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PROCESSING, MICROSTRUCTURE AND PROPERTIES OF LAMINATED NI-INTERMETALLIC COMPOSITES SYNTHESISED USING NI SHEETS AND Al FOILS

WYTWARZANIE, STRUKTURA ORAZ WŁASNOŚCI KOMPOZYTU WARSTWOWEGO Ni-FAZY MIĘDZYMETALICZNE UZYSKANEGO Z BLACHY NIKLOWEJ I FOLII ALUMINIOWEJ

The laminated Ni-(NiAl₃+Ni₂Al₃) and Ni-Ni₂Al₃ intermetallic composites were fabricated by reaction synthesis in vacuum using Ni sheets and Al foils. The aluminium layers were completely consumed due to the formation of intermetallic phases. The Ni-Al reaction at 620°C was studied by interrupting in steps the reaction process to observe the microstructural changes. The final microstructure consisted of alternating layers of intermetallic phases and unreacted nickel can be designed easily because the stable structures of the composites depend only on the treating time. Microstructural examinations using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray microprobe analysis (EDX) demonstrated that after 1h of treatment Ni₂Al₃ is the predominant intermetallic phase. The formation of the Ni₂Al₃ phase is thermodynamically favoured over the formation of the other phases and can be understood from the steps occurred through a series of solid state reactions. The tensile strength of the laminated composites increases with an increase of the volume fraction of the intermetallic products. However, it decreases after long heat treatment because the Ni₂Al₃/Ni₂Al₃ interfaces can very easily delaminate due to a very weak bonding caused by continuous Al₂O₃ inclusions. Observations show that the laminated composites exhibit a mixture of brittle fracture of intermetallics and ductile one of residual Ni layers.

Keywords: multilayer composite, microstructure, nickel aluminides, mechanical properties

Używając blachy niklowej i folii aluminiowej wytworzono kompozyty warstwowe Ni-(NiAl₃+Ni₂Al₃) oraz Ni-Ni₂Al₃. W wyniku reakcji syntezy zachodzących w temperaturze 620°C warstwy aluminium kompletnie przereagowały z częścią niklu i utworzyły fazy międzymetaliczne. Badano przebieg reakcji pomiędzy niklem i aluminium w temperaturze 620°C przerywając zachodzące reakcje i obserwując zmiany mikrostruktur. Stwierdzono, iż można łatwo sterować zmianami strukturalnymi wielowarstwowego kompozytu, gdyż zależą one jedynie od czasu wygrzewania. Badania z wykorzystaniem mikroskopu skaningowego, dyfraktometru oraz z zastosowaniem mikroanalizatora rentgenowskiego wykazały, że po 1 godzinie wygrzewania w 620°C dominującą fazą jest Ni₂Al₃, gdyż ma ona najniższą energię formowania w tej temperaturze. Wytrzymałość na rozciąganie kompozytów warstwowych Ni-fazy międzymetaliczne wzrasta wraz z czasem wygrzewania, a co za tym idzie, wraz ze wzrostem objętości faz międzymetalicznych. Jednak gdy czas wygrzewania jest dłuższy niż 2 godziny wytrzymałość na rozciąganie kompozytów zaczyna spadać. Spowodowane jest to występowaniem Al₂O₃ na styku uformowanych warstw Ni₂Al₃/Ni₂Al₃ i ich łatwą delaminacją. Obserwacje mikroskopowe wykazały, że przełom kompozytów warstwowych charakteryzuje się mieszanym charakterem, częściowo kruchym (dla faz międzymetalicznych) i częściowo ciągliwym (dla warstw niklu).

1. Introduction

Metal-intermetallic laminated (MIL) composites embody and exploit the concept of synthetic multifunctional materials. They offer an attractive combination of properties distinct from the separate constituent phases, including: high-temperature strength, room-temperature toughness and thermal stability. They also have the po-

tential to perform various functions, such as thermal management, ballistic protection, blast mitigation, heat exchange and vibration damping [1]. Among laminate composites, the Ti6Al4V-Al₃Ti laminate has a great technological advantage and attracts special attention for aerospace applications [2]. Instead Ni-Al-based laminate composites (especially Ni-NiAl and Ni-Ni₃Al) have high potential for substituting Ni-based superalloys and are

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considered as good candidate materials for high temperature structural and armour applications [3]. MIL composites can be produced by magnetron sputtering [4], electron beam evaporation [5], and vacuum plasma spraying [6]. In the last years a new technique, interlayer *in-situ* reaction process (called also reaction sintering [7] or reaction synthesis [3]), has been developed. In the method regularly distributed intermetallic layers are formed through reaction between alternatively laminated metal sheets at high temperature. The process is continued till one of the metals is fully consumed in the course of reaction. This technique involves relatively simple processing and the size and shape of the component that can be produced are not limited. In the way of the intermetallic phases synthesis Ti-intermetallics [1, 8], Fe-intermetallics [9], Mg-intermetallics [10], Nb-intermetallics [11], Cu-intermetallics [12, 13] and Ni-intermetallics [3, 7, 14] laminated composites have been processed. In the present study, this procedure was used to fabricate laminated Ni-(Ni₂Al₃+NiAl₃) and Ni-Ni₂Al₃ composites. The uniformly distributed intermetallic layers were formed through a high temperature reaction between the alternatively laminated Ni sheets and Al foils. The progress in the synthesis process with a prolonged time of reaction between the elemental

components was investigated. Hardness tests and tensile strength measurements were performed on the materials with different microstructures to establish the preliminary properties of the composites.

2. Experimental procedure

In the experiment, 600 μm thick sheets of nickel (99.57 at. % Ni, 0.11 at. % Cu, 0.09 at. % Co, 0.08 at. % Si, 0.07 at. % Mg, 0.07 at. % Fe, 0.01 at. % Al) and 150 μm thick foils of aluminium (99.53 at. % Al, 0.21 at. % Fe, 0.16 at. % Si, 0.05 at. % Zn, 0.03 at. % Cu, 0.02 at. % Ti) were used to fabricate laminated nickel-intermetallic composites. Nickel sheets and aluminium foils were cut into 50×10 mm rectangular pieces. Nickel sheets were ground with 800-grit abrasive paper. No special surface preparation treatment was applied to the aluminium foils prior to processing. Therefore, there were continuous Al₂O₃ films on the aluminium foils. Any contamination on the surface of sheets and foils was cleaned using water and then ethanol. After drying rapidly, they were laminated alternatively into nickel/aluminium multilayer samples (6 Ni and 5 Al layers) and then treated in a specially constructed furnace (Fig. 1).

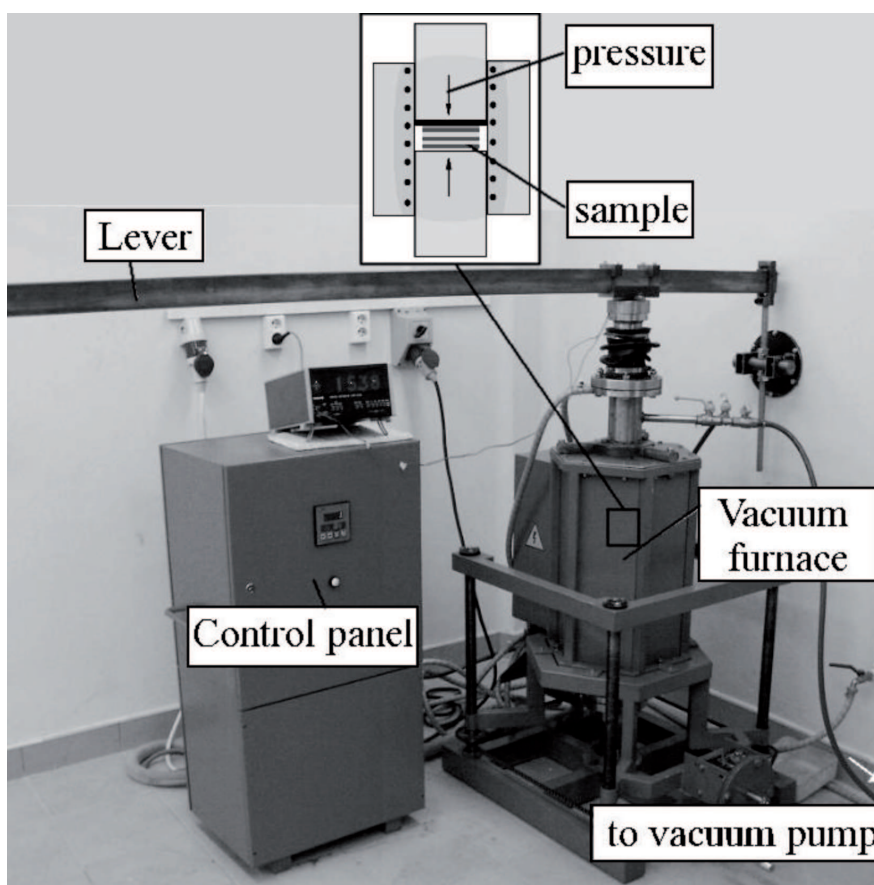


Fig. 1. Equipment used in the present study

A pressure of 5 MPa was applied at room temperature to ensure good contact between the metals. The temperature was raised to 620°C at a heating rate of 0.25°C/s. The samples were heated in vacuum (0,01 Pa) at 620°C for different treating time (0.17, 0.33, 0.5, 1, 2, 5, 10, 20, 50 h) under a uniaxial pressure of 1 MPa for the reaction synthesis and then furnace-cooled naturally to room temperature. In order to perform the observations of the reaction zone, the specimens were cut, mounted in a cold setting resin, initially mechanically ground with a grade 120-800 abrasive papers and finally polished using 1 μm diamond suspension. Microstructural observations were performed using a JEOL JMS-5400 scanning electron microscope (SEM) and a Carl Zeiss NEOPHOT 2 optical microscope. Before the samples were examined with the optical microscope they had been etched using an aqueous HF solution (5%)

to reveal the structure of the intermetallic layers. The chemical analysis was performed using EDX spectrometer (Oxford Instruments ISIS-300). Composition of the phases was determined by comparing the results of the microprobe analysis with the data in the binary Al-Ni phase diagram (Fig. 2).

In addition, an X-ray diffraction using a D/max RAPID2 diffractometer was employed to identify the intermetallic phases. Vickers measurements were performed by Hanemann microhardness tester mounted on NEOPHOT 2 microscope under load of 0.637 N for 15 s. Samples with dimensions of 50 mm \times 8 mm \times 4 mm, made from fabricated composites, were subjected to tension test on an INSTRON screw machine at a constant crosshead speed of 0.1 mm/min, corresponding to an initial strain rate of $1.68 \cdot 10^{-3}$ 1/s.

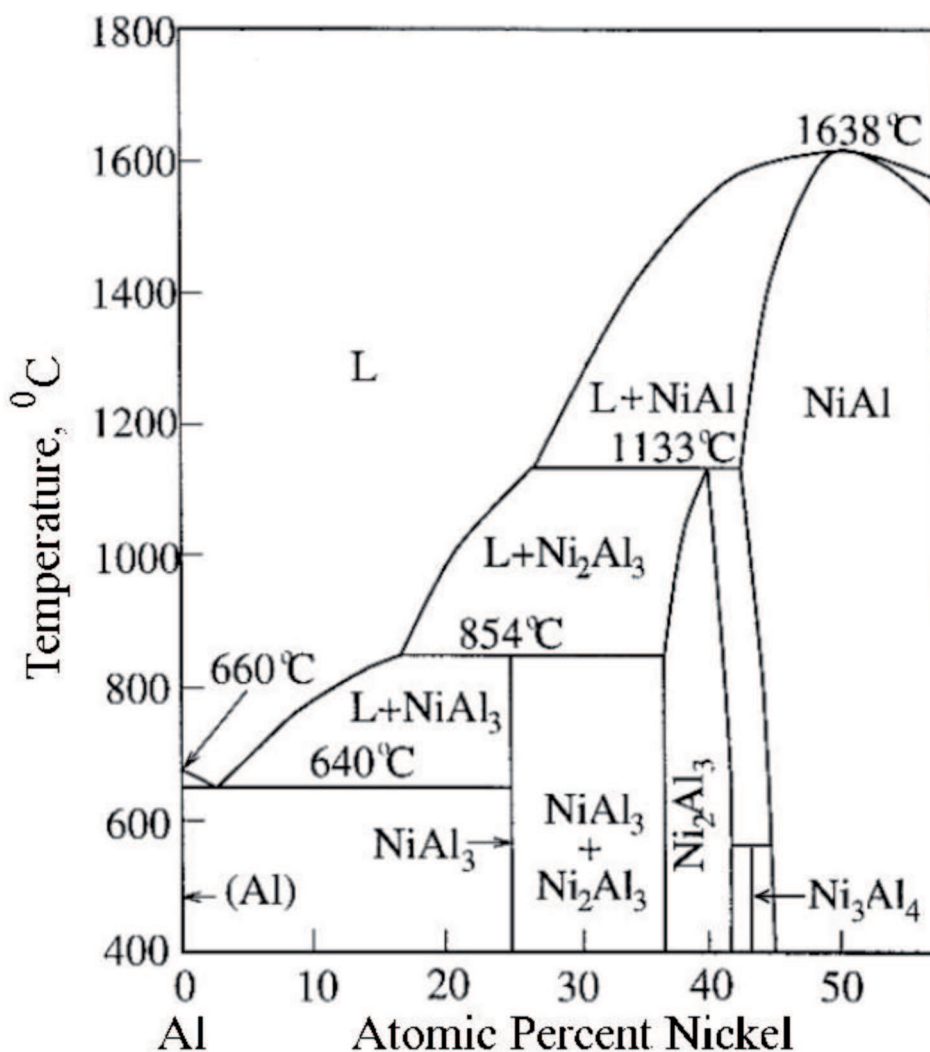


Fig. 2. Part of the Al-Ni binary phase diagram [15]

3. Results and discussion

Reaction synthesis between Ni sheets and Al foils under pressure resulted in a well-bonded, laminated composite microstructure with nickel layers sandwiched between intermetallics layers (Fig. 3).

An identification of the chemical compositions of the phases synthesised at the reaction zone was determined by SEM-EDX analysis. In principle, according

to binary Al-Ni phase diagram [16], six intermetallic phases could be produced during the reaction: NiAl_3 , Ni_2Al_3 , Ni_3Al_4 , NiAl , Ni_5Al_3 and Ni_3Al . Since it is obvious that temperature and annealing time are important factors for the formation of different intermetallics, the samples were heated at 620°C for 0.17, 0.33, 0.5, 1, 2, 5, 10, 20 and 50 hours. Figure 4 shows typical microstructures of the intermetallic layer of the samples held at a temperature of 620°C for 1 and 50 hours.

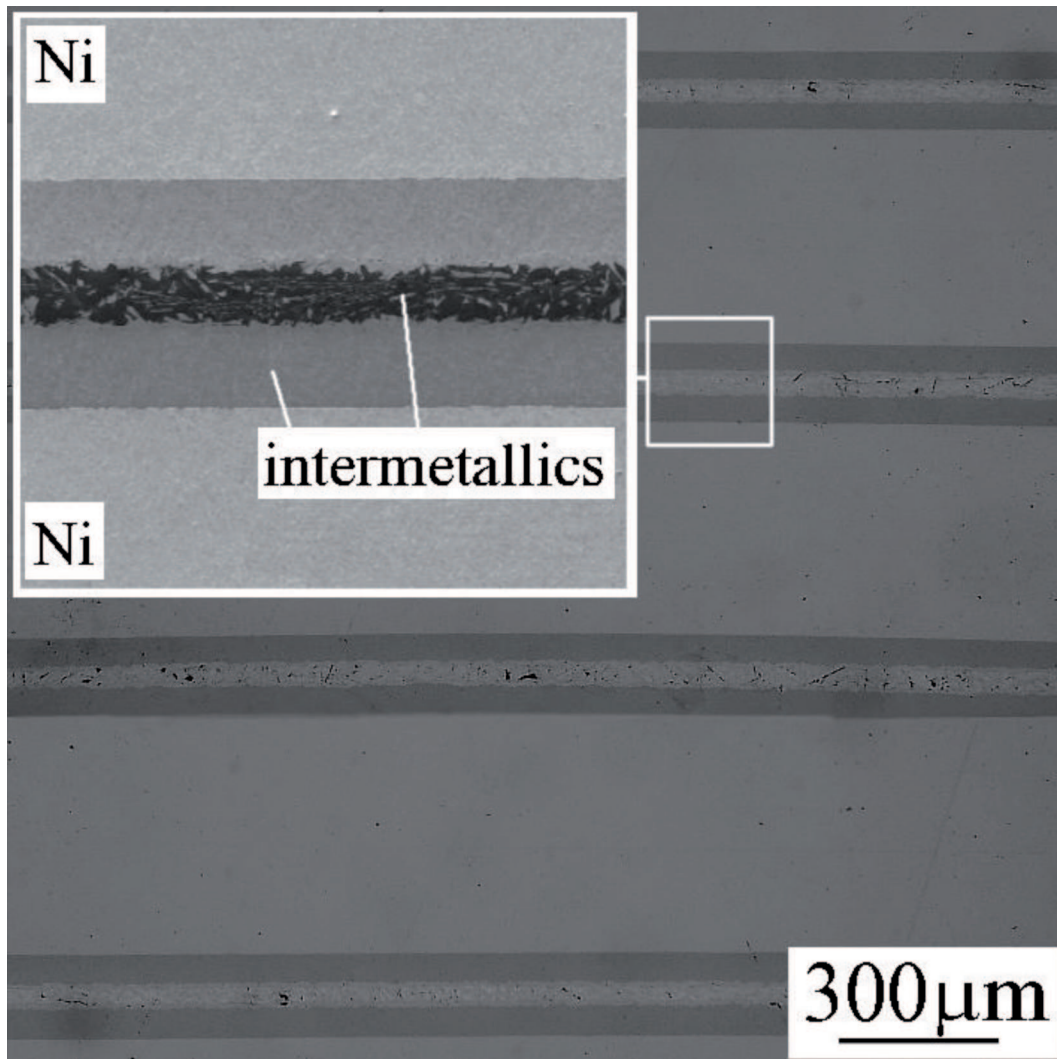


Fig. 3. Microstructure of the Ni-intermetallics laminated composite formed at 620°C for 1 h

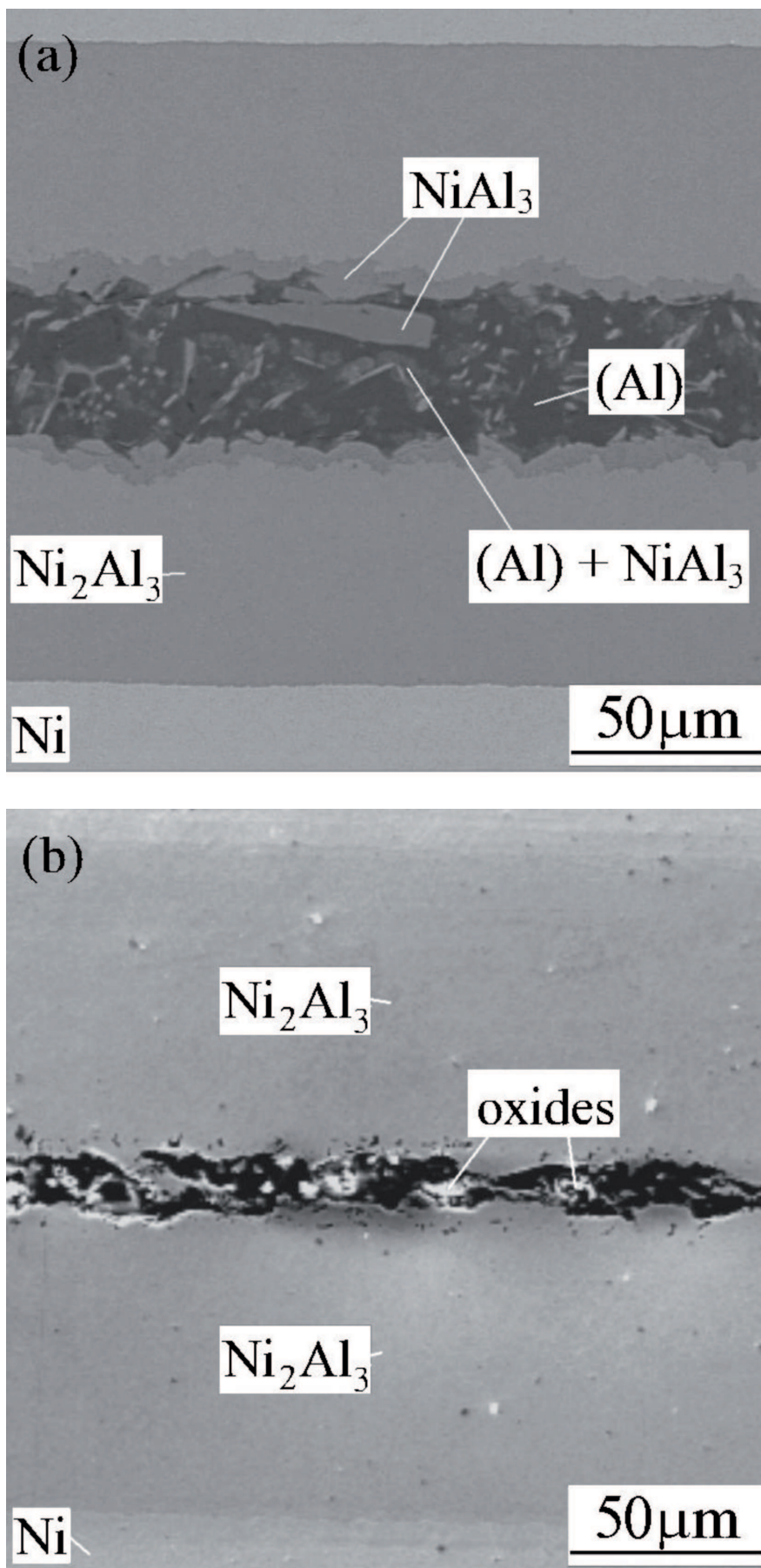


Fig. 4. Microstructure of the intermetallic layer formed after treatment for (a) 1 and (b) 50 h

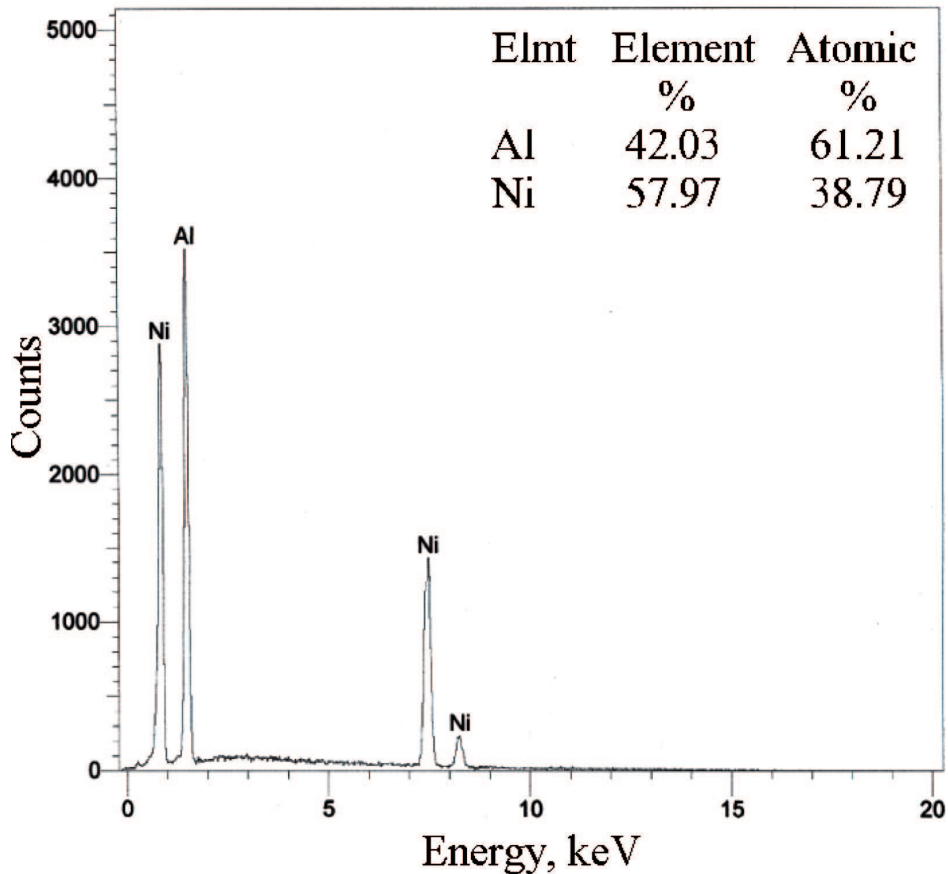


Fig. 5. X-ray spectrum for the Ni_2Al_3 intermetallic phase

The examinations of the above structures conducted by means of an X-ray spectroscopie showed that only two intermetallic phases and a solid solution were formed in the samples irrespectively of treating time (Fig. 5).

It was found that the wide layers in Fig. 4a neighbouring to Ni, containing 38.79 at. % Ni and 61.21 at. % Al, with the Ni : Al ratio about 2 : 3, are presumably the Ni_2Al_3 intermetallic phase [17]. Adjacent to Ni_2Al_3 , the deeply shaded area, containing 23.78 at. % Ni and 76.22 at. % Al, with the Ni : Al ratio about 1 : 3, is possibly the NiAl_3 intermetallic compound [17]. The dark shaded region with a blade-shaped islands contains between 0.47 and 15.63 at. % Ni and between 84.37 and 99.53 at. % Al. In the region X-ray radiation was simultaneously emitted by two phases of the structure: (Al) solid solution and NiAl_3 . The XRD results (Fig. 6) confirmed that the composites consisted of Ni, NiAl_3 and Ni_2Al_3 or only Ni and Ni_2Al_3 dependently on the treating time.

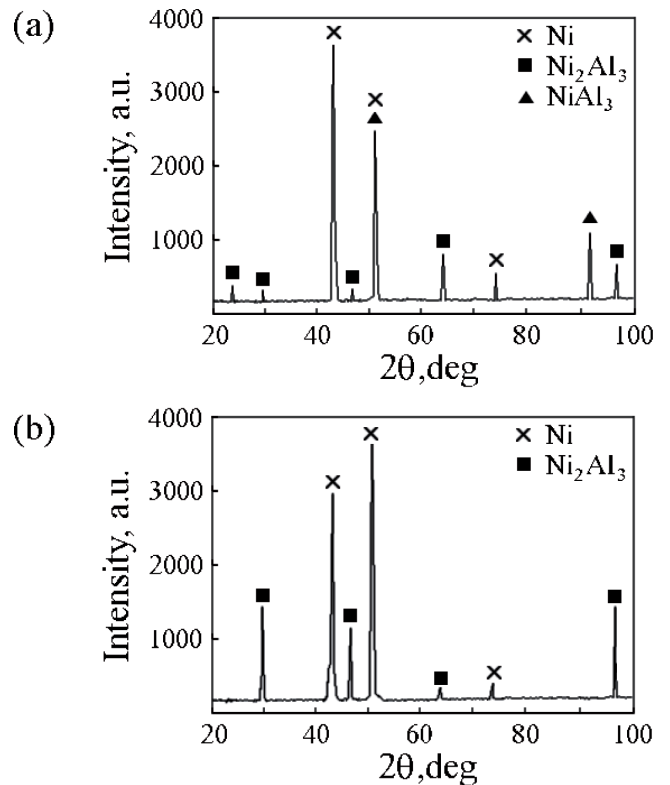


Fig. 6. XRD patterns of the cross-section of the laminated composites formed at 620°C for (a) 1 and (b) 50 h

The Gibbs free energies of formation for the compounds Ni_2Al_3 , NiAl_3 , NiAl and Ni_3Al at 620°C , are -309.9 , -166.2 , -131.9 and -41.6 kJ/mol, respectively [18, 19]. The formation of Ni_2Al_3 as the almost only product after 50 hours of the reaction between nickel and aluminium at 620°C is thermodynamically favoured and can be understood from the steps involved in another phases formation. Reactions between the Ni sheets and the Al foils depend on the diffusion of the Ni and the Al atoms through continuous and dense Al_2O_3 films on the surfaces of the Al foils. It is very profitable because the

Al_2O_3 films can be used as tracers [3]. There was observed migration of the oxide films from the surfaces of the Al foils to the middle of the formed intermetallic layers. The reaction between Ni and Al proceeds by means of diffusion of Al and Ni atoms through the Al_2O_3 films and formation of Ni_2Al_3 , NiAl_3 and (Al) solid solution (Fig. 7).

Figure 8 shows the map of elements obtained with SEM confirmed that both Al and Ni atoms could diffuse through the Al_2O_3 films.

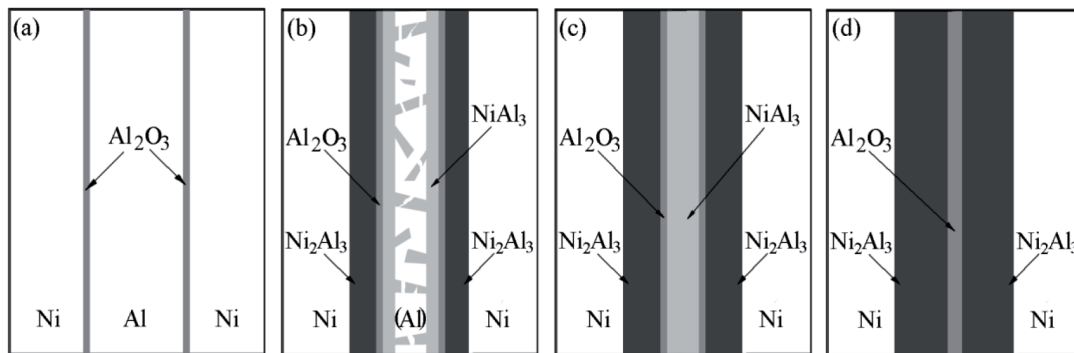


Fig. 7. Diagram showing observed reaction mechanisms between Ni and Al at 620°C

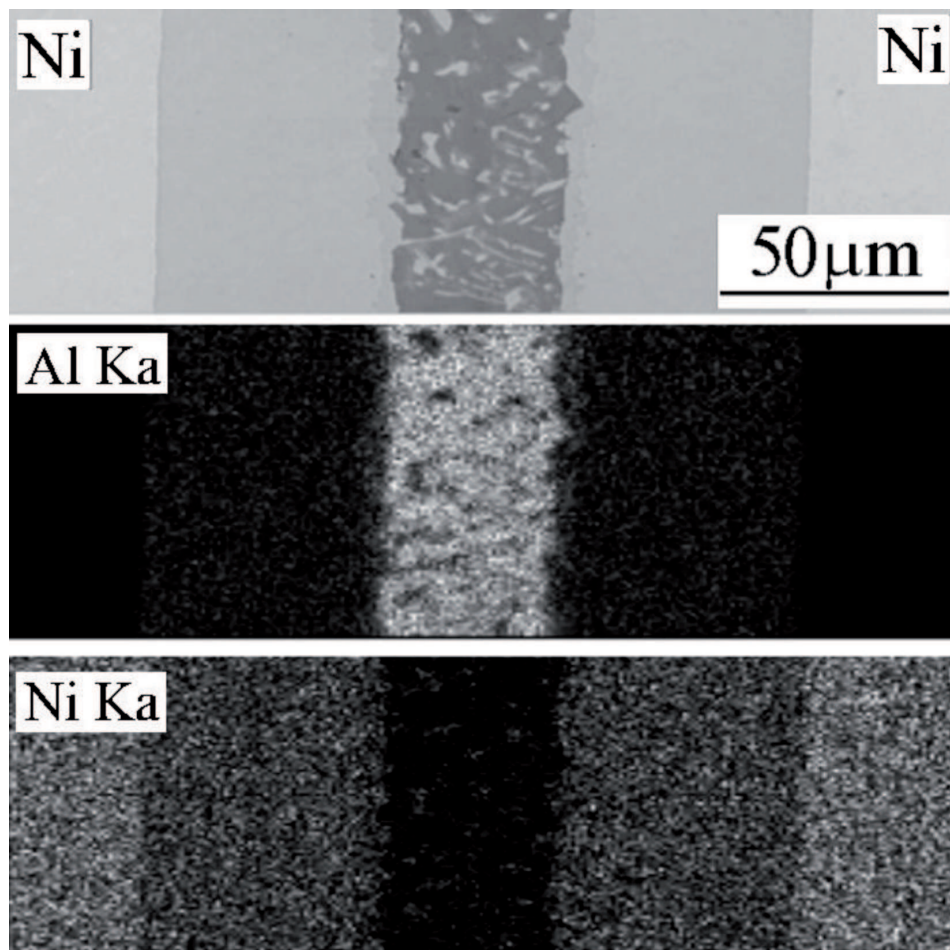


Fig. 8. SEM image of the Ni-Al reaction zone after treating at 620°C for 1 hour together with the maps of Al and Ni distribution

According to Xia and co-workers [20], there are three stages of formation of an intermetallic layer: intermetallic growth, transformation and stability. In the first stage both NiAl_3 and Ni_2Al_3 layers grow but the NiAl_3 layer grows more quickly because the diffusion reaction: $\text{Ni} + 3\text{Al} \rightarrow \text{NiAl}_3$ occurs very fast at the interface. After the completely consumption of Al, the layer consists of regular layers of Ni_2Al_3 (adjacent to Ni), irregular layers of NiAl_3 and the reaction zone consisting of NiAl_3 particles in (Al) matrix (Fig. 4a), which are thought to be produced by stresses resulting from the growth of the intermetallic layer. Generally, extensive lattice diffusion results in a uniform interface. On the other hand, diffusion along grain boundaries generates an irregular interface. The growth of Ni_2Al_3 layers at 620°C is limited by diffusion of Al atoms through the Al_2O_3 films. Therefore, diffusion of Al atoms along grain boundaries is inhibited, which results in straight, uniform interfaces between Ni and Ni_2Al_3 (Figs 4a and 4b). Thereafter the transformation follows, in which the Ni_2Al_3 layer develops by the diffusion of Ni atoms into the NiAl_3 phase. The irregular shape of the $\text{NiAl}_3/\text{Ni}_2\text{Al}_3$ interface indicates that the diffusion reaction: $\text{Ni} + \text{NiAl}_3 \rightarrow \text{Ni}_2\text{Al}_3$ does not generate equally fast. Further formation and growth of NiAl_3 requires a continuous supply of Ni atoms from

the Ni substrate through the Ni_2Al_3 layer. Since a large part of diffusing atoms is exhausted for the formation and growth of the Ni_2Al_3 layer, this causes a deficiency of Ni atoms for the growth of the NiAl_3 layer [21]. Therefore the thickness of the NiAl_3 layer is much smaller than that of the Ni_2Al_3 layer. When the NiAl_3 layers are consumed completely the stable stage comes, in which the structure keeps unchanged. The final stable structure at the temperature of 620°C is $\text{Ni}_2\text{Al}_3/\text{Ni}$ layers. Fig. 9 shows the thickness of Ni_2Al_3 and $\text{NiAl}_3 + (\text{Al})$ layers as a function of treating time at a temperature of 620°C .

The relationship between the thickness of the intermetallic layer and holding time can be given by the generally accepted equation

$$x = kt^n \quad (1)$$

where x is the thickness of Ni_2Al_3 layer, t is the holding time, n is the time exponent and k is a constant. It is well known that when $n=1$ the process is governed by the chemical reaction and when $n=0.5$ the process is controlled solely by the volume diffusion. It was found out that both mechanisms take place in the growth of Ni_2Al_3 layer. The first one (till 0.5 hour of annealing) with linear growth of the thickness of Ni_2Al_3 layer corresponds to

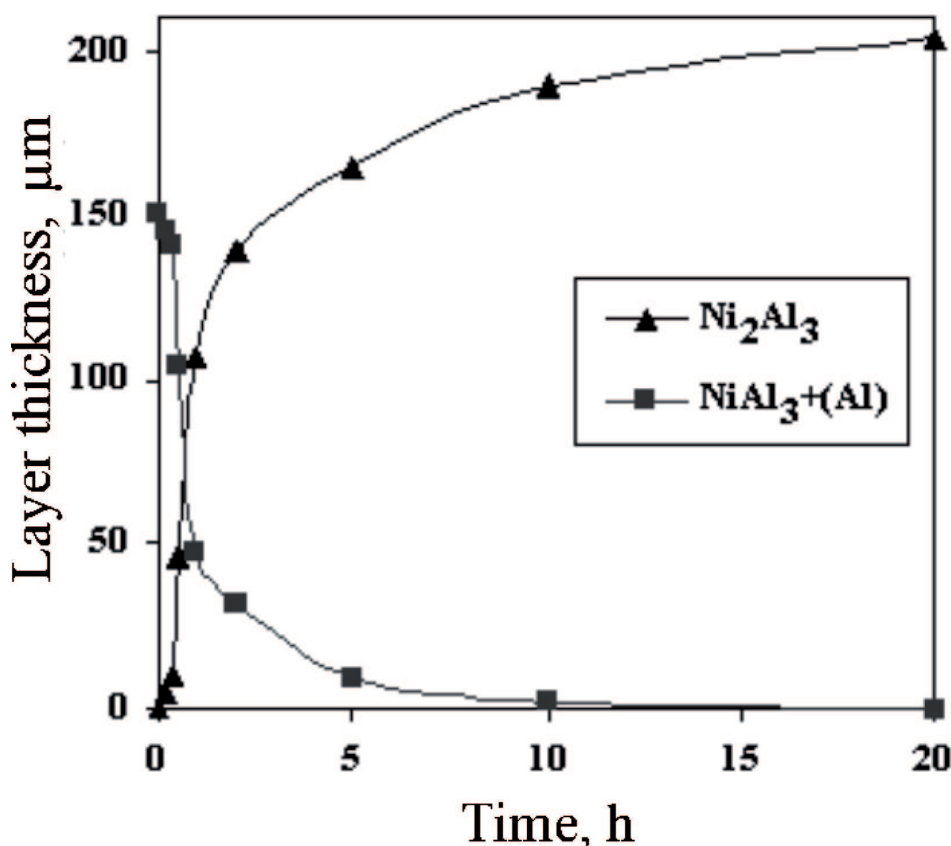


Fig. 9. The thickness of Ni_2Al_3 and $\text{NiAl}_3 + (\text{Al})$ layers as a function of time

reaction at the phase boundary and the second one (after 0.5 hour of annealing), with parabolic shape, which is attributed to the volume diffusion. The results are consistent with work of Pieraggi [22] and Wojewoda and Zięba [23]. On the basis of measurements a relationship between the thickness (expressed in μm) of the Ni_2Al_3 layer and the holding time (expressed in hours) after 0.5 hour of annealing has been derived

$$x = 45t^{0.5} + 67 \quad (2)$$

Ni_2Al_3 has $D5_{13}$ hexagonal crystallographic structure and its lattice parameters, a and c , are 0.403 and 0.489 nm, respectively [24]. By using the reported lattice parameters and the crystal structure at room temperature the density of Ni_2Al_3 was estimated to be 4.66 g/cm^3 . If the aluminium layer is transformed completely into Ni_2Al_3 , the thickness of the intermetallic layer can be expressed as [20]

$$x_{\text{Ni}_2\text{Al}_3} = \frac{\rho_{\text{Al}}}{\rho_{\text{Ni}_2\text{Al}_3}} \cdot \frac{L_{\text{Al}}}{1-m} = \frac{2.7}{4.66} \cdot \frac{L_{\text{Al}}}{1-m} = 0.579 \cdot \frac{L_{\text{Al}}}{1-m} \quad (3)$$

where L_{Al} is the thickness of the aluminium layer, m is nickel weight percent in the Ni_2Al_3 intermetallic phase, ρ_{Al} and $\rho_{\text{Ni}_2\text{Al}_3}$ are the density of the aluminium and intermetallic layers, respectively.

Various phases formed during synthesis were further confirmed by microhardness measurements. Values of $759 \pm 25 \text{ HV}$ and $510 \pm 7 \text{ HV}$ were obtained for Ni_2Al_3 and NiAl_3 phases, respectively. The large fluctuation in Ni_2Al_3 hardness is caused by possible variation in the Ni to Al ratio (Eleno et al. [17] reported that Ni_2Al_3 can contain between 59.5 and 63.2 at. % Al). Comparatively measured, the microhardness of nickel was 230HV. The aluminide phases (especially Ni_2Al_3) give high hardness and stiffness to the composite, while unreacted nickel provides the necessary high strength and ductility. Fig. 10 shows the tensile strength of the Ni-intermetallics laminated composites treated at a temperature of 620°C for different time.

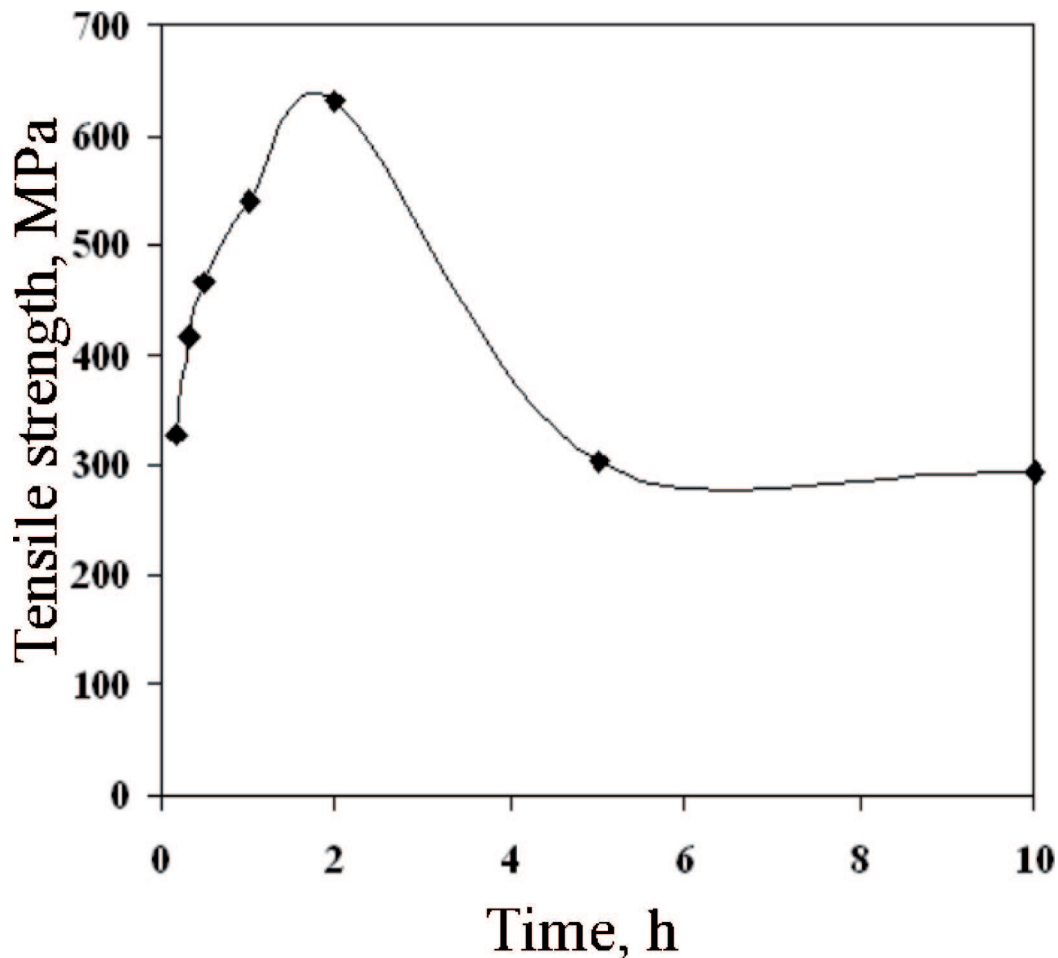


Fig. 10. Tensile strength of the Ni-intermetallics laminated composites as a function of time

At the initial treatment (after 0.17 h), the tensile strength was 328 MPa, that is equal to the results from the rule of mixture. With increasing the treating time the tensile strength increases up to a maximum value of 630 MPa (after 2 h) and then drops to a minimum value of about 294 MPa (when treating time is longer than 5 h). The increase of the tensile strength is due to the presence of the high-strength intermetallic layers. The strength decrease after long heat treatment is caused by the presence of Al_2O_3 inclusions that exist in a continuous state in the middle of the newly formed Ni_2Al_3 layers (especially at the $\text{Ni}_2\text{Al}_3/\text{Ni}_2\text{Al}_3$ interfaces), which cause very weak bonding between the Ni_2Al_3 layers (Figs 4b and 7d). The fracture surfaces of samples heat-treated longer than 2 hours were extremely ragged ($\text{Ni}_2\text{Al}_3/\text{Ni}_2\text{Al}_3$ interfaces were all delaminated) and therefore they were difficult to make into a specimens for SEM observations.

4. Conclusions

The laminated Ni-($\text{NiAl}_3+\text{Ni}_2\text{Al}_3$) and Ni- Ni_2Al_3 intermetallic composites were formed by reaction synthesis of Ni and Al foils at 620°C carried out under vacuum. The following conclusions can be drawn:

1. The well-bonded and fully dense layered structures can be designed easily. The stable structures of the composites depend only on the treating time at 620°C .
2. The microstructural characterisation by SEM, XRD and X-ray microprobe analysis indicated that after 1h of treatment Ni_2Al_3 is the predominant intermetallic phase.
3. The tensile strength of the laminated composites increases with an increase of the volume fraction of the intermetallic products. However, it decreases after long heat treatment because the $\text{Ni}_2\text{Al}_3/\text{Ni}_2\text{Al}_3$ interfaces can very easily delaminate due to a very weak bonding caused by continuous Al_2O_3 inclusions.
4. The fracture surface of the laminated composites exhibits a mixture of brittle fracture of intermetallics and ductile one of residual Ni layers.

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