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Peculiarities of the Mo/NiAl Interface Formed by SHS

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Abstract

This paper describes the possibility of welding (joining) the Mo substrate with NiAl intermetallic compound by the method of self-propagating high-temperature synthesis (SHS) without melting the Mo substrate. It was found that an intermediate layer is formed between the Mo substrate and the intermetallic welding, the main component of which is a cellular rod-like pseudobinary NiAl–Mo eutectic consisting of branched Mo threads with a 200 nm thickness and a NiAl matrix. The Mo dissolution in the Ni–Al melt, which resulted from the SHS reaction, was carried out by free transition of Mo atoms from the substrate surface to the liquid phase with subsequent diffusion and convective transfer from the interface to the melt volume. The Mo transfer to the melt volume proceeded relatively slowly, and during crystallization the hypoeutectic composition near the Mo substrate (up to 14 at. % Mo) was formed, and therefore, in the transition region both pseudobinary NiAl–Mo eutectic and nuclei of Mo-dendrites could be present.

Keywords

SHS, intermetallic compounds, NiAl, coating, mechanic activation treatment, pseudobinary NiAl–Mo eutectic

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Introduction

Due to the unique combination of high temperature strength, heat resistance, thermal conductivity and corrosion resistance, Ni–Al intermetallic compounds are widely used in the automotive industry, aerospace technology and power engineering. These materials are also known for their low plasticity and their tendency to brittle fracture, therefore, alloying additives are introduced into their composition to increase the strength properties [1–3]. High-melting metals W, Mo, and Ta are used for alloying Ni–Al-based intermetallic alloys, both with the aim of creating solid solutions and forming secondary phases. Such alloys have limiting values of plastic flow close to the materials traditionally used in turbine blades. The refractory metal Mo proved well in the form of an alloying additive that increases the temperature stability of multicomponent Ni-based superalloys [4]. At the same time, not only plasticity significantly increases, but also the crack resistance of the material improves [5]. At high temperatures (but

not in an oxidizing atmosphere), the strength of molybdenum exceeds the strength of most other metals.

Nickel aluminides are characterized by low ductility at room temperature and have a relatively low transition temperature from brittle to ductile state, about 200–400 °C [6, 7]. At relatively low temperatures NiAl has metal-like properties comparable with ceramics, which remain brittle even at temperatures around the melting point, and with compounds such as MoSi₂, which change from brittle to plastic at about 1300 °C [8].

The use of reinforcing fibers from W, Mo and Al₂O₃ in NiAl increases the plastic flow stress of NiAl by transferring the effective load from the matrix to the fibers [9]. Strong interfacial contact leads to an increase in high-temperature strength, but reduces low-temperature viscosity. It is also known that the eutectic NiAl–Mo alloy is stable during long-term annealing at 1400 °C, and the Mo fibers undergo minimal changes [10].

According to [11], Mo has a rather high solubility in both Ni and Al (up to 20 at. %). In [12, 13], the possibility of obtaining various intermetallic compounds in the Al–Mo system as a result of mechanical activation treatment of pure Al and Mo metal powders followed by heat treatment at 400–700 °C was described.

The creation of intermetallic Ni–Al-based coatings and welding on the surface of parts and products made of refractory metals is of great interest [14–16]. This task can be accomplished in the process of self-propagating high-temperature synthesis (SHS) from reaction mixtures of powders of metals Ni and Al [17]. Producing such materials by the SHS method has an advantage over traditional metallurgical technologies due to the use of the energy of a chemical reaction. The creation of coatings and surfacing on the basis of the NiAl intermetallic compound on the surface of molybdenum products in the SHS process is of great practical interest. It was shown that (NiAl) and NiAl–Mo make it possible to form coatings by the method of electro-spark alloying (ESA) [18]. NiAl–Mo-based alloys and coatings have high wear resistance in friction units, slip friction resistance on metal, with and without lubrication, and are used in the engineering industry as self-adhesive materials for friction clutches, machine elements, slip and abrasive wear, and also in the aviation industry.

The analysis of the literature has shown a limited amount of experimental work on the formation and structure of the transition zone between nickel aluminides and molybdenum substrates (products). The application of the SHS method is quite convenient and simple and allows a Ni–Al melt to be created during the highly exothermic chemical reaction, which interacts with Mo in a short reaction time and the melt crystallization. At the same time, the temperature of the SHS reaction products is much lower than the Mo melting point ($T_m = 2623$ °C).

In this work, we studied the interaction of a Mo substrate with a Ni–Al-based melt formed in the course of SHS, with special attention paid to the transition zone of intermetallic molybdenum.

Methods

For the experiments, Mo metal substrates (Alfa Aesar, purity 99.95 wt. %) in the form of cylinders of 6.35 mm (diameter) \times 6.35 mm (height) (Fig. 1a) weighing 2.0 g and Ni powders (Alfa Aesar, purity 99.9 wt.%, 3–7 microns) and Al (Alfa Aesar, purity 99.5 wt.%, <44 microns) were used. To prepare the reaction mixture, Ni and Al powders were mixed in a ratio (Ni + Al) – 50 \times 50 wt. %. The reaction mixture of powders together with

molybdenum cylinders was subject to mechanical activation (MA) treatment in a Fritsch Pulverizette-7 planetary mill. The MA treatment was carried out for 30 minutes (500 rpm, BPR = 15, 10 carbide balls with a diameter of 10 mm) for 4 g of reaction powders and 5 pieces of Mo cylinders in one atmosphere of air. Heat treatment (HT) of cylindrical substrates coated in the Ar (1 atm) was carried out at a temperature of (650 \pm 20) °C for 10 minutes.

The SHS experiments were carried out on special samples: Mo cylinders coated with an MA (Ni+Al) coating were pressed at a pressure of $P = 3$ Bar into a powder mixture (Ni+Al) – 50 \times 50 wt. % in the form of a tablet with a diameter of 20 mm and a height of 10 mm. The SHS experiments were carried out in air; the initiation of combustion was carried out using an electrically heated graphite tape.

The X-ray phase analysis was performed on a DRON-3M diffractometer with CuK_α radiation. The study of transverse thin sections was carried out on a Zeiss Ultra Plus ultra-high-resolution auto-emission scanning electron microscope with INCA 350 Oxford Instruments X-ray microanalysis unit.

Experimental

Mechanical activation and heat treatment

To apply coatings, Mo substrates in the form of cylinders were used. The appearance of the initial Mo substrates and after MA is shown in Fig. 1a, b. As a result of the MA treatment, a coating was formed on the Mo surface of the substrates from a mixture of reaction powders Ni and Al. The geometric dimensions of the samples after MA increased, the average coating thickness was 135 μm . The weight of the samples increased on average by 73 mg (3.75 %). The X-ray phase analysis of the processed MA substrates showed that the formed coatings on the surface of the substrates contained only the initial metals Ni and Al, the formation of intermetallic compounds in the coatings was not detected (Fig. 2a).

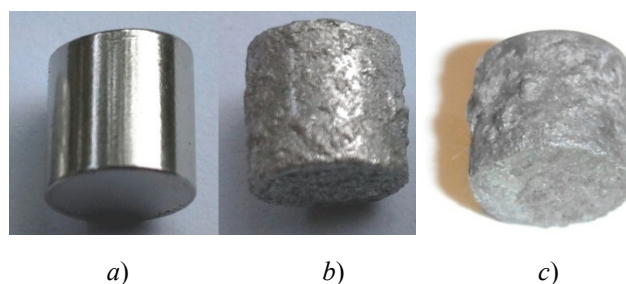
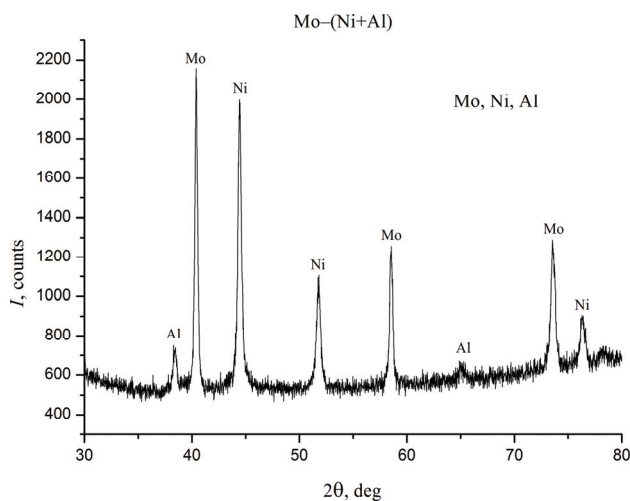
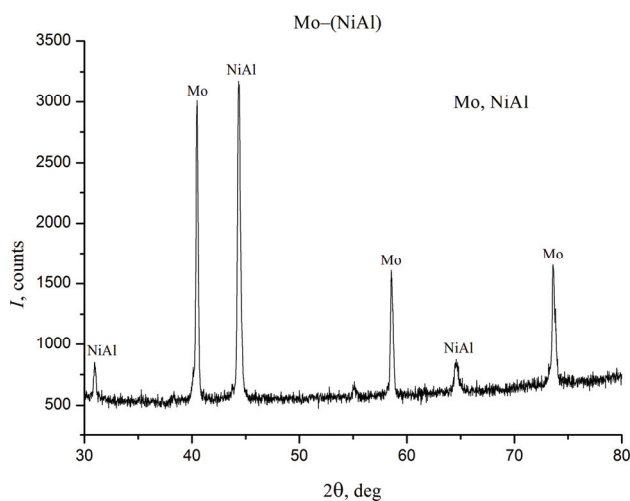


Fig. 1. The appearance of the samples:
a – the initial Mo substrate; b – Mo substrate after the MA;
c – Mo substrate after the HT



a)



b)

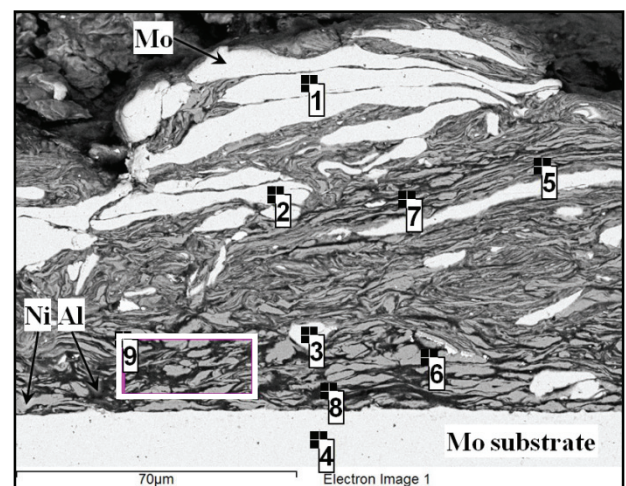
Fig 2. Radiographs from the surface of cylindrical substrates after MA (a) and after HT (b)

The study of the microstructure of the sample surface after the MA showed that the coating did not completely cover the substrate. It can be seen that the surface of the substrates in the uncoated zones was severely deformed as a result of the impact of the balls during the MA. This is a consequence of the fact that, as a result of the MA, not only the metal layer hardened, but also its destruction with removal of coating fragments occurred, thus leading to the formation of inhomogeneities and defects of the Mo surface of the substrate.

The applied coatings have an uneven, discontinuous, strongly developed relief layer with a thickness of 20 to 200 μm , having a laminate structure (Fig. 3), which is typical of powders subject to mechanical activation treatment [19]. The deposited

coatings also contain a large number of Mo particles of elongated shape with a size of up to 100 μm , which were separated from the substrates during the MA process. The energy dispersive analysis showed that Al particles contain up to 10 at. % oxygen, which is associated with the oxidation process in the process of MA, as the process was carried out in an atmosphere of air.

The conditions of heat treatment of samples with coatings deposited during the MA process were chosen taking into account the melting point of Al, at which the interaction between the reaction components of the coating occurs [20]. The heat treatment did not lead to noticeable changes in the shape, mass, and size of the samples (Fig. 1c). The X-ray phase analysis from the surface of heat-treated samples (Fig. 1b) showed that the NiAl intermetallic phase was formed in the



a)

Points	Mo	Ni	Al	O
1	97.9	0	2.1	
2	96.0	1.7	2.3	
3	94.9	3.2	1.9	0
4	96.1	1.5	2.4	
5		92.2	2.4	5.4
6		96.6	3.2	0.2
7	0	19.0	72.1	8.9
8		5.6	84.2	10.2
9		34.8	59.1	6.1

b)

Fig. 3. SEM of the transition zone of the coating on the samples after MA treatment (a) and the results of energy-dispersive analysis (b), at. %

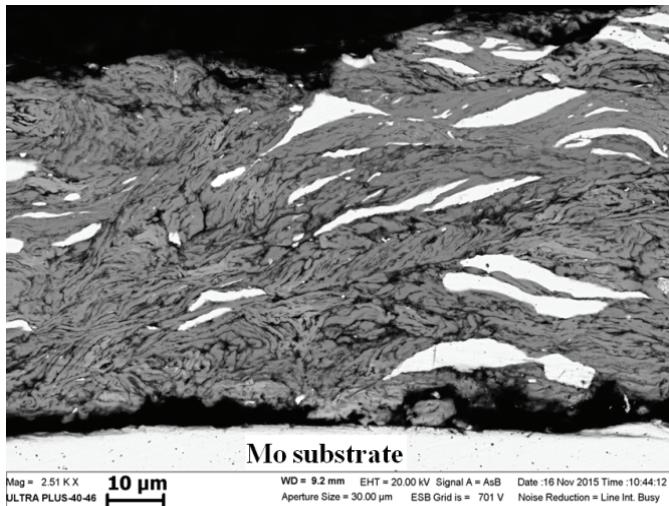


Fig. 4. SEM of transition zone coatings on the samples after HT

coating, and the metals Ni and Al were completely absent, which indicated the completeness of the chemical reaction (Ni+Al), (Fig. 2b). In the study of the microstructure of cross sections of heat-treated samples, partial exfoliation of the coating from the Mo surface of the substrates was found (Fig. 4). Most likely, this was due to a significant difference in the coefficients of thermal expansion of the Mo substrate and of the Ni-Al-based coating.

Mechanical Activation + SHS

Mo substrates with a mechanically activated (Ni+Al)-based coating were pressed into the reaction mixture of Ni and Al powders (50/50 wt.) in the form of a tablet with a diameter of 20 mm and a height of 10 mm at a pressing pressure of 3 tons. The resulting sample was pressed from above with a 4.5 kg punch. The SHS reaction was initiated with graphite tape in air. The appearance of the burnt sample is shown in Fig. 5a. To study the microstructure of the Mo/(Ni-Al) transition zone, a transverse section of the sample was fabricated (Fig. 5b).

During the SHS process, the Mo substrate did not undergo any noticeable changes in shape and size. The surfacing was a porous material based on the Ni₃Al and NiAl intermetallic phases, also containing oxide inclusions. At a distance of about 1 mm from the Mo substrate, there was about 4 at. % Mo. The intermediate layer, which was previously deposited on the Mo cylinder during mechanical activation (MA), after the SHS reaction, formed a denser non-porous layer than the main surfacing (Fig. 6a). The intermediate layer (Fig. 6b) consisted of

non-stoichiometric composition of nickel aluminide intermetallic grains elongated along the “substrate-surfacing” grain surface. Between the intermetallic grains there were aluminum oxide layers. Large Mo particles in the intermediate layer did not undergo changes in shape and size. Smaller Mo particles changed noticeably due to Mo diffusion from the surface of the particles into the intermetallic welding (Fig. 7). Figure 7a shows the precipitation of Mo precipitates between the NiAl grains. Recrystallized Mo particles were found on the Mo surface of the particles and inside the NiAl grains, as well as layers of oxides (Fig. 7b).

Mo dissolution in the Ni-Al melt, which was formed as a result of the SHS reaction, was carried out by free transition of Mo atoms from the substrate surface to the liquid phase with subsequent diffusion and convective transfer from the interface to the melt volume. It should be noted that the combustion temperature during the SHS reaction in the Ni-Al system was about 163 °C, which was much lower than the melting point of molybdenum ($T_m = 2623$ °C). Mo transfer to the volume of the melt proceeded relatively slowly, and during crystallization hypoeutectic composition near the Mo substrate (up to 14 at. % Mo) was formed, the therefore, in the transition region both pseudobinary NiAl-Mo eutectic and Mo-dendrite nuclei may be present. The equilibrium temperature of the pseudobinary system $L \leftrightarrow NiAl (\beta) + Mo(\alpha)$ was (1600 ± 7) °C, the eutectic point was 10 at. % Mo, the maximum solubility of Mo in the NiAl phase was less than 4 at. %.

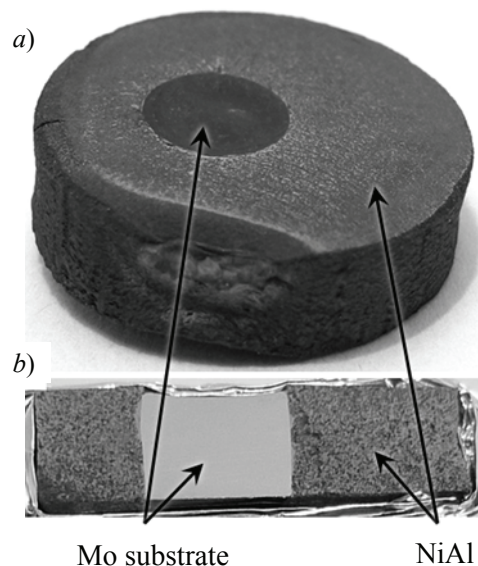


Fig. 5. The appearance of the sample after SHS (a) and its cross section (b)

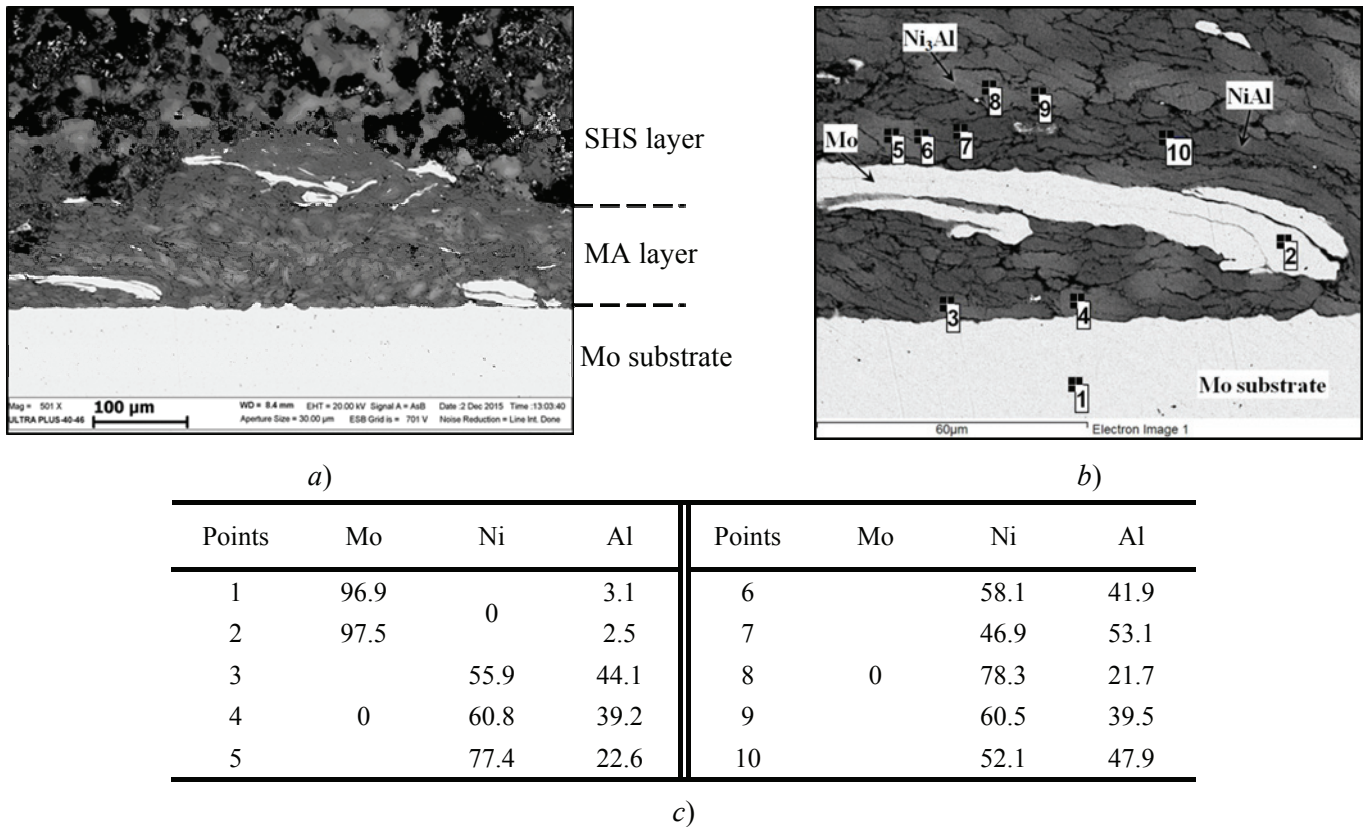


Fig. 6. SEM of transition zone of the coating on samples after SHS:
a – dense non-porous layer; *b* – intermediate layer; *c* – the result of energy dispersive analysis, at. %

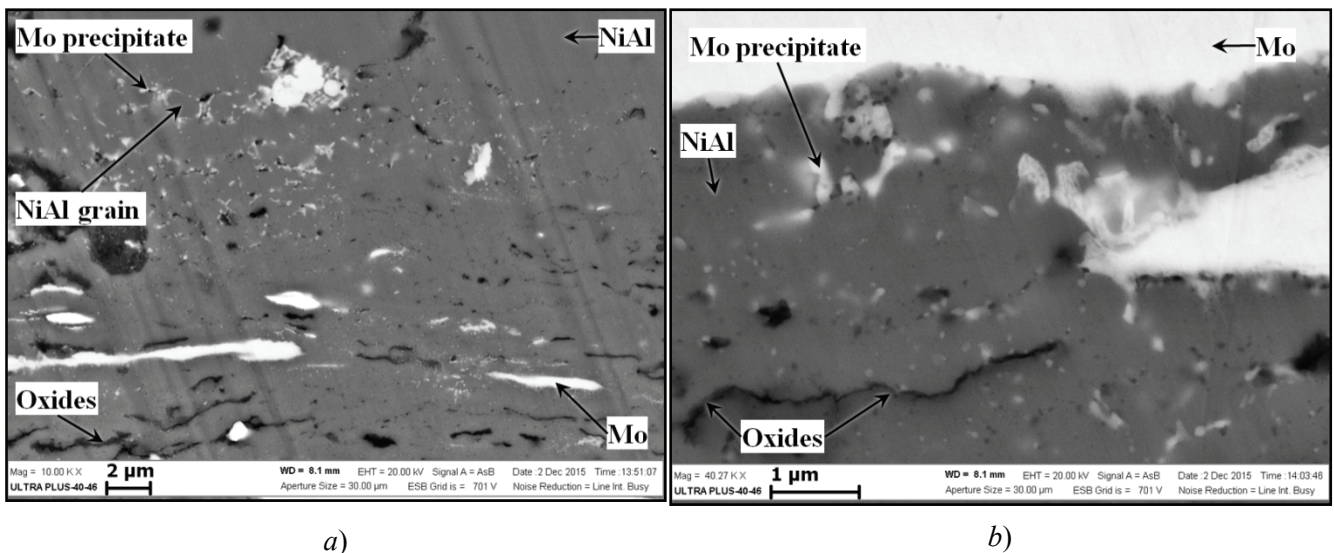


Fig. 7. SEM of transition zone of the coating on samples after SHS:
a – the precipitation of Mo between the NiAl grains; *b* – oxide layers

Conclusion

The possibility of applying reactive Ni–Al-based coatings on the surface of Mo substrate using mechanical activation, and their use to create intermetallic coatings on the molybdenum surface in the course of SHS has been shown.

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