Synthetic Effect of Cr and Mo Elements on Microstructure and Properties of Laser Cladding NiCr_xMo_y Alloy Coatings

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Received: 2 January 2020 / Revised: 23 February 2020 / Accepted: 22 March 2020 / Published online: 18 June 2020
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Abstract

NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1, 0.3$) alloy coatings were prepared on the Q235 substrate by laser cladding under the protection of argon. The phase composition, microstructure, corrosion behavior, and mechanical properties of the NiCr_xMo_y alloy coatings were investigated using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, electrochemical tests, X-ray photoelectron spectroscopy, microhardness, and nanoindentation tests. As the Cr content increased, the phase composition of the coatings changed from a single face-centered cubic (FCC) structure to a dual-phase structure coexisting with body-centered cubic (BCC) and FCC structures, while the addition of Mo promoted the precipitation of σ phase. The appearance of a homogeneous dual-phase structure and some amount of σ phase played a positive role in the corrosion resistance of NiCr_xMo_y coatings. Cr^{3+} ions and Mo^{6+} ions in the passive film enhanced the stability of the coatings. The nanoindentation tests showed that the nanohardness (6.71 GPa) and elastic modulus (184.40 GPa) of BCC phase were higher than those of the FCC phase (5.19 GPa and 155.26 GPa, respectively). Overall, the BCC phase and σ phase improved the mechanical properties of the coatings.

Keywords NiCrMo coating · Laser cladding · Corrosion behavior · Mechanical properties · Q235 substrate

1 Introduction

The booming marine equipment industry has made people committed to manufacturing marine corrosion-resistant products. The excellent pitting corrosion resistance and weldability of NiCrMo alloys make them ideal candidates for marine corrosion applications [1, 2]. It is also a promising coating material on mild steel to keep sound balance between the high cost and desired corrosion resistance. Nowadays, NiCrMo coatings are prepared using a variety

of methods, such as thermal spraying [3, 4], plasma spraying [5, 6], arc melting [7, 8], and laser remelting [1]. Rapid solidification using laser cladding can be used to obtain fine grains, small thermal deformations, metallurgical combinations of coatings and substrates, and show minor component segregation during non-equilibrium solidification [9–11]. Laser cladding is an important surface coating technology that has been used to prepare alloy coatings [12, 13]. Liu et al. [14] conducted a comparative study on the high-temperature corrosion of TP347H stainless steel, C22 alloy, and laser-cladded C22 coatings in molten chloride salts. The results showed that the C22 alloy was only slightly corroded, and layered (Ni, Cr, Mo)-rich corrosion products were formed on the C22 alloy at a low temperature. With increasing temperature, the dissolution and volatilization of some (Cr, Mo)-rich oxides in the outer product layer occurred, which accelerated corrosion. Despite their similar compositions and corrosion products, a laser-cladded NiCrMo coating showed a corrosion resistance that was superior to NiCrMo alloy, mainly due to the refined structure formed by rapid cooling. Therefore, the Cr and Mo contents in NiCrMo alloys strongly influence their corrosion resistance.

Available online at <http://link.springer.com/journal/40195>.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s40195-020-01081-5>) contains supplementary material, which is available to authorized users.

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Wang et al. [15] prepared a Ni–Cr–Mo coating on the surface of X70 steel with a high-power diode laser (HPDL) and compared its surface morphology and corrosion behavior with X70 and 316 stainless steel (316 SS). The results showed that the high Cr and Mo contents in the Ni–Cr–Mo coating increased the corrosion resistance of the dense oxide film compared with both X70 and 316 SS. He et al. [8] studied the microstructure, hardness, and phase of $\text{Ni}_2\text{CrFeMo}_x$ in the as-cast and annealed states. The hardness of the alloy significantly increased with increasing Mo content, and the phase stability of a single FCC solid solution decreased, resulting in the formation of σ phase at annealing temperatures of 600–900 °C. Li et al. [16] prepared Ni–Cr–Mo alloy coating on the biomass boiler superheater tube TP347H stainless steel using laser cladding technology and conducted fireside corrosion tests for 168 h at 650 °C and 700 °C. The results showed that the NiCrMo coating had the smallest weight gain in a corrosion environment, and the outer layer was mainly composed of Cr_2O_3 . Chou et al. [17] studied the electrochemical properties of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_x$ high-entropy alloy in 0.5 M H_2SO_4 , 1 M NaCl and NaOH solution. Increasing the Mo content improved the pitting corrosion resistance of the alloy in the chloride ion environment, but reduced the corrosion resistance in acidic and NaOH environments. Sadeghimeresht et al. [18] investigated the oxidation performance of high-velocity-air–fuel (HVOF) thermal sprayed NiCrAlY and NiCrMo coatings in a chloridizing-oxidizing environment and concluded that Mo in the NiCrMo coating improved the corrosion resistance by promoting the formation of a more protective Cr-rich oxide scale by reducing the diffusion of Cl^-/Cl_2 . Wang et al. [19] studied the corrosion resistance of FeCoCrMoCBy alloys with different Cr/Mo molar ratios and found that the passive current density of Fe-based amorphous alloy in 1 mol/L HCl solution decreased by about one order of magnitude, and meanwhile, the Cr/Mo molar ratio ensured the stability of the passive film. The appropriate Cr/Mo molar ratio can reduce the dissolution rate of passive films. The addition of Cr and Mo in passive films significantly contributes to their anticorrosion effects and also affects the microstructure and mechanical properties of the alloys [20]. However, the synthetic effect of Cr and Mo elements on phase structure and corrosion behavior of laser cladding NiCrMo coatings has rarely been studied. Therefore, we plan to simultaneously control the Cr and Mo contents to obtain a NiCrMo coating on Q235 steel which has excellent corrosion resistance.

In this paper, ternary NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1, 0.3$) alloy coatings were designed to investigate the combined effects of Cr and Mo on the phase composition and corrosion resistance. The corresponding relationship between structures and properties was explored. In addition, to achieve the versatility of coatings, we have further studied the mechanical properties of the most corrosion-resistant coating.

2 Experimental

Q235 steel was used as the substrate with dimensions of 140 mm × 40 mm × 10 mm. The substrate was polished with 150 grit SiC abrasive paper to remove contaminants and then cleaned by alcohol. High purity (> 99.5%) Ni, Cr, and Mo powders were employed as the NiCrMo alloy raw materials (compositions are summarized in Table 1), which were mixed for 10 h in a three-dimensional mixer. Images of the initial powder morphology are shown in Fig. 1. NiCrMo coatings were applied to the Q235 substrate using a laser cladding system (KUKA KR30/8T 5000 mm, Han's Laser) with a protective Ar gas device. The mixed powders were pre-coated on the matrix surface with a size of 80 mm × 30 mm × 2 mm. The laser cladding parameters were selected as laser power of 1200 W, scanning speed of 10 mm/s, spot diameter of 3 mm, and overlap ratio of 33%. The schematic diagram of the laser cladding process is shown in Fig. 2. To simplify, the NiCrMo coating cladded on the Q235 substrate was denoted as NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1, 0.3$) alloy coating.

X-ray diffraction (XRD, D/Max 2500PC, Rigaku) was used to characterize the crystal structure of the coatings using CuK_α radiation ($\lambda = 0.15405$ nm) at a scan rate of 4° min^{-1} and a step of 0.02° . The coating samples were polished and etched by a solution of aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$). A scanning electron microscopy (SEM, NANO FEI-450) equipped with an energy-dispersive spectroscopy (EDS, Apollo X) was used to characterize the microstructure and chemical composition of the coatings, respectively. Crystal structures were observed using transmission electron microscopy (TEM, JEM-2010) with selected area electron diffraction (SAED).

Electrochemical tests were performed using an electrochemical workstation (REF3000-32117, Gamry) with a traditional three-electrode cell in 3.5 wt% NaCl solution at 25 °C. A saturated calomel electrode (SCE) was used as the reference electrode, a Pt sheet as the counter electrode, and a coating with a working surface of 0.25 cm^2 as the working electrode. Degassing was done with nitrogen gas

Table 1 Compositions of NiCr_xMo_y alloy coating powders

Alloy coatings	Composition (at.%)		
	Ni	Cr	Mo
NiCr	50	50	–
NiCrMo _{0.1}	47.62	47.62	4.76
NiCrMo _{0.3}	43.48	43.48	13.04
NiCr _{1.5}	40	60	–
NiCr _{1.5} Mo _{0.1}	38.46	57.69	3.85
NiCr _{1.5} Mo _{0.3}	35.71	53.57	10.71

Fig. 1 Surface morphology of **a** Ni powder, **b** Cr powder, **c** Mo powder

Fig. 2 Schematic diagram of the laser cladding system

in 3.5 wt% NaCl test solution for 1 h before the test. Each sample was freely corroded for 30 min to achieve a quasi-stationary value of the open-circuit potential (OCP). The potentiodynamic polarization tests were measured at the OCP with a potential ranging from -0.15 to 1.5 V at a scan rate of 1 mV/s. The cyclic potentiodynamic polarization tests began at -0.5 V, and the forward scan was the same as the potentiodynamic polarization test. When the positive potential reached 1 V, the potential scan was reversed at the scan rate of 2 mV/s and returned to where the polarization began. Electrochemical impedance spectroscopy (EIS) measurements were conducted using an AC amplitude of 10 mV (peak to peak) at an OCP in the frequency range of 100 kHz to 10 mHz. The electrochemical tests for each sample were repeated at least three times to obtain repeatability.

The composition of the passive films formed on the NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1$) coatings after electrochemical tests in 3.5 wt% NaCl solution was investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) with an AlK_α X-ray excitation source ($h\nu = 1486.6$ eV). The binding energy (BE) scale was calibrated to the C $1s$ peak at 284.8 eV, and the XPS data were analyzed using XPSPEAK 4.1 software.

The cross section micro-hardness of the NiCr_xMo_y coatings was measured using an HVS-1000 Vickers micro-hardness tester with a load of 100 gf and a load dwell time of

Fig. 3 XRD patterns of NiCr_xMo_y alloy coatings

10 s. The nano-mechanical properties of NiCr_xMo_y coatings were characterized by a nanoindenter (UNHT CSM). Indentation was performed at a load of 15 mN and a load rate of 1.5 mN s^{-1} , and the maximum load was held constant for 15 s before being unloaded at the same rate as the loading. Each phase was tested at least 10 times to verify the accuracy of the data.

3 Results and Discussion

3.1 Microstructure of NiCr_xMo_y Alloy Coatings

Figure 3 displays the XRD patterns of NiCr_xMo_y alloy coatings. The peaks of the NiCrMo_y ($y = 0, 0.1, 0.3$) alloy coatings reveal the presence of a simple FCC phase, and distinct BCC phase peaks appear in the $\text{NiCr}_{1.5}\text{Mo}_y$ ($y = 0, 0.1, 0.3$) alloy coatings at 41.141° . Small σ phase peaks appear with increasing Mo content. In NiCr_xMo_y alloys, the peak position shifted to the left as the value of y increased, indicating that the addition of Mo with a larger atomic radius (Ni

Fig. 4 SEM micrographs of the NiCr_xMo_y alloy coatings: **a**, **a₁** secondary electron (SE) image of the NiCr coating, **b** SE image of the $\text{NiCrMo}_{0.1}$ coating, **b₁** backscattered electron (BSE) image of the $\text{NiCrMo}_{0.1}$ coating at high magnification, **c** SE image of the $\text{NiCrMo}_{0.3}$ coating, **c₁** BSE image of the $\text{NiCrMo}_{0.3}$ coating at high magnification, **d**, **d₁** SE images of the $\text{NiCr}_{1.5}$ coating, **e**, **e₁** SE images of the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating, **f**, **f₁**, **f₂** SE images of the $\text{NiCr}_{1.5}\text{Mo}_{0.3}$ coating

(1.24 Å), Fe (1.26 Å), Cr (1.28 Å), Mo (1.39 Å)) increased the lattice constant of the FCC phase. The calculated lattice parameters of NiCr coating to $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating increased from 3.596 Å to 3.606 Å. The results indicate that increasing the Cr content in the alloys promoted the formation of BCC phase, while increasing the Mo content led to the precipitation of σ phase. This is consistent with previous results [21–23].

The microstructures of NiCr_xMo_y alloy coatings are presented in Fig. 4. Table 2 lists the chemical compositions of different areas in the NiCr_xMo_y alloy coatings measured by EDS. As the Mo content increased, interdendrite (ID) regions emerged in the NiCrMo_y ($y=0, 0.1, 0.3$) alloy coatings and the fraction was significantly increased, as shown in Fig. 4a–c₁. NiCr alloy coatings exhibited a single-phase microstructure (Fig. 4a, b). The BSE images of the $\text{NiCrMo}_{0.1}$ and $\text{NiCrMo}_{0.3}$ alloy coatings shown in Fig. 4b₁ and c₁ indicate that they were composed predominantly of a dendrite (DR) region, an intercrystalline bright white region (marked as B), and an intercrystalline light-gray region (marked as IDM). EDS analysis showed that the IDM region has a similar composition with the DR region, and the B region has a very high Mo content. The EDS maps in Fig. 5a, b reveal that the (Cr, Mo)-rich phase increased with increasing Mo content. Therefore, the combination of the XRD results indicates that the ID and IDM regions were a (Ni, Fe)-rich phase with an FCC structure, while the B region was a (Cr, Mo)-rich phase. It has been reported that the as-cast CoCrFeNiMo_x alloy ($x=0.3, 0.5, 0.85$ alloys in this work) has a mixed FCC and σ microstructure, where the DR (A) and ID (B) regions have FCC structures, and the ID (C) region is a σ phase rich in Cr and Mo [22].

The $\text{NiCr}_{1.5}\text{Mo}_y$ coatings exhibited distinct DR and ID regions, and the ID fraction increased with increasing Mo content, which was the same trend observed in the NiCrMo_y coatings. Table 3 shows that the DR region of the $\text{NiCr}_{1.5}$ coating was mainly a Ni-rich phase; the ID region was a Cr-rich phase; and the ID region of $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ and $\text{NiCr}_{1.5}\text{Mo}_{0.3}$ was composed of a (Cr, Mo)-rich phase. Figure 4e–f₁ shows that there are many black speckled precipitates in the ID region.

In order to further determine the crystal structure and phase composition of DR, ID and the black speckled precipitates in the $\text{NiCr}_{1.5}\text{Mo}_y$ coating, TEM bright-field images, selected area electron diffraction (SAED), high-resolution

TEM (HRTEM) images and corresponding fast Fourier transformation (FFT) patterns of the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating were obtained (Fig. 6). The EDS composition of each phase is also given in Table 3. The $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating was composed of “A” and “B” regions, and severe dislocations and stacking faults appeared in the coating. The SAED pattern in Fig. 6g shows that the “A” region is an FCC phase along the [011] axis. In addition to the large area of the matrix phase (region C), different nano-scaled precipitates (regions D and E) appeared in region B. The high resolution TEM (HRTEM) morphologies of C, D, and E regions and the corresponding FFT of the images revealed that the strip-like Ni-rich phase (region E) had an FCC structure, and a (Cr, Mo)-rich σ phase (region D) with a stacking fault structure precipitated on the BCC phase (region C) along the [011] axis. The same BCC structure and similar electron configuration of Cr and Mo resulted in the formation of σ phase of Cr and Mo elements with large electron hole number [22, 24].

The combined solidification phase diagram of NiCrMo alloys (detailed phase diagrams are presented in the Supplementary Material) revealed an interesting phenomenon. At the initial solidification stage of the alloy coatings, the liquid phase was transformed into the high melting point Cr-rich BCC phase and (Cr, Mo)-rich σ phase in turn. At this time, the high melting point Cr-rich BCC phase preferentially nucleated and formed a skeleton structure and a uniform dual phase with the FCC phase. As solidification progressed, the FCC phase formed, and part of the BCC phase was transformed into a strip-like FCC phase. At this point, the microstructure of the coating finally changed to $L \rightarrow \text{BCC} \rightarrow \text{BCC} + \sigma \rightarrow \text{BCC} + \sigma + \text{FCC}$, and all the structures were interlaced with Cr-rich and Cr-depleted components. The solidification phase transition process and its schematic diagram are shown in Fig. 7.

3.2 Corrosion Behavior

3.2.1 Potentiodynamic Polarization

Figure 8 presents the potentiodynamic polarization curves of the NiCr_xMo_y alloy coatings in 3.5 wt% NaCl solution at room temperature. The electrochemical corrosion parameters obtained by the linear fit of the potentiodynamic polarization curves are listed in Table 4.

The curves all showed obvious passivation regions and a shift to the bottom right as the Mo content increased. The corrosion potential (E_{corr}) of NiCrMo_y and $\text{NiCr}_{1.5}\text{Mo}_y$ coatings first increased and then decreased, while the corrosion current densities (i_{corr}) showed the opposite trend. The potential at which the current density reached the value of $100 \mu\text{A cm}^{-2}$ was defined as transpassive potential (E_{tr}) [28]. The E_{tr} value increases with the addition of Mo content.

Table 2 Chemical composition (at.%) of different areas of the NiCr_xMo_y alloy coatings

Alloy coatings	Area	Ni	Fe	Cr	Mo
NiCr	DR	38.02	25.31	36.67	—
NiCrMo _{0.1}	DR	33.26	32.57	30.88	3.29
	IDM	31.92	29.94	33.66	4.48
NiCrMo _{0.3}	B	23.43	25.81	41.15	9.61
	DR	27.12	40.83	24.76	7.29
	IDM	27.62	39.78	25.07	7.52
NiCr _{1.5}	B	19.69	35.01	29.80	15.49
	DR	38.39	17.71	43.90	—
	ID	26.32	16.93	56.75	—
NiCr _{1.5} Mo _{0.1}	DR	34.35	25.08	37.56	3.01
	ID	19.71	23.02	52.01	5.27
NiCr _{1.5} Mo _{0.3}	DR	23.32	23.51	41.80	11.37
	ID	22.43	22.78	44.21	10.58

The smaller the E_{tr} value, the more defects it has and the more sensitive to break [29]. This indicates that the increase in Mo content further improved the stability of the coating passive films. The passive region width ΔE ($E_b - E_{pp} = \Delta E$) of the Mo-containing coatings with high Cr concentrations was more wider than that of the Mo-free coating with low Cr concentrations. This change may have been because the

relative concentrations of the easily passivated elements Mo and Cr in the NiCr_{1.5}Mo_y coatings were higher than that in the NiCrMo_y coatings [17, 30]. The NiCr_{1.5}Mo_{0.1} coatings exhibited lower i_{corr} values than the NiCrMo_{0.1} coatings, which implies that the NiCr_{1.5}Mo_{0.1} coatings possessed superior corrosion resistance. To gain further insight into the corrosion resistance of the coatings described in this paper, Table 5 lists the E_{corr} , i_{corr} , and E_{pp} values of the NiCr_{1.5}Mo_{0.1} and NiCr coatings as well as 304 SS and other Mo or Cr containing alloys in the literatures. The data show that the corrosion resistance of the coatings in this paper was relatively better than the corrosion resistance of the other listed alloys, and the coatings also have fewer alloy components.

3.2.2 Cyclic Potentiodynamic Polarization

Figure 9 shows the cyclic potentiodynamic polarization curves of NiCr_xMo_y coatings in 3.5 wt% NaCl solution at room temperature. A cyclic potentiodynamic polarization technique was adopted to better determine whether the NiCr_xMo_y coatings suffer from pitting corrosion and the susceptibility of alloy coating system. The arrows next to the cyclic polarization curves indicate the direction of the potential scan. The NiCrMo_y ($y = 0, 0.1, 0.3$) and NiCr_{1.5} coating showed positive hysteresis in the cyclic polarization curves, revealing that these four coatings were

Fig. 5 EDS maps of **a** NiCrMo_{0.1}, **b** NiCrMo_{0.3}, **c** NiCr_{1.5}Mo_{0.1} coatings

Table 3 Composition (at.%) in different regions marked in Fig. 6

Area	Ni	Fe	Cr	Mo
A	40.19	14.35	42.47	2.97
B	30.81	14.63	51.91	2.63
C	23.04	14.14	59.66	3.14
D	20.00	13.16	61.18	5.64
E	47.90	18.46	32.61	1.01

susceptible to pitting corrosion in 3.5 wt% NaCl solution. The area of the positive hysteresis loop is related to the degree of pit propagation that occurs during the cycle [31]. The pitting potential (E_{pit}) and protection potential (E_{prot}) in the cyclic polarization tests are important parameters for

evaluating the pitting behavior of materials [32, 33]. The E_{pit} of the NiCrMo_y ($y=0, 0.1, 0.3$) and $\text{NiCr}_{1.5}$ coatings were 843.5 mV, 906.7 mV, 800 mV, and 908.7 mV, respectively, and the E_{prot} were -24.62 mV, 819 mV, 678 mV, and 792.9 mV. Pits will expand at potentials higher than E_{pit} , but not below E_{prot} and the pits formed at potentials between E_{pit} and E_{prot} will continue to propagate without the formation of new pits [34]. The greater difference between E_{pit} and E_{prot} and the larger positive loop area indicate that the material has a lower pitting corrosion resistance [35, 36]. The addition of Mo reduced the difference between E_{pit} and E_{prot} and improved its ability to resist pits propagation. However, the negative hysteresis of the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ and $\text{NiCr}_{1.5}\text{Mo}_{0.3}$ coatings showed that no pits propagated below E_{pit} . The results showed that the

Fig. 6 TEM micrographs of $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ alloy coating: **a, b, c** bright-field (BF) images of the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating, **d** HRTEM image of region C, **e** HRTEM image of region D, **f** HRTEM image of region E, **g** SAED-pattern of region A in **a**, **h** corresponding fast Fourier transformation patterns of region in **d**, **i** corresponding fast Fourier transformation patterns of region in **e**, **j** corresponding fast Fourier transformation patterns of region in **f**

Fig. 7 **a** Solidification phase transformation process, **b** a schematic diagram of the NiCr_{1.5}Mo_{0.1} coating

Fig. 8 Potentiodynamic polarization curves of **a** NiCrMo_y alloy coatings, **b** NiCr_{1.5}Mo_y alloy coatings, **c** NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1$) alloy coatings

Table 4 Electrochemical parameters of the NiCr_xMo_y alloy coatings in 3.5 wt% NaCl solution

Alloy coatings	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{tr} (mV)	E_{pp} (mV)	E_{b} (mV)	ΔE
NiCr	-180.2	9.91×10^{-2}	917.5	339.8	708.7	368.9
NiCrMo _{0.1}	-167.4	4.88×10^{-2}	932.0	-53.4	907.8	961.2
NiCrMo _{0.3}	-321.7	1.79×10^{-1}	975.7	-184.5	970.9	1155.4
NiCr _{1.5}	-201.1	2.92×10^{-2}	847.5	72.7	847.5	774.8
NiCr _{1.5} Mo _{0.1}	-185.7	4.52×10^{-3}	941.7	101.9	912.6	810.7
NiCr _{1.5} Mo _{0.3}	-415.9	1.71	1002.0	-241.5	978.2	1219.7

E_{corr} , corrosion potential; i_{corr} , corrosion current density; E_{tr} , transpassive potential; E_{pp} , primary passivation potential; E_{b} , breakdown potential; ΔE , a potential difference between E_{b} and E_{pp}

pitting corrosion resistance of the Mo-containing alloys was effectively improved compared with the Mo-free alloys.

3.2.3 Electrochemical Impedance Spectroscopy

EIS is a key method for understanding corrosion and passivation processes. Figure 10a displays the Nyquist plots of the NiCr_xMo_y coatings in 3.5 wt% NaCl solution. The Nyquist curves of all coatings were characterized by a capacitive

semicircle. When the Cr content is the same, NiCrMo_{0.1} and NiCr_{1.5}Mo_{0.1} coating, respectively, had large capacitive loop radius, and NiCr_{1.5}Mo_{0.1} had the largest radius.

Figure 10b shows the Bode plots and a fitted electrical equivalent circuit. In the high frequency range, the impedance modulus was nearly constant, and the phase angle was close to 0°, indicating resistance behavior. The NiCr_{1.5}Mo_{0.3} coating exhibited two time constants, while the other coatings had only one time constant but a broadened phase angle. The heterogeneous surface caused by

Table 5 Corrosion properties of NiCr_{1.5}Mo_{0.1} alloy coating alongside other alloys reported in literature

Alloy	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{pp} (mV)	References
NiCr _{1.5} Mo _{0.1}	−185.7	4.52×10^{-3}	101.9	This work
NiCr	−180.2	9.91×10^{-2}	339.8	This work
Co _{1.5} CrFeNi _{1.5} Ti _{0.5}	−443	5.7×10^{-1}	−219	[17]
Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.1}	−381	1.3×10^{-1}	−215	[17]
Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.5}	−493	2.0×10^{-1}	−219	[17]
Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.8}	−551	4.1×10^{-1}	−189	[17]
45# steel	−601	1.028×10^{-2}	−343	[23]
AlCoCr _{0.5} FeNi	−458	7.622×10^{-3}	−161	[23]
AlCoCr _{0.75} FeNi	−326	1.687×10^{-4}	−276	[23]
AlCoCrFeNi	−270	7.113×10^{-5}	−208	[23]
AlCoCr _{1.5} FeNi	−163	2.455×10^{-5}	−105	[23]
AlCoCr ₂ FeNi	−357	3.177×10^{-4}	−86	[23]
304 SS	−272	1.35×10^{-1}	132	[25]
CoCrFeNiMo _{0.1}	−263	3.81×10^{-1}	−638	[26]
CoCrFeNiMo _{0.2}	−131	7.2×10^{-2}	−661	[26]
CoCrFeNiMo _{0.3}	−257	7.66×10^{-1}	−656	[26]
CoCrFeNiMo _{0.4}	−261	8.2×10^{-2}	−576	[26]
CoCrFeNiMo _{0.5}	−261	7.38×10^{-1}	−536	[26]
Ni–20Cr	−350.1	1.41×10^{-3}	–	[27]
Ni–40Cr	−270.6	1.35×10^{-4}	–	[27]

surface defects and/or the segregation of elements may result in the fact that this one time constant could in reality be the overlap of two time constants [37–40]. The impedance spectra were fitted by an equivalent circuit $R_s(\text{CPE}_1[R_1(R_2\text{CPE}_2)])$, where R_s represents the electrolyte resistance; R_1 and CPE_1 refer to the resistance and capacitance of the passive film, respectively; R_2 and CPE_2 are, respectively, the charge transfer resistance and double-layer capacitance. A constant phase element (CPE) was used instead of capacitance to account for the inhomogeneity in the system [34].

Table 6 lists the equivalent circuit fitting parameters for the NiCr_xMo_y coatings. The R_s value showed only in a small fluctuation and did not change significantly. The NiCr_{1.5} and NiCr_{1.5}Mo_{0.1} coatings have higher R_1 and R_2 values compared with the NiCr and NiCrMo_{0.1} coatings, which indicates decreased ion transport through the double charge layer in the NiCr_{1.5}Mo_y ($y=0, 0.1$) coatings, indicating its better corrosion resistance. The effective capacitance (C_{eff}) extracted from the passive film can be used to indicate the film properties and film thickness [41]. According to Brug et al. [42], its calculation formula is as follows:

$$C_{\text{eff}} = Y_0^{1/n} R_s^{(1-n)/n}. \quad (1)$$

where Y_0 represents the magnitude of CPE. R_s is the solution resistance, and n is the dispersion coefficient. The relationship between C_{eff} and the film thickness (d) is as follows [43]:

$$d = \frac{\varepsilon \varepsilon_0 A}{C_{\text{eff}}}. \quad (2)$$

where ε is the dielectric constant, ε_0 is the vacuum permittivity (8.8542×10^{-14} F/cm), and A is the surface area of the electrode. The passive film thicknesses of the coatings are shown in Fig. 11. The value of Y_0 can be used as an indicator for the change of layer thickness, and the layer thickness decreases as the Y_0 value increases, thereby reducing the corrosion resistance. The results show that the addition of a moderate amount of Mo increased the thickness of the passive film. According to the fitting parameters, n is a measure of the capacitance dispersion with values between 1 (ideal capacitance) and 0.7 (highly dispersed capacitance). The NiCr_xMo_{0.1} coating with middle Mo content showed a better corrosion resistance than the other coatings, and the increase in the Cr content had a positive effect on the corrosion resistance of the NiCr_xMo_y coatings [44]. The EIS results are consistent with the potentiodynamic polarization curve trend. Section 3.1 shows that excessive amount of Mo formed many (Cr, Mo)-rich phases and (Cr, Mo)-depleted phases in NiCr_xMo_{0.3} ($x=1, 1.5$) coatings, and the resulting potential difference caused the (Cr, Mo)-depleted phases to act as anodes, which reduces their corrosion resistance. The addition of a moderate amount of Mo enhanced the corrosion resistance of NiCr_xMo_{0.1} ($x=1, 1.5$) coatings, although the appearance of a homogeneous multiphase structure and a small number of σ phases were also observed in the coatings.

Fig. 9 Cyclic polarization curves of NiCr, NiCrMo_{0.1}, NiCrMo_{0.3}, NiCr_{1.5}, NiCr_{1.5}Mo_{0.1}, and NiCr_{1.5}Mo_{0.3} in 3.5 wt% NaCl solution

Fig. 10 EIS plots of samples measured in 3.5 wt% NaCl solution at room temperature: **a** Nyquist plots, **b** Bode plots, and **c** equivalent electrical circuit diagram of NiCr_xMo_y alloy coatings

Table 6 Equivalent circuit parameters obtained by fitting the EIS results of NiCr_xMo_y alloy coatings in 3.5 wt% NaCl solution at room temperature

Alloy coatings	R_s ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	R_2 ($\Omega \text{ cm}^2$)	CPE ₁ parameters		CPE ₂ parameters	
				Y_{0-1} ($10^{-5} \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_1	Y_{0-2} ($10^{-5} \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_2
NiCr	15.14	9.463×10^5	1.460×10^6	0.762	0.899	0.723	0.803
NiCrMo _{0.1}	13.81	1.498×10^6	1.912×10^6	0.702	0.919	0.869	0.938
NiCrMo _{0.3}	16.19	2.485×10^5	7.323×10^5	0.956	0.891	0.835	0.905
NiCr _{1.5}	12.62	2.640×10^6	2.726×10^6	0.751	0.896	0.528	0.861
NiCr _{1.5} Mo _{0.1}	13.80	5.407×10^6	5.692×10^6	0.668	0.862	0.472	0.825
NiCr _{1.5} Mo _{0.3}	14.81	7.741×10^3	4.868×10^3	3.108	0.778	6.675	0.839

Fig. 11 Passive film thickness (d) of NiCr_xMo_y coating in 3.5 wt % NaCl solution at room temperature

3.2.4 XPS Analysis of NiCr_xMo_y Alloy Coatings

The chemical compositions of the passive films formed on the NiCr_xMo_y coatings were characterized by XPS due to the obvious passivation regions of the potentiodynamic polarization curve. The XPS spectra of the O 1s, Cr 2p, Mo 3d,

Ni 2p, and Fe 2p for the NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1$) coatings after electrochemical tests in 3.5 wt% NaCl solution are presented in Fig. 12. Table 7 shows the calculated proportions of different components in the NiCr_xMo_y ($x = 1, 1.5$; $y = 0, 0.1$) coating and the relative proportions in each detailed spectra.

The O 1s spectrum (Fig. 12a) showed that all coatings contained O^{2-} species (530.2 eV), OH^- species (531.8 eV), and H_2O (533 eV), which corresponded to metal oxides, hydroxides, and bound water, respectively. The bound water can be used to capture dissolved metal ions, which will form a new film that can resist further corrosion [45, 46]. The Cr 2p spectrum represents the Cr^{3+} oxide state. From the proportion of Cr_2O_3 and $\text{Cr}(\text{OH})_3$, the Cr_2O_3 is the main chromium species in the passive film formed on the NiCr_xMo_y coatings. The Ni 2p spectra in the NiCr_xMo_y coatings included the NiO and $\text{Ni}(\text{OH})_2$ peaks, while the metallic Ni peak appeared in the Mo-free alloy coatings. NiO is the main Ni component in the passive film. The Fe 2p peaks were determined to be Fe^{2+} and Fe^{3+} oxides. The relative intensity of the peaks shows that Ni and Fe were less readily oxidized than Cr and Mo. The Mo 3d peaks are composed of Mo^{4+} and Mo^{6+} peaks, and the Mo^{6+} peaks at 232–233 eV and 235–236 eV belong to $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$, respectively. As the Cr content increased, the relative peak intensity of Mo^{6+} exceeded that of Mo^{4+} and the $\text{Mo}^{4+}/$

Fig. 12 XPS spectra of **a** O, **b** Cr, **c** Mo, **d** Ni, **e** Fe elements in the passive film on NiCr_xMo_y ($x = 1, 1.5; y = 0, 0.1$) alloy coatings after potentiodynamic polarization tests in 3.5 wt% NaCl solution

Mo^{6+} ratio decreased. According to the overall composition, the composition of Ni and Fe elements did not greatly change, and Cr oxide became the main product in the passive film. When the Cr content of the coating was the same, the relative content of Fe, Ni, Cr, and O was nearly the same.

The oxidation products of Mo in the passive film were determined to play a key role in the corrosion resistance, and the corrosion resistance improved as more Cr oxides were formed.

Table 7 Overall composition and percentages from the detailed XPS spectrum of the surface of NiCr_xMo_y ($x = 1, 1.5; y = 0, 0.1$) alloy coatings

Alloy coatings			Peak%	at. %
NiCr	Cr 2p _{3/2}	Cr _{ox}	54.8	8.8
		Cr _{hy}	45.2	
	Fe 2p _{3/2}	Fe ²⁺	44.3	4.8
		Fe ³⁺	55.7	
	Ni 2p _{3/2}	Ni ₀	8.8	2.6
		Ni _{ox}	55.1	
		Ni _{hy}	36.1	
	O 1s	O ²⁻	43.3	83.8
		OH ⁻	35.1	
		H ₂ O	21.6	
NiCrMo _{0.1}	Cr 2p _{3/2}	Cr _{ox}	56.8	9.3
		Cr _{hy}	43.2	
	Fe 2p _{3/2}	Fe ²⁺	51.5	3.4
		Fe ³⁺	48.5	
	Ni 2p _{3/2}	Ni _{ox}	79.4	3.2
		Ni _{hy}	20.6	
		O ²⁻	36.1	82.4
	O 1s	OH ⁻	38.5	
		H ₂ O	25.4	
		Mo ⁴⁺	63.3	
NiCr _{1.5}	Cr 2p _{3/2}	Cr _{ox}	60.4	11.0
		Cr _{hy}	39.6	
	Fe 2p _{3/2}	Fe ²⁺	49.5	3.0
		Fe ³⁺	50.5	
	Ni 2p _{3/2}	Ni ₀	11.7	1.6
		Ni _{ox}	54.9	
		Ni _{hy}	33.4	
	O 1s	O ²⁻	37.7	84.4
		OH ⁻	41.2	
		H ₂ O	21.1	
NiCr _{1.5} Mo _{0.1}	Cr 2p _{3/2}	Cr _{ox}	57.8	11.0
		Cr _{hy}	42.2	
	Fe 2p _{3/2}	Fe ²⁺	53.6	4.0
		Fe ³⁺	46.4	
	Ni 2p _{3/2}	Ni _{ox}	78.1	1.5
		Ni _{hy}	21.9	
		O ²⁻	32.8	81.8
	O 1s	OH ⁻	46.3	
		H ₂ O	20.9	
		Mo ⁴⁺	44.8	
	Mo 3d	Mo ⁶⁺	55.2	1.6

Based on the above analysis of the passivation film components in the NiCr_xMo_y coatings, we can propose the following anode and cathode reactions:

where M is the metal atom. At the beginning of corrosion, the formation of a stable Cr oxide layer on the surface of the sample caused the coating to become passivated. Meanwhile, the dissolved metal ions passed through the barrier layer and hydrolyzed at the barrier layer/solution interface to form metal hydroxides [37]:

Chloride ions continuously eroded the weak spots (such as pores and inclusions) of the passive film which accelerate the transport of ions. Upon the addition of Mo, the Mo-based oxide precipitated on the sample surface, which enhanced the stability of the Cr₂O₃ passive film. The Mo-based oxide was further oxidized to MoO₄²⁻, whose formation has been reported to improve the pitting resistance of coatings [47, 48]:

The passive film of the NiCr_{1.5}Mo_{0.1} coating contains higher Cr³⁺ and Mo⁶⁺ oxide states, which indicates the existence of dense passive film [1, 26]. The results show that the corrosion resistance of the coating was mainly related to the formation of Cr₂O₃ passive film and the addition of Mo element.

3.3 Mechanical Properties of NiCr_xMo_y Alloy Coatings

Figure 13 shows the microhardness curves along the cross sections of the NiCr_xMo_y coatings. The microhardness curves indicated the three parts of the coating, the transition zone and the substrate. The existence of a transition zone reduced stress concentration at the interface and inhibited the initiation and propagation of interface cracks. Increasing

Fig. 13 Microhardness of NiCr_xMo_y alloy coatings

Cr and Mo contents significantly improved the hardness of coatings, and the hardness of $\text{NiCr}_{1.5}\text{Mo}_y$ coatings with two-phase structure was even more obvious. In order to further investigate the reasons, nanoindentation tests were carried out on the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating. The load–depth curves of different phases in the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating are shown in Fig. 14a. The indentation depth of the FCC phase was significantly greater than that of the BCC phase, indicating that the BCC phase was more resistant to plastic deformation. The average hardness and elastic modulus values were calculated using the Oliver–Pharr method [49] from the load–depth curves as shown in Fig. 14b. The average nanohardness of the FCC and BCC phases was 5.19 GPa and 6.71 GPa, while the elastic modulus was 155.26 GPa and 184.40 GPa, respectively. Increased Cr and Mo contents resulted in the formation of the hard BCC phase and σ phase

in the ID region and the relative volume fraction of the ID region with the increase in Mo content is one of the reasons for the increase in its microhardness. In addition, the solid solution strengthening effect caused by the higher lattice parameter of the FCC phase also played an active role in the improving the microhardness of the coating. A larger atomic radius difference and higher solute content led to a better solid solution strengthening effect [50]. The increase in the number of grain boundaries also increased the microhardness of the coatings. Mo plays a leading role in improving the microhardness. Therefore, the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating is a multifunctional coating with excellent properties.

4 Conclusions

In this study, the phase composition, microstructure, corrosion properties and mechanical properties of NiCr_xMo_y alloy coatings by laser cladding were investigated. The main conclusions are summarized as follows:

- (1) The x value increased from 1 to 1.5, and the phase structure changed from a single FCC phase to a dual-phase structure containing FCC and BCC phases, while the increase in y value promoted the precipitation of σ phase.
- (2) The addition of Mo improved the passivation range (ΔE) of the coatings and enhanced the pitting resistance. The $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating with relatively high content of Cr^{3+} ions and Mo^{6+} ions formed a dense passivation film which slowed down the corrosion of the coating and thus had the best corrosion resistance. The corrosion resistance of the homogeneous multi-phase structure was better than that of the single-phase structure.

Fig. 14 **a** Nanoindentation load–depth curves, **b** average nanohardness and elastic modulus of the different phases in the $\text{NiCr}_{1.5}\text{Mo}_{0.1}$ coating

- (3) The increase in Cr and Mo initiated phase transition and solid solution strengthening due to lattice distortion, which enhanced the microhardness and mechanical properties of the coatings.

Acknowledgements This work was financially supported by the Distinguished Taishan Scholars in Climbing Plan (No. tspd20161006) and the National Natural Science Foundation of China (Nos. 51772176 and 51971121).

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