EROSION OF MOLD-STEEL SURFACE OXIDATION AND NITRIDING LAYERS DUE TO A DIE-CASTING ALUMINUM ALLOY

EROZIJSKA OBRABA OKSIDIRANIH IN NITRIRANIH PLASTI POVRŠINE JEKLENEGA ORODJA MED TLAČNIM LITJEM ALUMINIJEVE ZLITINE

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The resistance to erosion due to A356 aluminum-alloy melt of H11 die steel treated with two different surface-treatment technologies (oxidation treatment and nitriding treatment) was investigated by employing a hot-dip-aluminum (immersion) experiment. The microstructure, chemical constituents, phase compositions, heat-flux variation and activation energy were analyzed, using a scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Compared to the nitrided samples, the oxidized samples have a smaller erosion area and a lower mass loss. Moreover, the nitrided samples require lower Gibbs free energy to react with the aluminum-alloy melt. Compared to the samples with the oxidation treatment, the activation energy of the reaction between the nitrided samples and aluminum alloy is smaller. These results indicate that the H11 die steel surface-treated with oxidation tends to exhibit a better erosion resistance to aluminum-alloy melt than the steel surface-treated with nitriding.

Keywords: erosion resistance, oxidation treatment, nitriding treatment, immersion test

Avtorji prispevka so raziskovali erozijsko odpornost površine orodja iz orodnega jekla H11 zaradi oplakovanja s talino Al zlitine A356 med tlačnim litjem. Površina jeklenega orodja je bila obdelana na dva različna načina; s tehnologijo površinske oksidacije in z nitriranjem. Odpornost proti eroziji so ugotavljali s preizkusom potapljanja v vročo talino Al zlitine. Mikrostrukturo, kemijsko in fazno sestavo, spreminjanje toplotnega toka in aktivacijsko energijo so avtorji analizirali s pomočjo vrstičnega elektronskega mikroskopa (SEM), energijske disperzijske spektroskopije (EDS), rentgenske difrakcije (XRD) in diferencialne vrstične kalorimetrije (DSC). Vzorci z oksidirano površino so imeli v primerjavi z nitriranimi manjše poškodbe površine zaradi erozije in manjšo izgubo mase. Nadalje so površinsko nitrirani vzorci zahtevali manjšo Gibbsovo prosto energijo za reakcijo s talino Al zlitine. Aktivacijska energija za začetek reakcije med površino nitriranih vzorcev in Al zlitino je bila manjša v primerjavi s površinsko oksidiranimi vzorci. Rezultati raziskave so tako pokazali, da je površinsko oksidirano H11 jekleno orodje za tlačno litje bolj odporno proti eroziji Al taline kot orodje, ki ima nitrirano površino.

Ključne besede: odpornost proti obrabi zaradi erozije, obdelava površine orodja z oksidacijo ali nitriranjem, preizkus potapljanja orodja v talino

1 INTRODUCTION

Aluminum is a widely used material in the automotive industry and the requirement for the quantity and quality of aluminum alloys has been enhancing.[1] Die casting is one of the most efficient forming methods used for aluminum components.[2] A mold affects not only the productivity but also the die-casting performance, such as surface finishing and microstructure refinement. So, many researchers focus on improving the mold quality and prolonging the service life of a mold.[3] It is well known that one of the main reasons for a reduced service life of a mold is the fact that the die surface becomes eroded due to the high temperature of aluminum-alloy melts.[4]

During a die-casting process, erosion occurs because high-temperature melt continuously scours the die surface and produces a mechanical shock and chemical corrosion.[5] When the die is drawn, a part of the casting may be left on the die surface, or the mold may be torn apart, causing a permanent failure of the mold.[6] Therefore, preventing the erosion of a mold is a very important task taken to prolong its life. A suitable surface treatment of a mold is one of the most effective technologies, and many researches reported on it. G. H. Farrahi et al.[7] found that shot peening increased the fatigue life of D3 steel by about 14 %, while nitrocarburizing and single-stage nitriding decreased the fatigue life of D3 steel by about 29 % and 50 %, respectively. Bo Wang et al.[8] investigated the effect of nitrided-layer microstructure control on the wear behavior of the AISI H13 hot-work

die steel. The nitrided surface layer consisting of the ε-$Fe_{2-3}N$ and γ'-Fe_4N phases showed excellent wear resistance at a light load but a seriously deteriorated performance at a heavy load. Jose Mario Paiva et al.[3] held that an $AlCrN/Si_3N_4$ nanocomposite PVD coating showed an optimum combination of hardness, adhesion, soldering behavior, oxidation resistance and stress state. It provided an efficient stress barrier, preventing the crack propagation caused by dynamic pressing. The application of the nanocomposite coating increased the lifespan by approximately three times as compared to the benchmark AlCrN coating. Ildiko Peter et al.[9] tested the corrosion and thermal fatigue resistance of nickel-based-alloy-coated samples and magnesia-stabilized-zirconia-coated samples by cyclically dipping them in a molten aluminum alloy. Both coatings failed due to thermal stresses and no signs of corrosion were detected. Marcin Adamiak et al.[10] investigated the changes in the surface-layer property after the high-power diode-laser (HPDL) treatment of hot-work tool steels with CrN, (Ti,Al)N and Ti(C,N) coatings. The employment of a laser beam at a 0.7 kW power for the laser treatment of the samples with the Ti(C,N) coatings causes a clear coating-adhesion growth because of the diffusive processes induced by the heat release. The laser treatment of the samples with the CrN coating with a power above 0.5 kW causes the development of a network of cracks associated with different thermal-expansion coefficients of both the substrate materials and the coatings.

The two methods of surface treatment, surface oxidation and nitriding, are of great significance for the service of a die. However, the erosion resistance of die steel and its mechanism after the surface-oxidation and nitriding treatments do not get the attention they deserve. In this research, the H11 die steel and A356 aluminum alloy were used, and a hot-dip (immersion) experiment was carried out. SEM, EDS, XRD and DSC were used to investigate the morphology, chemical composition, phase species, change in the heat flow and activation energy. Through these analysis and characterization methods, the erosion resistance of die steel and its mechanism after surface oxidation and nitriding were investigated to provide the basis for prolonging the service life of a die.

2 EXPERIMENTAL PART

The selected experimental materials were the A356 die-casting aluminum alloy and H11 die steel; their chemical compositions are shown in **Tables 1** and **2**, respectively.

Eroded rectangular H11 steel specimens with dimensions of (20 × 20 × 105) mm and thermal-analysis samples with dimensions of ϕ3 mm × 1 mm were used in the experiment. Firstly, these specimens were heat treated as follows: the highest austenitizing temperature was 1015 °C and the specimens were tempered twice at 550 °C to reach a hardness of 48 HRC. Then the samples were treated with oxidation and nitriding and numbered as shown in **Table 3**. In this experiment, the vapor-oxidation treatment and nitrocarburizing treatment were used. The vapor-oxidation treatment included vapor oxidation at 550 °C for 1.5 h under a water-vapor pressure of 150 kPa. The nitrocarburized samples were first heated at 470 °C under an N_2 atmosphere. After that, the samples were heated to 565 °C and the N_2, NH_3 and CO_2 gasses with a composition of 47.5 % N_2 + 47.5 % NH_3 + 5 % CO_2 were blown into the furnace. The specimens were held in this condition for 2.5 h. Finally, the nitriding samples were cooled under the N_2 atmosphere until the temperature reached 120 °C and taken out of the furnace.

Table 1: Chemical composition of A356 (*w*/%)

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
A356	6.50–7.50	0.20	0.20	0.10	0.25–0.45	0.10	0.20	Bal.

Table 2: Chemical composition of H11 die steel (*w*/%)

Element	C	Si	Cr	Mo	V	Mn	Fe
H11	0.35–0.40	~	5.0	2.2	0.5	<0.4	Bal.

Table 3: Identification numbers and treatment processes for the specimens

Immersion time	0.5 h	1 h	2 h
Oxidation treatment	A1	A2	A3
Nitriding treatment	B1	B2	B3

The eroded samples with different surface treatments (oxidation, nitriding) were immersed into the A356 aluminum-alloy melt (680 °C) under a protective argon atmosphere. After a given time (0.5, 1 or 2) h, these samples were taken out and cooled in air. Then the samples were soaked in a saturated NaOH solution for 12 h. Afterward, they were placed in an ultrasonic cleaner to remove the residual aluminum alloy from the surface, washed with distilled water, dried and weighed. Therefore, comparing the current state of the samples with their quality found before the experiment, the mass-loss rate could be calculated. Finally, the sample were prepared for different characterization analyses (SEM+EDS, XRD).

The surfaces of thermal-analysis samples were covered completely with the A356 aluminum-alloy powder and they were put in a TGA (thermal gravimetric analyzer)/DSC special crucible, respectively. The samples were heated from room temperature to 700 °C under a protective argon atmosphere at three different heating rates (10, 15 and 20) K/min and the changes in the thermal flow were recorded.

3 RESULTS AND DISCUSSION

3.1 Results for the sample mass loss

The mass-loss rate of each sample was calculated according to the quality recorded before and after the test; the results are shown in **Figure 1**.

$$\dot{M} = \frac{Q_{Pre} - Q_{Post}}{Q_{Pre}} \times 100\% \qquad (1)$$

where $\dot{M}$ is mass-loss rate, Q_{Pre} pre-experimental quality, Q_{Post} post-experimental quality.

According to **Figure** 1, the mass loss of the samples increases gradually with the time of the experiment. After the immersion for (0.5, 1 and 2) h, the mass-loss rates for the oxidized samples are (0.67, 1.26 and 1.77) %, respectively. The mass-loss rates for the nitrided samples are (1.63, 1.82 and 2.87) %, respectively. Obviously, the oxidation layer can protect the mold and decrease the mass loss more effectively. This indicates that the erosion resistance of the H11 die steel treated with surface oxidation is better than that of the H11 die steel treated with nitriding.

3.2 Microstructure

Figure 2 shows the microstructures of the samples with different treatments after the immersion for (0.5, 1 and 2) h. According to the figures, a small amount of a second phase starts to form on the sample surface after 0.5 h. This indicates that mutual diffusion between Fe and Al atoms occurred at a temperature of 680 °C, resulting in a reaction forming Fe-Al intermetallic compounds on the die surface. As the time increases to 1h, the second phase grows, accumulates and extends on the surface and into the matrix. After 2 h, corrosion pits form and connect with each other, as shown in **Figures 2c** and **2f**. Obviously, the erosion area of the nitrided samples is larger than that of the oxidized samples.

According to the analysis above, the nitrided specimens are more prone to be corroded. On the other
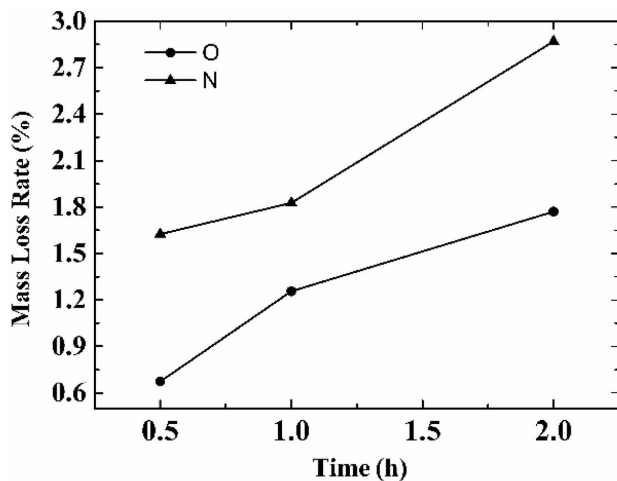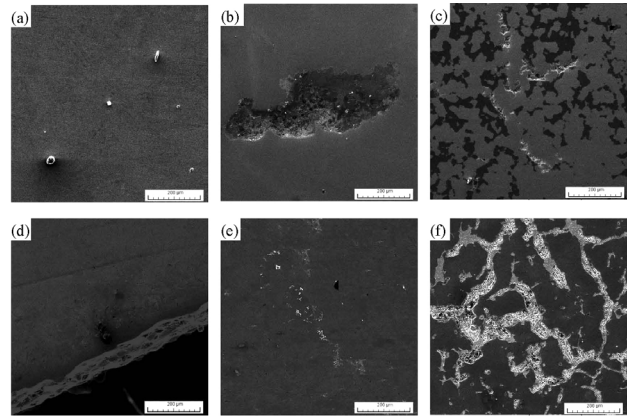

Figure 2: Scanning electron micrographs of oxidation samples after immersion for: a) 0.5 h, b) 1 h, c) 2 h; scanning electron micrographs of nitriding samples after immersion for d) 0.5 h, e) 1 h, f) 2 h

hand, this may relate to the chemical-reaction rate for Fe and Al, which mainly depends on the speed of the atom diffusion. V. Joshi et al.[11] hold that chemical reactions and diffusion in a melt are the dominant mechanisms behind an intermetallic formation and soldering, and that the movement of a liquid-solid diffusion results in a mass loss or erosion. Die steel forms a protective film after its surface treatment. This film plays a role in preventing the process of atomic diffusion. Compared with the nitriding layer, the oxidation layer can prevent the mutual diffusion between the Fe and Al atoms and slow down the reaction process more effectively, improving the erosion resistance of die steel and prolonging the service life of a die. On the other hand, this may be associated with the reaction between the aluminum melt
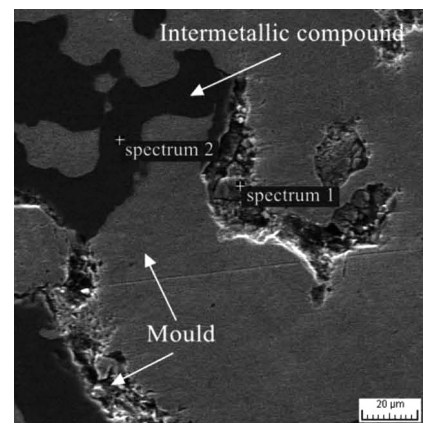

Figure 3: Chemical composition of sample A3 at S1 and S2

Element	Weight (%)		Atomic (%)	
	S1	S2	S1	S2
Fe	90.03	44.08	86.47	27.95
Al	2.37	53.78	4.70	70.69
Si	1.14	–	2.17	–
Cr	6.46	–	6.66	–

Figure 1: Mass-loss rate after the immersion
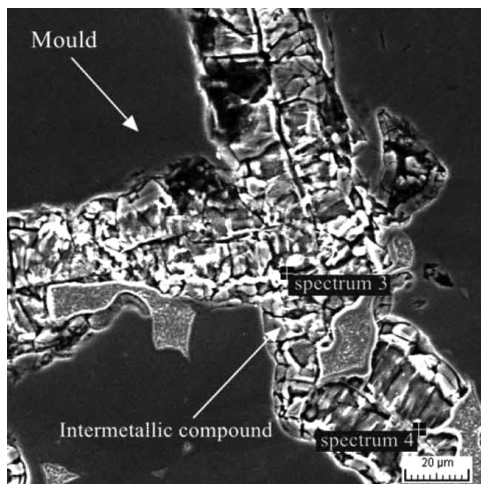
Figure 4: Chemical composition of sample B3 at S3 and S4

Element	Weight (%)		Atomic (%)	
	S1	S2	S1	S2
Fe	87.81	79.07	77.72	68.22
Al	11.69	13.76	21.40	24.57
Si	0.50	0.72	0.88	1.23
Cr	–	6.45	–	5.98

and the protective film. Compared with the oxidation layer, the reaction between the aluminum melt and nitriding layer is more violent, which may be related to the microstructure of the surface layers or the rate of the reaction between the phase components contained in
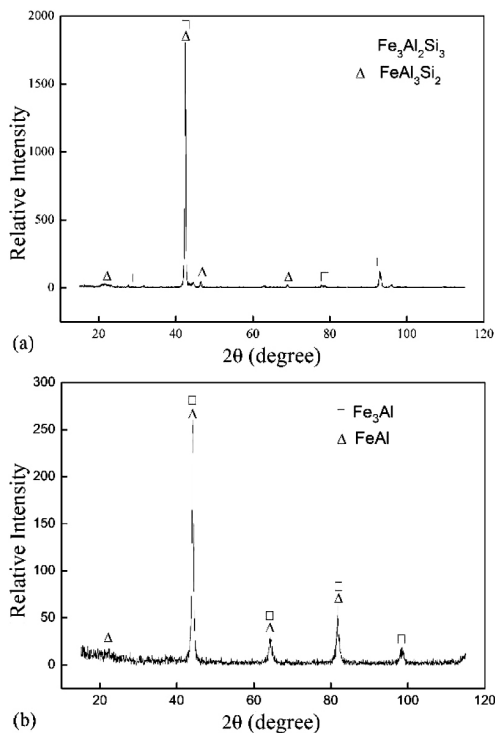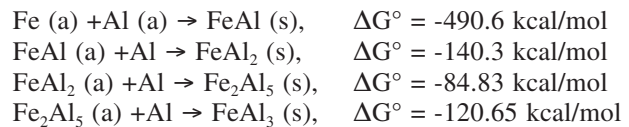

Figure 5: X-ray diffraction diagrams for samples: a) A3 and b) B3

these surface layers and aluminum melt. These options need our further discussion and research.

3.3 Microstructure and phase analysis

The morphology of the sample surfaces after the immersion and the elemental content are shown in **Figures 3** and **4**. On the erosion areas of the samples, there are intermetallic compounds or a solid solution, containing Fe, Al and Si. According to the atomic percent in **Figure 3**, there is a small amount of Al diffused in the iron substrate at S1 on the surface of oxidation sample A3. The Si element was not detected, so the phase can be determined as Fe_2Al_5 at S2. According to the atomic percent in **Figure 4**, the phase is close to Fe_3Al at S3 and S4 on the surface of nitriding sample B3. To further determine the phases on the surfaces of the samples, an XRD experiment was performed. According to **Figures 3**, **4** and **5**, the surface of oxidation sample A3 contains Fe_2Al_5 binary alloy, and $Fe_3Al_2Si_3$ and $FeAl_3Si_2$ ternary alloy, while the surface of nitriding sample B3 only contains Fe_3Al and $FeAl$ binary alloy.

Four reactions between Fe and Al can occur at 680 °C; the Gibbs free energy[11] is shown with the formula below:

$$Fe\ (a) +Al\ (a) \rightarrow FeAl\ (s), \qquad \Delta G° = -490.6\ kcal/mol$$
$$FeAl\ (a) +Al \rightarrow FeAl_2\ (s), \qquad \Delta G° = -140.3\ kcal/mol$$
$$FeAl_2\ (a) +Al \rightarrow Fe_2Al_5\ (s), \qquad \Delta G° = -84.83\ kcal/mol$$
$$Fe_2Al_5\ (a) +Al \rightarrow FeAl_3\ (s), \qquad \Delta G° = -120.65\ kcal/mol$$

The surfaces of the nitriding samples contain FeAl whereas the surfaces of the oxidation samples contain Fe_2Al_5. The Gibbs free energy of the FeAl generation is significantly lower than that of the Fe_2Al_5 generation, indicating that the driving force of the FeAl generation is lower than that of the Fe_2Al_5 generation. In other words, the reaction between the nitriding layer and aluminum-alloy melt is easier to occur.

3.4 Thermal analysis and activation-energy calculation

Figure 6 shows how the heat flow changes with the temperature while heating the A356 aluminum-alloy powder and H11 die steel. The range of 500–650 °C was selected in order to observe the process more intuitively and the heat changes are shown in **Table 4**.

Table 4: Heat changes of the thermal-analysis samples with two different surface treatments (J/g)

	Oxidation treatment	Nitriding treatment
10 K/min	-124.27	-143.43
15 K/min	-25.07	-44.51
20 K/min	-16.17	-26.05

As shown in **Figure 6**, the DSC curves for the thermal-analysis samples with two different surface treatments have the same shape and trend. The aluminum
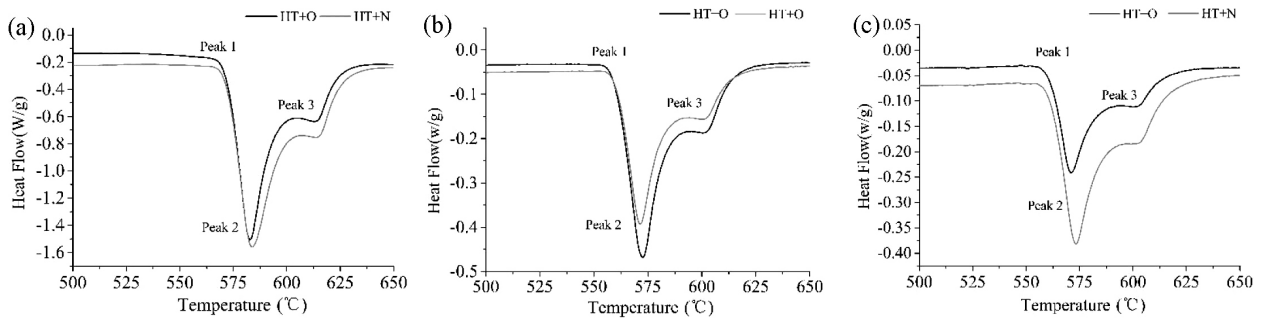
Figure 6: DSC results of the thermal analysis of the samples with two different surface treatments: a) 10 K/min; b) 15 K/min; c) 20 K/min
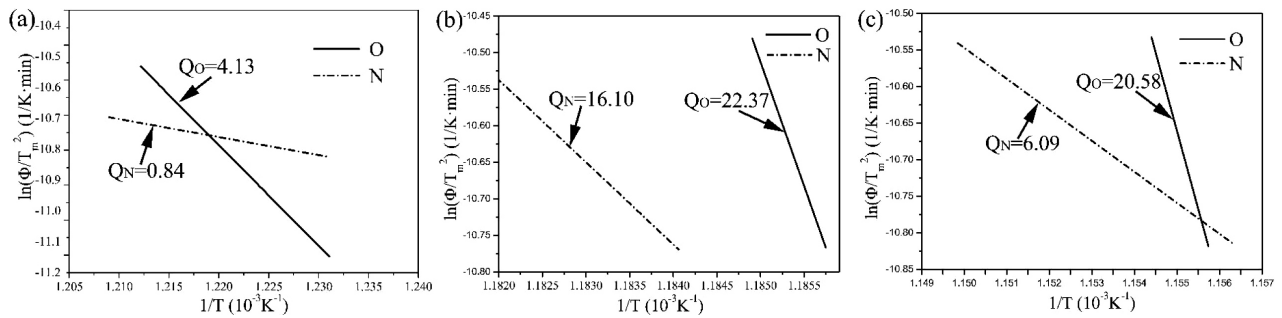

Figure 7: Activation energy (unit: eV/atom) of the reaction between A356 aluminum alloy and die steel with two different surface treatments at a) peak 1, b) peak 2 and c) peak 3 (the positions of peaks 1, 2 and 3 are shown in **Figure 6**)

alloy began to melt at peak 1. Peak 2 is an endothermic melting peak and peak 3 is a weak exothermic peak. **Table 4** shows that, at the same heating rate, the heat released by the nitrided samples is larger than that released by the oxidation samples. The heat release of the oxidation samples is only 25.07 J/g when the heating rate is 15 K/min, while that of the nitrided samples is up to 44.51 J/g. The heat release of the nitrided samples is still much larger than that of the oxidized samples when the heating rate is 20 K/min. It shows that the oxidation layer can more effectively inhibit the reaction between the aluminum alloy and die steel, protecting the die steel from erosion due to molten aluminum and prolonging the service life of a die.

Using the Kissinger formula,[12,13,14] the activation energy for the reaction can be calculated:

$$\frac{d\left(\ln \dfrac{\Phi}{T_{\mathrm{m}}^{2}}\right)}{d\left(\dfrac{1}{T_{\mathrm{m}}}\right)} = -\frac{Q}{k} \qquad (2)$$

where k is the Boltzmann constant; T_{m} is the peak temperature; and ϕ is the heating rate. The activation energy Q is not a constant (unit: eV/atom) and it is related to the peak temperature T_{m} and the heating rate ϕ. The activation energy of a reaction can be obtained by plotting $\ln (\phi/T_{\mathrm{m}}^{2})$ as a linear function of $1/T_{\mathrm{m}}$. The slope of the line plotted is equal to $-Q/k$. **Figure 7** shows the activation energy of the reaction between the A356 aluminum alloy and two kinds of samples.

According to **Figure 7**, the activation energy of the reaction between the surface oxidation layer and aluminum alloy is 22.37 eV/atom and 20.58 eV/atom at peak 2 and peak 3, respectively, which is much higher than the activation energy (4.13 eV/atom) at peak 1. The activation energy of the reaction between the surface nitriding layer and aluminum alloy is only 0.84 eV/atom at peak 1, while the activation energy at peak 2 and peak 3 is 16.10 eV/atom and 6.07 eV/atom, respectively. Clearly, at the same peak, the reaction between the oxidized samples and aluminum alloy needs much more activation energy, especially at peak 1. The high activation energy results from the atomic activity of permutation diffusion, which can limit the solid-phase transformation and obstruct the formation of intermetallic compounds[7]. It indicates that the oxidation layer can more effectively inhibit the reaction between aluminum alloys and die steel.

This phenomenon can be explained in two ways. On the one hand, a surface nitriding layer may not be uniform and compact. The aluminum melt can wet the mold more easily and permeate through it, quickly damaging the surface layer. Therefore, it cannot hinder the mutual diffusion between the Fe and Al atoms. On the other hand, aluminum melt can react with some phases from the nitriding layer more violently and these reactions are exothermic, further promoting the subsequent reaction between the Fe and Al atoms and speeding up the formation of intermetallic compounds. When intermetallic compounds accumulate on the die surface to a certain degree, soldering may occur. In summary, the erosion resistance of the H11 die steel surface-treated with

oxidation is better than that of the H11 die steel treated with nitriding.

4 CONCLUSIONS

The resistance to erosion due to A356 aluminum alloy of H11 die steel surface-treated with two different technologies (oxidation treatment and nitriding treatment) was investigated with immersion experiments.

(1) After immersions for (0.5, 1 and 2) h, the mass-loss rates of the oxidized samples are (0.67, 1.26 and 1.77) %, respectively. The mass-loss rates of the nitrided samples are (1.63, 1.82 and 2.87) %, respectively, and their erosion areas are larger.

(2) The Gibbs free energy of the reaction between the nitrided samples and aluminum-alloy melt is lower than that of the oxidized samples, namely the reaction is easier to occur.

(3) The thermal analysis (a DSC experiment) was analyzed and the activation energy was calculated. At the same heating rate, the heat released by the nitrided samples is larger than that released by the oxidation samples. The reaction between the oxidation samples and aluminum alloy needs much more activation energy. This shows that an aluminum-alloy melt reacts more violently with the nitrided samples.

Thus, the H11 die steel surface-treated with oxidation tends to perform better, exhibiting higher resistance to erosion due to aluminium-alloy melt than that surface-treated with nitriding.

Acknowledgements

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