Postprint: Wear Characteristics of Two NiAl-Based Alloys Under Acid Corrosion Conditions

Authors: Wang Zhensheng, Yang Shuangshuang, Peng Zhen, Tan Qingqi, Guo Jianting, Zhou Lanzhang

Date: 2023-03-18T00:00:00+00:00

Abstract

The corrosion-wear characteristics of NiAl-2.5Ta-7.5Cr-x(0, 1)B alloys in 5% H2SO4 solution were investigated. The results show that: under acidic corrosion conditions, the NiAl-2.5Ta-7.5Cr-1B alloy exhibits superior corrosion resistance compared to the NiAl-2.5Ta-7.5Cr alloy, readily passivating to form a film, with a static corrosion rate of 0.007 mg/(cm2 · h1), a passivation current density of 0.299(mA · cm-2), and a natural corrosion potential of -0.213 V, demonstrating good acid corrosion resistance and stability. The material film completely covers the wear surface of the NiAl-2.5Ta-7.5Cr-1B alloy, inhibiting the accelerating effect of corrosion on wear; the corrosion-wear rate of the NiAl-2.5Ta-7.5Cr-1B alloy is reduced by 2-8 times compared to that of the NiAl-2.5Ta-7.5Cr alloy. The tribocorrosion of the NiAl-7.5Cr-2.5Ta-1B alloy is controlled by corrosion-wear and the protective effect of the complete material film. The tribocorrosion mechanism of the NiAl-2.5Ta-7.5Cr alloy is controlled by corrosion-wear and abrasive wear.

Full Text

Corrosive-Wear Properties of Two NiAl-Based Alloys in Sulfuric Acid Solution

WANG Zhensheng[1],[2], YANG Shuangshuang[1], PENG Zhen[1], TAN Qingqi[1], GUO Jianting[3], ZHOU Lanzhang[3]

[1] Engineering Research Center of Advanced Mining Equipment, Ministry of Education, Hunan University of Science and Technology, Xiangtan 411201, China
[2] Hunan Provincial Key Laboratory of National Defense Science and Technology for High Temperature Wear Resistance Materials and Preparation Technology, Hunan University of Science and Technology, Xiangtan 411201, China

[3] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

Abstract

The corrosion-wear properties of NiAl-2.5Ta-7.5Cr-x(0, 1)B alloys in 5% H_2SO_4 solution were investigated at room temperature. The results demonstrate that NiAl-2.5Ta-7.5Cr-1B alloy exhibited superior corrosion resistance compared to NiAl-2.5Ta-7.5Cr alloy in 5% H_2SO_4 solution, with a passive current density of 0.299 $\mathrm{A \cdot cm^{-2}}$ and a free corrosion potential of -0.213 V. The key factor is the formation of a passive film on the surface of NiAl-2.5Ta-7.5Cr-1B alloy. The corrosion-wear rate of NiAl-2.5Ta-7.5Cr-1B alloy was 2–8 times lower than that of NiAl-2.5Ta-7.5Cr alloy. The abrasion mechanism for NiAl-7.5Cr-2.5Ta-1B alloy was dominated by the synergistic effect of corrosion-wear and the protectiveness of the passive film, whereas that for NiAl-7.5Cr-2.5Ta alloy was primarily controlled by corrosion-wear and abrasive wear.

Keywords: metallic materials, NiAl-2.5Ta-7.5Cr alloy, NiAl-2.5Ta-7.5Cr-1B alloy, H_2SO_4, corrosive wear, abrasion mechanism

Funding: Supported by Natural Science Foundation of Hunan Province (No. 13JJ8015) and National Natural Science Foundation of China (No. 51101055).

Received: November 10, 2014; Revised: February 1, 2015

Correspondence: WANG Zhensheng, Tel: 13298528387, E-mail: zswang@imr.ac.cn

---

The ordered intermetallic compound NiAl possesses a high melting point (1640°C), high thermal conductivity (70–80 $\mathrm{W/m \cdot K}$), low density (5.86 $\mathrm{g/cm^3}$), and excellent corrosion resistance. Over the years, researchers have improved the high-temperature creep resistance and room-temperature fracture toughness of NiAl alloys through alloying and the fabrication of endogenous and exogenous composites, employing methods such as solid solution strengthening, second-phase strengthening, and oxide dispersion strengthening (ODS). Although NiAl-based alloys are difficult to achieve 2% room-temperature tensile ductility, they exhibit good compressive strength and compressive plasticity. Given the natural compressive stress state in wear conditions, scholars have investigated the wear performance of various NiAl materials. Results indicate that under room-temperature wear conditions, tensile ductility becomes a secondary performance indicator compared to hardness, strength, compressive plasticity, and work-hardening capacity. Dry friction wear is controlled by plastic deformation, demonstrating good wear resistance. Under atmospheric and dry friction conditions, the alloy exhibits excellent self-lubricating and wear-resistant characteristics at 700–900°C, with friction coefficients and wear rates lower than those of Ni-based self-lubricating alloys (containing W, Mo, Co), and the self-lubricating properties are durable. Additionally, through alloying element additions, NiAl-based alloys can develop self-lubricating properties from room temperature to 900°C, providing research ideas for practical applications. Considering that NiAl has a highly stable long-range ordered crystal structure with surfaces that can be stabilized at the atomic scale, it can be used as a substrate material for catalysis research, including studies on the adsorption of S, CO, O, and Xe. Therefore, exploring the friction and wear characteristics of NiAl-based alloys under corrosive conditions, combined with their good tribological properties, is significant for broadening their practical application range.

1.1 Sample Preparation

High-purity Ni, Al, Ta, Cr, and Ni-B (>99.9%, mass fraction) were used as raw materials to prepare alloys with nominal compositions of NiAl-2.5Ta-7.5Cr and NiAl-2.5Ta-7.5Cr-1B (at.%) using a VAM-I high-vacuum arc furnace. Wear test specimens with a thickness of 4 mm, static corrosion specimens measuring 4 mm × 10 mm × 10 mm, and electrochemical polarization curve specimens measuring 4 mm × 10 mm × 10 mm with grooves cut on the side surfaces were prepared by wire electrical discharge machining. All specimen surfaces were ground to 1200-grit SiC paper, ultrasonically cleaned in acetone and alcohol, and dried. Analytical-grade H_2SO_4 and distilled water were used to prepare a 5% H_2SO_4 solution by mass fraction.

1.2 Static Immersion Corrosion Test

Following ASTM31-72 standard, static corrosion specimens measuring 4 mm × 10 mm × 10 mm were ultrasonically cleaned in anhydrous ethanol and acetone, dried, and weighed before being immersed in H_2SO_4 solution for 72 h. After corrosion testing, specimens were cleaned, dried, and reweighed. The mass loss due to corrosion was calculated as the difference between the two measurements. The static corrosion rate was calculated using the formula V = (W_{before} - W_{after})/St, where W_{before} is the initial mass (mg), W_{after} is the final mass (mg), S is the specimen area (cm^2), and t is the test duration (h).

1.3 Electrochemical Corrosion Test

Potentiodynamic polarization curves were measured using a CHI760E electrochemical workstation with a three-electrode system: the specimen as the working electrode, a large-area Pt sheet as the auxiliary electrode, and a saturated calomel electrode as the reference. Electrochemical specimens were sealed with epoxy resin, with one end connected to a lead wire and 1 cm^2 exposed as the working surface. After ultrasonic cleaning in anhydrous ethanol and acetone, specimens were dried and immersed in the corrosive medium for 10 min. Once the open-circuit potential stabilized, polarization curves were measured at a scan rate of 5 mV/s over a range of $±$0.3 V relative to the open-circuit potential. The self-corrosion current density was determined using the software integrated in the CH660E system.

1.4 Corrosion-Wear Test

The friction and wear properties of both materials were evaluated using an HRS-2M high-speed reciprocating friction and wear tester. The counterface specimen was a Si_3N_4 ceramic ball with a diameter of 4 mm. The load was applied to the ball while the specimen reciprocated in a holder, creating sliding wear at the ball-specimen contact surface. Tests were conducted at room temperature in H_2SO_4 solution under loads of 10 N and 45 N, sliding speeds of 0.05 m/s and 0.1 m/s, a reciprocating distance of 10 mm per cycle, and a wear duration of 60 min. The friction coefficient was monitored and recorded by the equipment. Wear volume was measured using a NanoMap-500LS three-dimensional contact surface profilometer. The wear rate was calculated as $W = V/(F \cdot L)$, where V is the wear volume loss, F is the load, and L is the sliding distance. The average of three wear tests was reported.

The microstructure and worn surface morphologies were observed using an S-3400N scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). Vickers hardness was measured using an HV-50 hardness tester with a load of 500 g and loading time of 15 s. Room-temperature compressive strength was tested using a universal mechanical testing machine at a compressive strain rate of 2.78×10^{-3} s^{-1}.

2. Results and Discussion

2.1 Static Corrosion of Alloys

After 72 h of static corrosion, the H_2SO_4 solution showed no discoloration or precipitation for either alloy, and both specimen surfaces appeared gray-black. The static corrosion rate of NiAl-2.5Ta-7.5Cr alloy was 0.009 mg/($cm^2 \cdot h$), while that of NiAl-2.5Ta-7.5Cr-1B alloy was 0.007 mg/($cm^2 \cdot h$). According to the Chinese four-level corrosion resistance standard, both alloys fall into the second level, indicating good corrosion resistance in 5% H_2SO_4 solution.

[Figure 1: see original paper] shows SEM images of both alloys before and after corrosion. Combined with EDS analysis and comparison of Figs. 1a and 1b, a reaction product layer formed on the NiAl-2.5Ta-7.5Cr alloy surface, with significant pitting corrosion cavities and a few cracks at the alloy phase boundaries. Comparison of Figs. 1c and 1d reveals that NiAl-2.5Ta-7.5Cr-1B alloy also formed a reaction product layer, but exhibited exfoliation corrosion and numerous cracks at the phase boundaries. The volume of insoluble corrosion products at the phase boundaries exceeded that of the consumed matrix metal, creating wedge-shaped tensile stresses on surrounding grains. Simultaneously, the phase boundaries experienced tensile stress, accelerating crack initiation and propagation. When corrosion progressed to a certain extent, crack propagation caused delamination and spalling, i.e., exfoliation corrosion occurred.

[Figure 2: see original paper] presents XRD patterns of both alloys before and after corrosion. The patterns show that NiAl-2.5Ta-7.5Cr alloy formed a reaction product film composed of $NiCrO_3$, Al_2O_3, and $AlH(SO_4)_2$, while NiAl-2.5Ta-7.5Cr-1B alloy formed a film consisting of $NiCrO_3$, B_2O, and TaO.

2.2 Electrochemical Corrosion of Alloys

The polarization curves for both alloys are shown in [Figure 3: see original paper]. Both alloys exhibit similar curve shapes. When the polarization potential reached approximately -0.20 V (the self-corrosion potential), the alloys entered the active dissolution region. As the potential increased further to approximately -0.15 V (the passivation potential) and the current density reached the critical passivation current density, the polarization current density slightly decreased with increasing potential, indicating that both alloys underwent passivation in H_2SO_4 solution.

lists the electrochemical test parameters for both alloys in H_2SO_4 solution. NiAl-2.5Ta-7.5Cr alloy had a free corrosion potential of -0.236 V and a passive current density of 3.524 $\mathrm{A \cdot cm^{-2}}$, whereas NiAl-2.5Ta-7.5Cr-1B alloy showed a free corrosion potential of -0.213 V and a passive current density of 0.299 $\mathrm{A \cdot cm^{-2}}$. These results indicate that NiAl-2.5Ta-7.5Cr-1B alloy possesses a more positive free corrosion potential and lower passive current density, demonstrating better passivation performance and corrosion resistance compared to NiAl-2.5Ta-7.5Cr alloy.

2.3 Corrosion-Wear Behavior

2.3.1 Corrosion-Wear Test Results [Figure 4: see original paper] shows the friction and wear properties of both alloys in H_2SO_4 solution. The friction coefficient of NiAl-2.5Ta-7.5Cr-1B alloy was lower than that of NiAl-2.5Ta-7.5Cr alloy under all conditions except 10 N + 0.05 m/s. The wear rate of NiAl-2.5Ta-7.5Cr-1B alloy ranged from 0.695 to 1.69×10^{-15} $\mathrm{m^3/(m \cdot N)}$, representing a 2–8 fold improvement over NiAl-2.5Ta-7.5Cr alloy. This demonstrates that boron addition significantly reduced the acid corrosion-wear rate of NiAl-2.5Ta-7.5Cr alloy.

2.3.2 Wear Morphology of NiAl-2.5Ta-7.5Cr Alloy [Figure 5: see original paper] presents the worn surface morphologies of NiAl-2.5Ta-7.5Cr alloy in H_2SO_4 medium. The alloy surface clearly reveals the underlying microstructure. Under 10 N + 0.05 m/s conditions, the surface exhibited shallow plowing grooves with numerous pitting cavities and a relatively loose structure ([Figure 5: see original paper]a). As the sliding speed increased to 0.1 m/s, the worn surface became smoother, with plowing features becoming shallower and narrower and pitting characteristics diminishing ([Figure 5: see original paper]b). With the load increased to 45 N, pitting features weakened while plowing features slightly increased, and white wear debris particles appeared ([Figure 5: see original paper]c). When both load and speed increased to 45 N + 0.1 m/s, distinct plowing features were observed with numerous white wear debris particles distributed discontinuously along the grooves ([Figure 5: see original paper]d).

EDS analysis indicated that the white particles consisted of 33.35% O, 16.07% Al, 1.68% Cr, and 48.9% Ni (at.%), likely comprising Al_2O_3, $NiCrO_3$, and NiAl.

For NiAl-2.5Ta-7.5Cr alloy, corrosion accelerates wear due to microstructural inhomogeneity. Corrosion damages the integrity of grain boundaries and phase boundaries, reducing their bonding strength. The corroded material surface becomes porous and loose, making it easily scraped off by the wear counterpart and increasing material loss. This results in a decreased ratio of reaction film formation rate (composed of $NiCrO_3$, Al_2O_3, and $AlH(SO_4)_2$) to sliding speed, causing the film to be sheared more rapidly and increasing the wear rate. Rapid shearing of the reaction film may expose fresh metal substrate, leading to higher friction coefficients as wear proceeds on the fresh metal surface.

Wear accelerates corrosion because wear-induced dislocation concentration, particularly under high loads, generates vacancies through dislocation intersection. The vacancy concentration correlates with plastic deformation magnitude, increasing with applied load. These vacancies disrupt the regular atomic lattice arrangement, causing elastic distortion in the surrounding crystal and increasing the internal energy of the worn surface, thereby reducing corrosion resistance. Consequently, under 45 N loading, more reaction film formed on the alloy surface, which was then plowed off by the counterpart, generating numerous white wear debris particles that subsequently caused additional plowing. This enhanced plowing features and increased material loss. The abundant white debris particles may also transform the wear mechanism from sliding to rolling during reciprocating friction, reducing the friction coefficient while simultaneously causing plowing damage. Therefore, the corrosion-wear behavior of NiAl-2.5Ta-7.5Cr alloy in H_2SO_4 medium is controlled by corrosion-wear and abrasive wear.

2.3.3 Wear Morphology of NiAl-2.5Ta-7.5Cr-1B Alloy [Figure 6: see original paper] shows the worn surface morphologies of NiAl-2.5Ta-7.5Cr-1B alloy in H_2SO_4 solution. Unlike the previous alloy, the worn surface did not reveal the underlying microstructure, indicating that a surface film completely covered the wear track. Under 10 N + 0.05 m/s conditions, the surface was relatively flat and smooth, with white punctate and flake-like substances distributed within the surface film, along with large pitting cavities and blocky spalling features ([Figure 6: see original paper]a). As sliding speed increased to 0.1 m/s, spalling features diminished while plowing grooves appeared and white substances increased ([Figure 6: see original paper]b). With load increased to 45 N, spalling features again weakened, plowing features intensified, and white substances increased further. At 45 N + 0.1 m/s, the worn surface exhibited plastic deformation and deep plowing grooves formed as Si_3N_4 asperities penetrated the surface film, acting as cutting tools that sheared, plowed, or cut the surface. EDS analysis revealed that the white substances likely consisted of TaB, B_2O_3, and Al_2O_3. [Figure 6: see original paper]d shows that these white substances exhibited good ductility under friction forces, firmly adhering to the surface film and helping maintain its complete coverage during sliding wear, completely isolating the alloy from direct contact with Si_3N_4 and creating a film/Si_3N_4 wear condition.

Thus, the corrosion-wear behavior of NiAl-2.5Ta-7.5Cr-1B alloy in H_2SO_4 medium is controlled by corrosion-wear and the protective effect of the intact surface film.

Material loss caused by corrosion-wear is not simply the sum of pure wear and pure corrosion, but is significantly greater than either alone. In 1949, Zelder first proposed the synergistic interaction between corrosion and wear, where corrosion accelerates wear and wear promotes corrosion, thereby accelerating material degradation. Only by controlling either wear or corrosion can the synergistic increment be reduced, substantially decreasing material loss.

NiAl-2.5Ta-7.5Cr-1B alloy readily passivates and forms a film in acid solution. The resulting surface film exhibits good corrosion resistance and effectively inhibits material loss. The white substances within the film demonstrate good plasticity and ductility under friction forces, firmly adhering to the surface film and helping maintain its complete coverage during sliding wear, thereby suppressing corrosion-accelerated wear.

NiAl-2.5Ta-7.5Cr alloy shows slightly poorer corrosion resistance than NiAl-2.5Ta-7.5Cr-1B alloy in acid solution. The corroded surface is porous and loose, easily scraped off by the wear counterpart and increasing material loss, leading to corrosion-accelerated wear. The plowing action of hard oxides such as Si_3N_4 on NiAl-2.5Ta-7.5Cr alloy results in higher wear rates compared to NiAl-2.5Ta-7.5Cr-1B alloy.

In summary, boron addition enhances the passivation tendency, acid corrosion resistance, and acid corrosion-wear resistance of NiAl-2.5Ta-7.5Cr alloy.

Conclusions

1. NiAl-2.5Ta-7.5Cr-1B alloy exhibits superior corrosion resistance compared to NiAl-2.5Ta-7.5Cr alloy, readily forming a passive film with a static corrosion rate of 0.007 mg/($cm^2 \cdot h$), passive current density of 0.299 $A \cdot cm^{-2}$, and free corrosion potential of -0.213 V, demonstrating excellent acid corrosion resistance and stability.
2. In 5% H_2SO_4 solution, the wear rate of NiAl-2.5Ta-7.5Cr-1B alloy was 2–8 times lower than that of NiAl-2.5Ta-7.5Cr alloy because the intact surface film covering the worn surface reduced corrosion-accelerated wear.
3. The corrosion-wear mechanism of NiAl-2.5Ta-7.5Cr alloy is controlled by corrosion-wear and abrasive wear, whereas that of NiAl-7.5Cr-2.5Ta-1B alloy is controlled by corrosion-wear and the protective effect of the intact surface film.

References

1. GUO Jianting, *Ordered Intermetallic Compound NiAl Alloy* (Beijing, Science Press, 2003) p. 75.
2. Noebe R D, Bowman R R, Nathal M V. Physical and mechanical properties of the B2 compound NiAl. *Inter Mater Rev*, 38(4), 193 (1993).
3. Miracle D B. The physical and mechanical properties of NiAl. *Acta Metall Mater*, 41(3), 649 (1993).
4. WANG Zhenshen, GUO Jianting, ZHOU Lanzhan, XIE Yi, SHENG Liyuan, HU Zhuangqi. Investigation of friction and wear behavior of NiAl-based alloys at room temperature. *Chinese Journal of Materials Research*, 23(3), 225 (2009).
5. Mishra S C, Satapathy Alok, Chhaithanya M. Wear characteristics of plasma-sprayed nickel-aluminum composite coatings. *Journal of Reinforced Plastics and Composites*, 28(23), 2931 (2009).
6. WANG Zhenshen, GUO Jianting, ZHOU Lanzhan, SHENG Liyuan, HU Zhuangqi. High temperature wear behavior of NiAl-Cr(Mo)-Ho-Hf eutectic alloy. *Acta Metallurgica Sinica*, 45(3), 297 (2009).
7. WANG Zhenshen, ZHOU Lanzhan, GUO Jianting, HU Zhuangqi. Wear behavior of in situ composite NiAl-Al_2O_3-TiC at high temperature. *Tribology*, 28(6), 497 (2008).
8. WANG Zhenshen, GUO Jianting, ZHOU Lanzhan, ZHANG Guangye, HU Zhuangqi. Friction and wear behavior of NiAl-Cr(Mo)-Cr S self-lubricating composite. *Tribology*, 30(6), 589 (2010).
9. WANG Zhenshen, ZHANG Meng' en, YANG Shuangshuang, GUO Jianting, ZHOU Lanzhan, CHEN Zhigang. Microstructure, mechanical properties, and friction-wear characteristics of NiAl-2.5Ta-7.5Cr-1B alloy. *Acta Metallurgica Sinica*, 49(11), 1325 (2013).
10. WU Haipeng, LI Wenjing, GUO Li, PAN Yanfei, XU Xiufen. Effect of promoter species and precursors on catalytic activity of alkali metal promoted NiAl mixed oxides for N_2O decomposition. *Journal of Fuel Chemistry and Technology*, 39(7), 550 (2011).
11. WANG Fengping, KANG Wanli, JING Hemin. *Electrochemical Fundamentals, Methods and Applications* (Beijing, Chemical Industry Press, 2008) p. 62.
12. LIU Yonghui, ZHANG Peifen. *Principles and Applications of Metal Corrosion* (Beijing, Aviation Industry Press, 1993) pp. 87–88.
13. ZHANG Jingyu, LIU Qingfeng, LIU Qian. Effect of Ti on the corrosion resistance of Zn-Al alloy films. *Acta Metallurgica Sinica*, 49(10), 1168 (2009).

14. JIANG Xiaoxia, LI Shizhuo, LI Shu. *Corrosive Wear of Metals* (First Edition) (Beijing, Chemical Industry Press, 2003) pp. 198–308.

15. LEI Ali, LI Gaohong, FENG Lajun, DONG Nan. Structure and abradability of Cu-Al_2O_3 gradient coatings fabricated by plasma spraying. *Transaction of the China Welding Institution*, 29(5), 65 (2008).

16. Zelder. Corrosion in slurry pipelines. *Corrosion*, 30(8), 285 (1974).

Note: Figure translations are in progress. See original paper for figures.