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# Coating of metals with intermetallics by mechanical alloying

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## **1. Introduction**

The available experimental data show that aluminide phases of the Ni–Al system can be used as a protective coating for industrial alloys because the Ni–Al intermetallic compounds offer a combination of good oxidation resistance and useful mechanical properties at high temperatures [\[1–3\]. T](#page-2-0)he Ni–Al coatings can be especially attractive for the low-melting point alloys such as Al alloys. However, there are some difficulties in fabricating intermetallic coatings on the Al alloys using conventional coating techniques because of considerable differences in the physical properties of the substrate and aluminide phases such as their melting points, bonding properties, and low deposition rates. One of the new methods that could be effectively used for fabrication aluminide coatings is mechanical alloying (MA)[\[4–7\]. I](#page-2-0)n present paper, the formation of the Ni–Al intermetallic coatings on the Al alloy by MA method was studied.

# **2. Experimental details**

In the present experiments, the duralumin plates of dimensions  $2$  mm  $\times$  20 mm  $\times$  15 mm were used as substrates. The hardness of the substrate was 55 HV. The Ni (99.9%, <50  $\mu$ m) and Al (99.7%,  $<$ 50  $\mu$ m) powders were used as raw materials for MA deposition. The Ni and Al powders were mixed at the composition of Ni—50 at.% Al and Ni—25 at.% Al. The MA was carried out in a planetary ball mill AGO-2U with water-cooling. Steel balls with a diameter of 6 mm

## ABSTRACT

The Ni–Al coatings were fabricated on the duralumin substrate by mechanical alloying method. The NiAl and Ni<sub>3</sub>Al aluminide phases could be directly formed during mechanical milling as a result of reaction between Ni and Al. The phase composition of the coatings could be optimized by the combinations of key factors such as milling intensity, milling duration, the composition of the powder mixture and subsequent annealing treatment. The hardness of the coating on the substrate was more than ten times that of the initial duralumin substrate.

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weighing 100 g were used for the coating deposition. The weight of the powder mixture for all cases was 10 g. The coatings were fabricated at two rotation speeds of vial: 620 and 840 rpm, termed low intensity and high intensity process, respectively. No process control agent was added to these powders. The temperature inside the chamber was about 150–200 $\degree$ C at rotation speed of 620 rpm and 400–450 $\degree$ C at rotation speed of 840 rpm [\[8\].](#page-2-0) After that, assynthesized samples were annealed in Ar atmosphere at 550 ◦C and were then cooled in the furnace. In all cases, the annealing time was 2 h.

The phase composition of the coatings was characterized by Xray diffraction (XRD) analysis using a Dron diffractometer with the Cu K $\alpha$  radiation. The weight fractions of the phases were calculated from the intensities of the diffraction peaks with an accuracy  $\pm 5\%$ . The cross-sectional microstuctures of the coatings were observed by using a Hitachi TM 1000 scanning electron microscope (SEM). Microhardness measurements were carried out using an automated load HVS-1000 hardness testing machine at a load of 100 g and a dwell time of 10 s. Ten measurements were taken for each sample and the average value obtained.

## **3. Results and discussion**

During mechanical milling, the substrate surface was subjected to high-energy ball impacts. The powder particles trapped between the ball and substrate became cold-welded to the substrate surface. It was found that the Ni–Al intermetallic compounds could be form on the surface as a result of the reaction between Ni and Al during mechanical activation process.

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Fig. 1. X-ray diffraction of the coating fabricated from Ni-25 at.% Al powder mixture.

Fig. 1 shows the XRD patents of the coating fabricated from the Ni—25 at.% Al powder mixture. The phase composition and the volume fraction of the aluminide phases may be directly associated with the power involved in the milling process and the milling duration. During the low intensity process at the rotation speed of 620 rpm, NiAl (around 20 wt.%) and Ni<sub>3</sub>Al (around 15 wt.%) were formed after 60 and 120 min of milling. Milling for 120 min at the rotation speed of 840 rpm increased the volume fraction of the NiAl phase up to 35 wt.% and decreased the volume fraction of the Ni3Al phase up to 5 wt.%. The subsequent annealing treatment of the coating fabricated at the rotation speed of 840 rpm at 550 ◦C resulted in the formation of around 95 wt.% Ni<sub>3</sub>Al and 5 wt.% NiAl. After annealing of the coating fabricated at the rotation speed of 620 rpm at 550 $\degree$ C, the main phase was NiAl (around 60 wt.%), only  $40$  wt.% of Ni<sub>3</sub>Al was formed. The differences in the phase composition could be attributed to the different defect structure that formed under the ball collisions and the different level of the strains that was introduced into the materials. The temperature inside the chamber at the rotation speed of 840 rpm was almost twice that at 620 rpm. On the one hand, the higher temperature increased mobil-



**Fig. 2.** X-ray diffraction of the coating fabricated from Ni—50 at.% Al powder mixture.

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Fig. 3. The Ni-Al coating fabricated by MA method: (a) and (b) Ni<sub>3</sub>Al coating, cross-sectional microhardness of NiAl coating.

#### **Table 1**

Microhardness of Ni3Al and NiAl intermetallic coating fabricated on duralumin substrate by MA and subsequent annealing at 550 ◦C.



ity of the atoms; on the other hand the high temperature decreased the defect density and led to strain relaxation. It is likely that these factors strongly influence the atom distribution during mechanical alloying. The local distribution of the atoms had a great effect on the further reaction between Ni and Al, and order of the phase transformation.

It is interesting to note that when the Ni—50 at.% Al powder mixture was used for deposition of the coatings, only formation of the NiAl phase was observed. [Fig. 2](#page-1-0) shows the example of the XRD spectra of as-fabricated coatings. The phase composition of as-fabricated coatings was around 90 wt.% of NiAl and 10 wt.% of Ni. The annealing treatment at 550 ℃ did not change strongly the phase composition. The coating was stable. These results suggest that the NiAl intermetallic coating can be directly fabricated during mechanical alloying without annealing treatment.

Fig. 3a and b shows the examples of the cross-sectional microstructure of the Ni aluminide coatings fabricated by MA method and subsequent annealing treatment. The thickness of the coating was around 100–150  $\mu$ m. The coatings were rather dense and uniform. Fig. 3c shows the cross-sectional microhardness of the coatings and substrate. The microhardness of the coatings is listed in Table 1. The hardness of the duralumin substrate coated with the Ni–Al compounds increased dramatically. The hardness of the coating on the substrate was more than ten times that of the initial substrate.

#### **4. Conclusions**

The Ni–Al coatings were fabricated on the duralumin substrate by mechanichal alloying method. The NiAl and  $Ni<sub>3</sub>Al$ aluminide phases could be directly formed during mechanical milling as a result of reaction between Ni and Al. The phase composition of the coatings could be optimized by the combinations of key factors such as milling intensity, milling duration, the composition of the powder mixture and subsequent annealing treatment. The hardness of the coating on the substrate was more than ten times that of the initial duralumin substrate.

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#### **References**

- [1] C. Sierra, A.J. Vázquez, Surf. Coat. Technol. 200 (2006) 4383–4388.
- [2] G. Prévot, D. Schmausa, S. Le Moal, Surf. Sci. 604 (2010) 77–770.
- [3] Hongbo Guo, Yongjing Cuia, Hui Penga, Shengkai Gonga, Corrosion 52 (2010) 1440–1446.
- [4] S. Romankov, Y. Hayasaka, G. Kalikova, S.V. Komarov, N. Hayashi, E. Kasai, Surf. Coat. Technol. 203 (2009) 1879–1884.
- [5] S. Romankov, S. Kaloshkin, Y. Hayasaka, N. Hayashi, E. Kasai, S.V. Komarov, J. Alloys Compd. 484 (2009) 665–673.
- [6] S.V. Komarov, S. Romankov, N. Hayashi, E. Kasai, Surf. Coat. Technol. 204 (2010) 2215–2222.
- [7] S. Romankov, S.V. Komarov, N. Hayashi, S. Ueno, S. Kaloshkin, E. Kasai, Surf. Coat. Technol. 202 (2008) 4285–4290.
- [8] A.V. Tikhomirov, A.A. Aksenov, E.V. Shelekhov, S.D. Kaloshkin, V.Yu. Zadorozhnyi, Yu.A. Skakov, G.S. Milovzorov, Russian J. Non-Ferrous Met. 49 (3) (2008) 193–203.