keyless cards, the maximum width of the MKH depended on the minimum length of the key groove. Table 2 presents statistics related to the spoon-tooth ends for the groove-shaped keys. Pneumatic fingers were used to complete the key-holding assembly based on MKH size, which resulted in a time-saving approach for precise selection.

As the executive components of cold-sprayed zinc-modified MKH undergo relatively complex actions, a programmable logic controller (PLC) was required to produce them. To meet the functional requirements of automatic spraying in sequence, we created a PLC module for the nozzle control system, as shown in Figure 2. Nozzle rotation was performed by the motors and corrected using cylinders. The motor was driven by a position-sensing circuit. During cold galvanisation, the MKH could be moved horizontally to the established automation equipment. A Delta 10.9-inch touchscreen was used for the man-machine interface, which sustained the association of PLC-signal pathway and displayed the nozzle state.



Figure 1. Configuration of the MKH and groove-shaped keys.

Table 2. Dimensions of the spoon-tooth ends.

Batch	Length (mm)	Amount	Structure
1#	10.5	6	Single-row shrapnel blade
2#	11.4	7	Straight-groove marble blade
3#	11.7	6	Double-row bullet
4#	12.6	5	Double-row arc-shaped billiard
5#	13.9	6	Straight-groove billiard

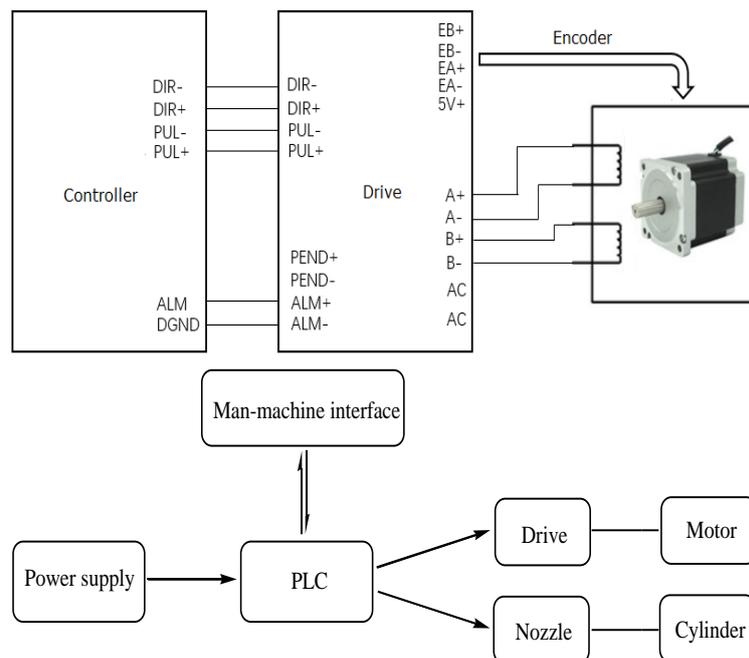


Figure 2. Electronic control system for nozzle.

Two options were considered for the cold-spraying design: position adjustment for the key slot and automatic adjustment of the jet nozzle. Clamping the MKH through the key head using image scanning was determined to be convenient. For the MKH in the drive-mode direction, the nozzle moved in the sense-mode direction, and assembly deviation of the cold spraying was within a small range. The spraying procedure indicated that the MKH was fixed for primary corrosion of zinc at the coating interface under the constraint of the key-slot fixture.

The corrosion behaviours of the MKH and cold-sprayed zinc-modified MKH were investigated in a humid environment. Figure 3 shows the surface topographies derived from micro-area SEM analysis, where the spoon-tooth end was marked by dashed circles. The top views of the specimens were confirmed using a digital camera inserted at the upper right. The initial MKH state had a flat surface (Figure 3A). During the 90-h NSST,

the oxidation reaction with humid air was represented by electron transfer resistance, and rust was formed over the MKH substrate (Figure 3B). MKH coated with zinc exhibited only small rusty areas after 90 h of salt-fog exposure (Figure 3C), which was observed in the composite coatings of ZnO and ZnCO₃.

Following post-heat treatments, the bonding strength between the coating and substrate ensured durability in terms of the process parameters. The chemical corrosion resistance of the dense coatings displayed enhanced prevention efficiency, particularly for a lower incidence of cracks. No obvious changes were observed in the modified MKH, and the formation of corrosion products interfered with the penetration of the corroded steels. For the salt-spray resistance of cold-sprayed zinc, the hundred micron-thick film contributed to the normal service of keys consistent with those of locks.

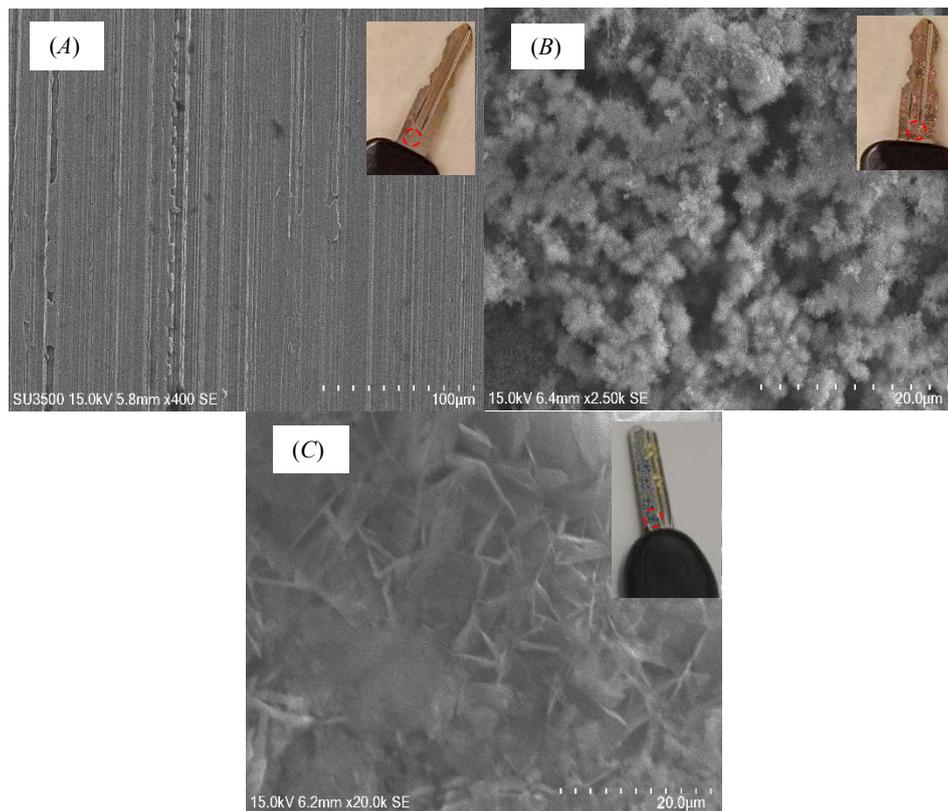


Figure 3. Surface topographies of MKH specimens (*A*: initial state; *B*: after 90-h NSST; *C*: coated with cold-sprayed zinc after 90-h NSST).

To explore further the anti-corrosive effects of the galvanisation technology, a white-light interferometer was used to measure the corrosion pits on the MKH surfaces. Regular damages of the cold-sprayed zinc-modified MKH incessantly appeared. The variation in exposure duration was rationalised by its anti-corrosive performance of the composite coatings, leading to a delay in the corrosion pits. These observations revealed no apparent rust stains along the interface. ZnO and ZnCO₃ acted as protective films that limited erosion of the entire surface, where the average degree of corrosion of the MKH specimens showed parabolic relations over time (Figure 4). The corrosion degree of the modified MKH increased rapidly in the range of 0–40 h, and then its tendency for coating corrosion gradually slowed. Therefore, a lower corrosion degree of the cold-sprayed zinc-modified MKH ($< 0.19 \mu\text{m h}^{-1}$) was determined as compared with that of raw MKH ($< 1.23 \mu\text{m h}^{-1}$) within 90 h.

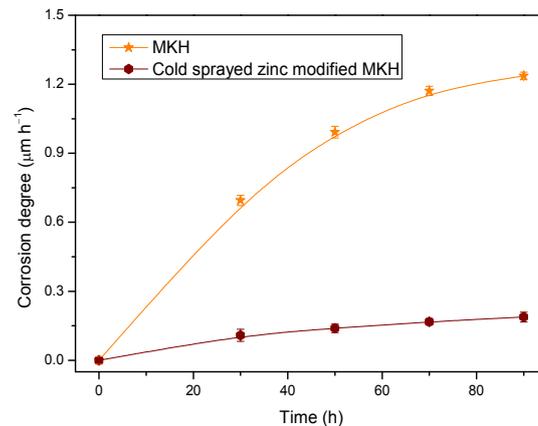


Figure 4. Comparison of the corrosion degree for MKH and cold-sprayed zinc-modified MKH.

IV. Conclusion

Cold-sprayed zinc-modified MKHs were fabricated using direct cold spraying and post-heat treatment. A PLC module for the nozzle control system was adopted to meet the functional requirements of automatic spraying. The prevention efficiency of humidified oxygen was drastically facilitated as a result of the compact film of the modified MKH and its chemical corrosion resistance in a salt-fog atmosphere. A lower corrosion degree of modified MKH ($<0.19 \mu\text{m h}^{-1}$) was determined than that of raw MKH ($<1.23 \mu\text{m h}^{-1}$) during the 90-h NSST, indicating parabolic relations over time. We demonstrated that the limited number of rust stains during salt-fog corrosion did not affect the bonding strength between the coating and MKH substrate. We also revealed the constraint ability of hundred micron-thick coatings (100–140 μm). Moreover, cold spraying is an environment-friendly technique and can potentially prolong the service life of keys.

References

- [1]. Kudláek J, Svoboda J, Zoubek M, Kania H and Saternus M 2022 Technology of repairs of anticorrosion protection of smaller parts of historic steel structures using hot-dip galvanizing *Advances in Manufacturing III* pp. 189-201
- [2]. Li X, Zhang Z, Du B, Li W and Suo S 2020 Development status of anti-corrosion technology for power transmission tower's steel structure *IOP Conference Series: Earth and Environmental Science* **546**052010
- [3]. Maqsood M F, Raza M A, Rehman Z U, Abid M and Iqbal S 2021 Corrosion study of zinc rich epoxy ester paints for cold galvanizing of mild steel *Surface Review and Letters* **28**2150064
- [4]. Rekha M Y and Srivastava C 2021 Electrogalvanization using Zn-graphene oxide composite coatings with enhanced corrosion resistance performance *Journal of Coatings Technology and Research* **18**753-760
- [5]. Valentini C R, Fiora J and Iglesias A M 2008 Corrosion behavior of chromated zinc-electroplated mild steel *CORROSION* **64** 891-899
- [6]. Pan Z W, Tao J, Zhu Y M, Huang J F and Paranthaman M P 2010 Spontaneous growth of ZnCO_3 nanowires on ZnO nanostructures in normal ambient environment: Unstable ZnO nanostructures *Chemistry of Materials* **22** 149-154
- [7]. Chavan N M, Kiran B, Jyothirmayi A, Phani P S and Sundararajan G 2013 The corrosion behavior of cold sprayed zinc coatings on mild steel substrate *Journal of Thermal Spray Technology* **22** 463-470
- [8]. Wang Y, Wu M, Lu P, Zhou W, Shi X, Yang K and Miao X 2022 Mechanical and corrosion resistance of cold sprayed zinc (CSZ) nano composite coating enhanced by SiO_2 -GO hybrid material *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **632** 127824
- [9]. Xie C, Li H X, Zhou X L and Sun C C 2019 Corrosion behavior of cold sprayed pure zinc coating on magnesium *Surface and Coatings Technology* **374**797-806
- [10]. Li W Y, Li C J and Yang G J 2010 Effect of impact-induced melting on interface microstructure and bonding of cold-sprayed zinc coating *Applied Surface Science* **257**1516-1523
- [11]. Zhao D and Zhang S T 2021 Environment-friendly hydrophobic moisture-resistant cold zinc spraying sealing agent and construction method thereof *Chinese Invention Patent* CN112760004A
- [12]. Huang G S, Li X B and Xing L K 2016 Corrosion behavior of low pressure cold sprayed Zn-Ni composites coating *Anti-Corrosion Methods and Materials* **63** 461-469
- [13]. Peng L, Yang F X, Yu Z, Wang X L, Han B and Wang X T 2020 Comparative experimental study on the anticorrosive properties of cold sprayed zinc and hot galvanized zinc *Total Corrosion Control* **34** 1-6
- [14]. Che X H, Yuan R H, Tang L C, Xiong Y D, Wu M F and Zhu M H 2021 Study of catecholate-functionalized zinc complex on carbon steel and its application to corrosion resistance *Journal of Physics: Conference Series* **1978** 012009
- [15]. ISO 9227:2017. Corrosion tests in artificial atmospheres — Salt spray tests. Geneva: International Organization for Standardization
- [16]. Qu S P, Pang X L, Wang Y B and Gao K W 2013 Corrosion behavior of each phase in low carbon microalloyed ferrite-bainite dual-phase steel: Experiments and modeling *Corrosion Science* **75**67-77