Study of long-term post-SHS phase kinetics in Ni/Al reactive multilayer nanofoils

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Abstract. We present the results of the recent experiments with two species of Ni/Al reactive multilayer nanofoils (RMNFs) supporting the self-propagating high-temperature synthesis (SHS) reaction. SEM method was used to evaluate their general structure and quantitative chemical composition before and after reaction. Phase composition was determined from XRD spectra. Special attention was paid to the stability of phase composition over relatively long time intervals after SHS reaction – order of the hours and days. In some cases, XRD spectra showed notable evolution of crystalline structure, which can have significant impact on practical application of SHS, for instance, in soldering technologies. To our knowledge, similar effect has been previously observed only for SHS-reactive powder mixtures.

1. Introduction

Reactions of self-propagating high-temperature synthesis (SHS) in reactive multilayer nanofoil (RMNFs) drew substantial interest in the recent decade due to the possibilities of their practical application in different areas, such as mechanical joining of dissimilar or sensitive materials or energy storage [1-4]. Typically, RMNFs comprise thousands of alternating of nanolayers of reactive metals. Specific area of inter-layer boundaries in this system is very large. Therefore, the highly exothermic SHS reaction producing the corresponding intermetallic product, once initiated, propagates along the foil at very high speed – up to a few kilometers per second. The released heat can melt thin adjacent layers but the temperature rapidly decreases with time (~ms) and with distance from the RMNF. This allows to produce very quickly the soldered or welded joints meeting all the requirements concerning mechanical strength, as well as electrical and thermal conductivity, while not damaging deeper layers of joined details.

Obviously, the quality of such solder joints depends critically on the crystalline structure of the SHS reaction product [5]. The latter is determined by the processes of diffusion and phase kinetics developing not only near the propagating SHS reaction front but also during later, much slower stages of the reaction [1, 3, 6]. A large amount of research has been devoted to this issue. For instance, in [7, 8] the Ni/Al RMNF structure was studied while the SHS wave was “frozen” by introduction of an efficient local heat sink. This allowed the experimenters to access the crystalline structure before, in the course of and after the SHS reaction, at the periphery of the “freezing zone”. This experiment confirmed that at relatively slow heating rates formation of the intermetallic reaction product in RMNFs occurs both along the interface of the reagents and along grain boundaries of the less refractory component (Al). In addition, the reaction “route” (succession of phase transitions) significantly depends on the reaction speed [2, 3, 9]. During slow annealing of RMN foils, several intermediate products are formed and converted in a series. In rapid SHS reactions, the most stable product and the liquid phase are usually formed.
immediately. In turn, the reaction speed strongly depends on many factors including chemical composition of the foil, bilayer thickness, ambient temperature, initiation method, etc. Our new experiments were made with the most extensively studied pair of reactive metals: Al and Ni. The work was mainly focused at the late, very slow stages of SHS reactions and their final products for Ni/Al RMNFs having different chemical composition – close to 1Ni:1Al and 3Ni:Al.

2. Experimental

2.1. Sample fabrication

The studied Ni/Al RMNF samples were fabricated by the method of magnetron sputtering on copper substrates with the use of a QUBE unit (by Mantis Deposition Ltd) allowing precise thickness control of the grown nanofoils at the level of several Å. Targets of pure (about 99.99%) Ni and Al were taken. Surface oxide layers were mechanically removed from the targets to prevent contamination in the grown structures. The growth process was performed at the standard argon pressures in the chamber ca. 10⁻² bar and consisted of alternating deposition of atoms of the two metals sputtered from the clean targets by magnetron discharge in argon. At each moment, one of the two deposition cells (with either Al or Ni target) was mechanically screened from the substrate without magnetron discharge quenching. Deposition rate did not exceed 2Å/s. It was limited mainly by thermal conductivity of the substrate/fabricated foil. Its surface temperature had to be kept below 320 K to inhibit pre-mixing of the metals. The molar ratio of Al and Ni in the RMNF was controlled via the corresponding layers’ thickness. Full thickness of the composite foil amounted to a few tens of μm. After deposition, the foils were mechanically detached from the substrates.

The deposition regimes used for fabrication of specimens for this study were adjusted for the 3Ni:Al atomic ratio in the RMNF, which corresponds to one of non-equimolar intermetallic crystalline phases Ni₃Al. The growth process was interrupted by a few 8-hour-long breaks without vacuum chamber opening. Nonetheless, oxidation during these breaks separated the RMNF into macroscopic strata with relatively poor mutual adhesion. The product of this process is further designated as “Sample 2” or “S2”.

For reference, we took the commercially available material Nanofoil® [2], further referred as “Sample 1” or “S1”. This product is known to have approximately equimolar stoichiometry (atomic ratio ca. 1Ni:1Al) and minor content of vanadium. The foils are fabricated in an uninterrupted growth process and their structure is macroscopically uniform.

The compared Ni/Al RMNF varieties had the same bilayer thickness (sum of thicknesses of two adjacent Ni and Al layers) 100 nm. The major difference consisted in different molar ratio between its Ni and Al components. All experiments reported below were made with free-standing narrow strips (a few mm wide) cut out of these two Samples (large RMNF sheets).

2.2. Characterization techniques

The structure and chemical composition of samples before and after SHS reaction were studied using LYRA3 TESCAN scanning electron microscope (SEM) with EDS unit. Crystalline structure of the samples was investigated using Super Nova (Oxford Diffraction) 4-circle single-crystal diffractometer. Sample strip 5 by 2 mm in dimensions was mounted on the goniometer head and aligned to be in rotation center. Measurements were performed using Cu-cathode X-Ray tube with the sample rotated along the axis perpendicular to X-Ray beam, which gave us diffraction intensity distribution in reciprocal space. At this stage, full 3 d data were reduced to powder diffraction patterns by integrating over the sample rotation angle in the range ±30°, and then – over the polar angle within the CCD image. To cover whole angle range of interest, each dataset was recorded at closest detector’s distance (50 mm) from the sample and at 3 detector’s angle positions (0°, 65°, 95°)

Diffractometer operation were controlled via Crysalis Pro software. This software was also used for preliminary data processing. Final data processing and analyzing were performed in MATLAB program package.
3. Results

3.1 SEM/EDS study
High-resolution SEM images of both RMNF Samples in their unreacted, as-fabricated state confirmed presence of alternating contrast planar layers, as well as the bilayer thickness value ~100 nm. Figure 1 presents overview images of the Samples with lower resolution and EDS chemical composition data averaged over the outlined areas.

Quantitative chemical analysis estimates weight % of Ni in mean composition of the Sample 1 foil as 80, which corresponds to ~65 atomic %. Nonetheless, this popular RMNF type taken for reference is known to be approximately equiatomic [2], which shows that the EDS method notably overestimates relative Ni content for the tested structures.

![Figure 1](image.png)

**Figure 1.** (a), (b): data for as-fabricated RMNF Sample 1. (c), (d): data for as-fabricated Sample 2. (b), (d): SEM images. (a), (c): EDS spectra for the outlined squares.

Sample 2 has substantially lower (~2 times) relative Al content than presumably equimolar Sample 1, in sensible agreement with the intended 3Ni:Al stoichiometry. Chemical contaminants are present only in trace quantities.

Figure 2 presents images and EDS data for the same two Samples after SHS reaction. For Sample 1, the reacted films comprise rounded crystallites with characteristic size ~1 μm. No traces of the initial 100 nm-wide layers can be distinguished. Crystalline domains in reacted Sample 2 foil are much smaller (sub-μm). This observation agrees with the general tendency following from the modern models of SHS reactions in Ni/Al nanofoils [9]: in Ni-rich structures, the reaction develops in so-called “dissolution/precipitation” mode with the product growing from numerous nuclei appearing at interlayer boundaries; in contrast, equimolar or Al-rich multifoils are fully melted during the SHS and very large (μm-scale) product domains grow from rare nuclei in continuous melt.
EDS analysis shows little or no presence of Al in the SHS reaction products for both Samples. This discrepancy can be explained by certain heterogeneity of chemical composition in the product. The showed SEM images represent side surfaces of RMNF strips mechanically broken after reaction, and the EDS analysis is made for these surfaces. Crystallization process may selectively expel Ni onto grain boundaries where Ni concentration can be therefore much higher than average.

Bottom SEM images in figures 1 and 2 show that delamination of Sample 2 RMNF becomes more pronounced after SHS reaction. Reaction-related mechanical stresses break the relatively weak adhesion at the oxidized strata boundaries, and the opening breaches are not “healed” by material melting in free-standing of insufficiently compressed foils. This conclusion may be important for practical applications of RMNFs. However, this phenomenon cannot be expected to have strong impact onto crystalline phase kinetics studied in this work.

3.2 XRD study
XRD experiments with both Samples were made in accordance with the following scheme: 1. Fixation of a small RMNF strip in sample holder of the diffractometer; 2. XRD spectrum acquisition for the Sample in its as-fabricated state; 3. In-situ initiation of SHS reaction in the RMNF strip with electric spark; 4. Acquisition of XRD spectrum immediately after the SHS reaction; 5. The sample is left in the holder and spectrum measurement is repeated after 24 hours; 6. The measurement is repeated in 168 hours (a week) after reaction. This experiment scheme was aimed at registration of long-term residual kinetics of phase composition in SHS reaction products.
Figure 3. Powder XRD spectra for free-standing RMNF strips before (black curves) and immediately after (red curves) SHS reaction. (a): Sample 1 (ca. Ni:Al); (b): Sample 2 (ca. 3Ni:Al).

XRD spectra for as-fabricated and reacted RMNF strips are compared in figure 3. In the former case (black curves), only peaks associated with the reactants (Al and Ni) are present; for Sample 2, relative heights of Al peaks are much lower. Diffraction peaks at angles below 35°, characteristic for intermetallic phases, cannot be discerned in these (black-line) spectra, which suggests that pre-mixed fraction in the as-fabricated RMNFs is negligible. The intermetallic-related peaks appear after SHS reaction (red curves in figure 3) while the features of the reactants disappear. They can be unambiguously attributed to NiAl and Ni$_3$Al [10] for Samples 1 and 2, respectively. The reaction product peaks have distinctly lower width than the peaks of reactants which agrees with greater mean size of the product crystallites showed in SEM images in figure 2, in comparison with possible dimensions of reactant grains.

Figure 4(b) shows three XRD spectra measured with Sample 2 RMNF immediately after SHS, then after 24 hours, and then after 168 hours after the reaction. As noted above, their pattern matches the known one for Ni$_3$Al intermetallic [10]. The spectrum did not change in any details over the observation time suggesting that the final product is stable and there is no detectable long-term (hour- or day-scale) phase kinetics. This is not so for Sample 1. Different strips of this foil gave slightly different XRD spectra with notable post-reaction long-term evolution. A set of such spectra measured for the same RMNF strip at times 0, 24 and 168 hours after reaction is showed in figure 4(a). All major peaks here have satellites, and changes in the intensity distribution over the time were reliably detected (compare with spectra in the right part of the same figure). This leads to conclusion that recrystallization processes in the SHS product for near-equimolar Ni/Al RMNFs can proceed for as long as days or weeks.

Figure 4. XRD spectra of SHS products measured at times 0, 24 and 168 hours after reaction. (a): Sample 1 (the foil strip with the most notable post-reaction phase kinetics). (b): Sample 2.
4. Discussion and conclusions

Phase transitions in RMNFs during SHS reactions are known to occur for the most part at the time scale of milliseconds or faster (up to fractional second [11] and down to nanoseconds [9]). Long-term (minute-scale) recrystallization after SHS reaction has been reported [12-14] for powder systems generally characterized by slower reaction kinetics because of much smaller specific area of interface boundaries. Authors of [13] also mentioned relatively bad reproducibility of fine spectral features. In those publications, the phenomenon of long-term re-crystallization of the NiAl product was explained by the fact that it has very broad homogeneity zone in the equilibrium phase diagram, especially at elevated temperatures. Solid NiAl domains grow from the surrounding melt with elemental composition corresponding to the homogeneity zone edge [15], different at different temperatures. Therefore, at room temperature their composition turns out to be far from equilibrium and non-uniform. Low atomic mobility at room temperature slows re-crystallization rates to the observed day-scale values. In [16], the authors ascribed complicated and unstable phase structure at grain boundaries of SHS reaction product to the presence of vanadium in the commercial RMNFs with near-equimolar stoichiometry (taken in this work as the reference Sample 1).

In contrast, solid intermetallic phase Ni$_3$Al, has very narrow homogeneity zone in the phase diagram. Consequently, crystallizations of Ni$_3$Al SHS reaction product directly produces stoichiometrically correct domains which excludes the late re-crystallization stage.

The result obtained in the reported work can be of importance for practical applications of RMNFs. Long-term re-crystallization can either deteriorate or improve parameters, for instance, of soldered or welded joints. In some cases, the choice could be made in favor of RMNF stoichiometry types having lower specific stored chemical energy but better long-term product stability.

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