20-24 SEPTEMBER 2015 KRYNICA-ZDRÓJ POLAND

# XXIII CONFERENCE ON APPLIED CRYSTALLOGRAPHY

## PROGRAMME & ABSTRACTS

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# XRD *in-situ* heating of large period Ni/Al reactive multilayer

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**Keywords:** Ni/Al multilayers, thermal stability, *in-situ* X-Ray studies

The Ni/Al multilayers, capable of strong exothermic reaction of SHS type, might found application in joining heat sensitive materials or serve as imbedded heat reservoir, which could be activated by proper heat pulse. The DSC constant heating rate experiments proved that the large to medium period multilayers, i.e. $\Lambda$ ~ (100 - 25 nm) show highest transformation rate, i.e. strongest effect in tightest temperature range producing eventually the expected NiAl phase [1, 2]. However, attempts to determine an exact phase transformation sequence with XRD method gave conflicting results, especially as it concerns the presence of metastable $Al_9Ni_2$ phase [2, 3]. Therefore, the aim of the present work was to carry out an *in-situ* X-ray diffraction study of thermal stability of Ni/Al multilayer of nominal period $\Lambda$ = 100 nm. It was deposited on (001)-oriented monocrystlline silicon substrate using double target magnetron systems with rotating table as described in detail elsewhere [4]. The overview of the microstructure of Ni/Al multilayer is presented in Fug. 1*a*.

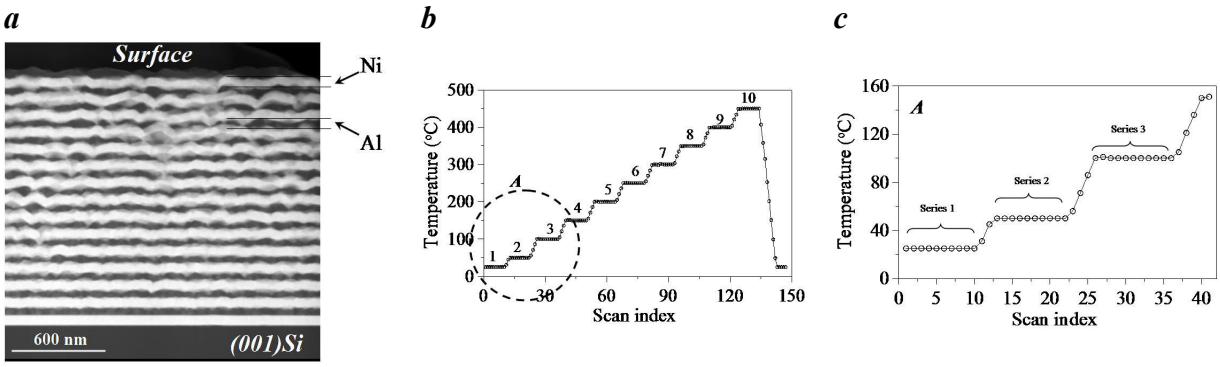


Fig. 1. The Al/Ni multilayer HAADF-STEM microstructure (a) and the heating/cooling curve used in the thermal stability investigations (***b***, ***c***).

Wide angle X-ray scattering (WAXS) measurements were performed using Bruker D8 Discover (Germany) diffractometer operating at voltage 40 kV and current 40 mA. CuKα radiation was used (λ= 1.5406 Å). Measurements were performed in reflection mode, using Bragg-Brentano geometry, with focusing optics consisting of Goebel mirror with deflection 0.677 $^{o}$ and 1 mm slit and two Soller collimators of axial divergence 2.5 $^{o}$ applied on both sides. The measurements were performed in temperature range from 25 $^{o}$C to 450 $^{o}$C using Anton-Paar TTK 450 temperature chamber equipped with liquid nitrogen cooling system. The sample was subjected to temperature program consisting of heating the sample at rate 20 K/min to temperature steps 25, 50, 100, 150, 200, 250, 300, 350 and 450 $^{o}$C, followed by cooling to 25 $^{o}$C at rate 30 K/min (see Fig. 1*b*, *c*). At particular temperature step the sample was scanned ten times at high sampling rate, 0.045 second per point, with angular resolution 0.04 $^{o}$ in 2θ range 30 – 60 $^{o}$. Thus, a single scan required 37.26 seconds and total time at particular temperature step, i.e. 10 scans, required 431 seconds. Additional measurements at 25 $^{o}$C were performed before and after the in-situ experiment. These scans were registered at broader 2θ range 30 -105 $^{o}$, at offset (θ angle) 0 $^{o}$ and 6 $^{o}$, at low sampling rate 0.5 seconds per point. Structure refinement was performed using the whole-pattern decomposition (Profile Matching) procedure (also known as LeBail fitting [5]), as implemented in the FullProf program [6]. The lattice parameters were precisely determined by Dicvol04 program [7]. The X-ray diffraction data were analyzed using the crystallographic database PDF4 [8].

From the analysis of the X-ray diffraction pattern, using the data contained in the database PDF4 [8], it is evident that the produced multilayer consists from an alternating layers of solid solution of Ni(Al) and Al(Ni). Their unit cell parameters were estimated at $a$ = (3.5281 ± 0.0009) Å for Ni(~1.45wt.%Al) and $a$ = (4.0365 ± 0.0011) Å for Al(~6.97 wt.% Ni). The beginning of phase transformation in the multilayer structure is observed already at 200 °C, as at that temperature small peaks from the orthorhombic phase $Ni_3Al$ were detected (Fig. 2*a*). An increase of the temperature up to 250 °C leads to an increase of the fraction of the $Ni_3Al$ phase and complete disappearance of the Al(Ni) (Fig. 2*b*). The heating of the Ni/Al multilayer up to 300 °C results in the crystallization of cubic NiAl phase (space group Pm-3m (221)). Still higher temperature (350 ° C), causes results

not only in disappearance of $Ni_3Al$ phase and lowering of NiAl-phase and Ni(Al) fractions, but also in the crystallization of $Ni_3Al$ (space group Pm-3m (221)) cubic phase (Fig. 3*a*). The heating of the Ni/Al multilayer up to 400 °C continues the process of substitution of NiAl with $Ni_3Al$. It should be noted that the solid solution Ni(Al) is still present in a small amount up to a temperature of 450 °C (Fig. 3*b*). After annealing at 450 °C, the multilayer structure has only two phases: cubic NiAl and cubic $Ni_3Al$.

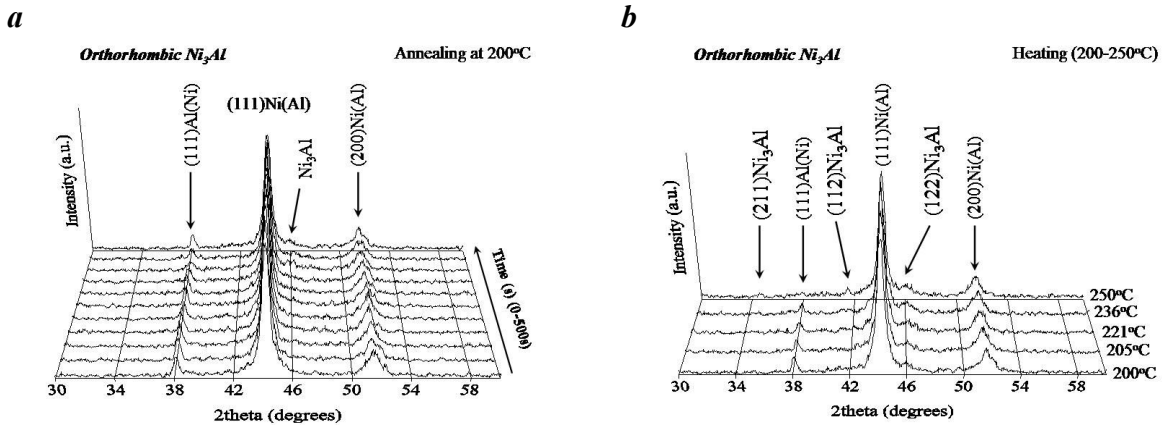


Fig. 2. The X-ray diffraction patterns of Al/Ni multilayer recorded during annealing at 200 °C (*a*) and during heating up to 250 °C (*b*).

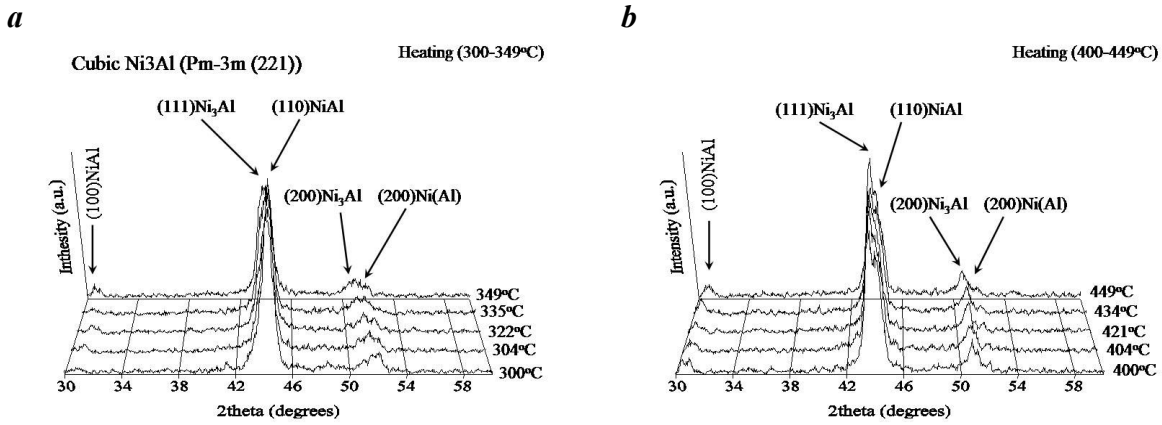


Fig. 3. The X-ray diffraction patterns of Al/Ni multilayer recorded during heating from 300 up to 349 °C (*on the left*) and during heating from 400 up to 450 °C (*on the right*).

**Summary**

The XRD *in-situ* heating of the Ni/Al multilayer of $\Lambda$ ~100 nm up to 450°C indicated, that such treatment causes following sequence of phase transformations:

$$Ni(Al) + Al(Ni) \rightarrow Ni(Al) + \text{orthorhombic } Ni_3Al \rightarrow Ni(Al) + \text{orthorhombic } Ni_3Al + \text{cubic NiAl} \rightarrow$$
$$\rightarrow Ni(Al) + \text{cubic NiAl} + \text{cubic } Ni_3Al \rightarrow \text{cubic NiAl} + \text{cubic } Ni_3Al .$$

**Acknowledgments**

The research was performed in a frame of the project no DEC-2012/05/B/ST8/01794 supported by National Science Centre (NCN) of Poland

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