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Analysis of Catalytic Properties of Ni_3Al Thin Foils for the Methanol and Hexane Decomposition

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***Abstract*—**Intermetallic Ni_3Al – based alloys belong to a group of advanced materials characterized by good chemical and physical properties (such as structural stability, corrosion resistance) which offer advenced technological applications. The paper presents the study of catalytic properties of Ni_3Al foils (thickness approximately 50 μm) in the methanol and hexane decomposition. The egzamined material posses microcrystalline structure without any additional catalysts on the surface. The better catalytic activity of Ni_3Al foils with respect to quartz plates in both methanol and hexane decomposition was confirmed. On thin Ni3Al foils the methanol conversion reaches approximately 100% above 480 ^{o}C while the hexane conversion reaches approximately 100% (98,5%) at 500 ^{o}C. Deposit formed during the methanol decomposition is built up of carbon nanofibers decorated with metal-like nanoparticles.

***Keywords*—**hexane decomposition, methanol decomposition, Ni_3Al thin foils, Ni nanoparticles

I. Introduction

INTERMETALLIC Ni_3Al – based alloys belong to a group of advanced materials with interesting physical properties. Due to good resistance to oxidation and corrosion, high melting point and relatively low density this material can be used in the automotive, aerospace and mechanical engineering industry [1, 2].Thermal resistance, high structural stability and large surface to volume ratio of Ni_3Al thin foils predispose the material to be a good catalyst for decomposition of various organic compounds. It was found that the alkali-leached Ni_3Al powders show a high catalytic activity for the methanol decomposition ($CH_3OH \rightarrow 2H_2+CO$) [3]. Authors reported that the oxidized Ni_3Al powders exhibit catalytic properties in methane decomposition [4]. It was reported that the fine Ni particles are formed on the surface of the Ni_3Al powder, and the surface of these Ni particles is covered with a thin layer of oxides and hydroxide after the alkali leaching process. [5]. At present, there is a need for low-cost, efficient heterogeneous catalysts with high surface to volume ratio for application in microchanell reakctors or as a warp of the catalyst layer. For such applications the most suitable catalysts are the materials in solid form, for example thin intermetallic foils. As reported in literature [6], research results indicate that the Ni_3Al catalysts are highly promising as a good catalyst for chemical reactions, especially for methanol decomposition.Methanol is a chemical compound who can be future fuel. There are a number of publications talking about the attractiveness of this fuel [7,8,9]. Methanol is readily available; it can be easily recovered from biomass or biogas, or also be synthesized catalytically from basic elements.

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The choice of methanol as a substrate was caused by a possibility to produce hydrogen during its decomposition.

Hexane is produced during the refining of crude oil. It is widely used in industry, but it is also one of the volatile organic compounds and can be decomposed by catalytic oxidation [10]. The choice of hexane as a substrate was dictated by a possibility of using it as a method to purify the air.The aim of this study is to analyze the catalytic properties of Ni_3Al thin foils for methanol and hexane decomposition. Ni_3Al foil was used as a catalyst to produce hydrogen in methanol decomposition.

II. Experimental

The thin Ni_3Al foils with chemical composition (at.%): Ni - 22.13Al-0.26Zr - 0.1B , with a thickness of 50 μm and an average grain diameter (equivalent diameter) of approximately 10 μm, was studied. Before the experiment, the foils were mechanically cut into small pieces with dimensions of 6 x 2 mm. Every time in the study 0.4 g of the test material was used.The investigations of catalytic activity was carried out in a fixed-bed quartz reactor. The flow rate was about 3 dm^3/h with argon as carrier gas. The process of decomposition was performed for two substrates: methanol (concentration of approximately 111000 ppm) and hexane (concentration of approximately 34000 ppm). In both cases the reference material was quartz in similar amount. Each decomposition reactions was carried out in the temperature range of 100 - 600^{o}C during 30 minutes for each temperature. The analysis of the composition of the reaction mixture was performed using a mass spectrometer Perkin Elmer Clarus 560s.After methanol and hexane decomposition the surface of the Ni_3Al foils was observed by SEM (Quanta 3D FED).The phase structure of the surface products after decomposition was invastignated by X-ray diffraction using Seifert 3003 diffractometer with CoKα radiation.

III. Results And Discussion

Catalytic activity of Ni3Al foils in methanol decomposition reaction starts from above 280 °C (Fig. 1(a)). With increasing temperature the conversion of methanol is growing rapidly and at 480 °C the conversion is approximately 100% (99%). Methanol conversion on quartz starts at the same temperature as on the Ni_3Al foils but with less effectiveness – maximum conversion (approximately of 65%) was carried out at 530 ^{o}C. In the hexane decomposition clear differences in the efficiency of these processes carried out on thin foils Ni_3Al and quartz can be distinguished. Decomposition temperature has an influence of hexane conversion. At temperature below 230 ^{o}C

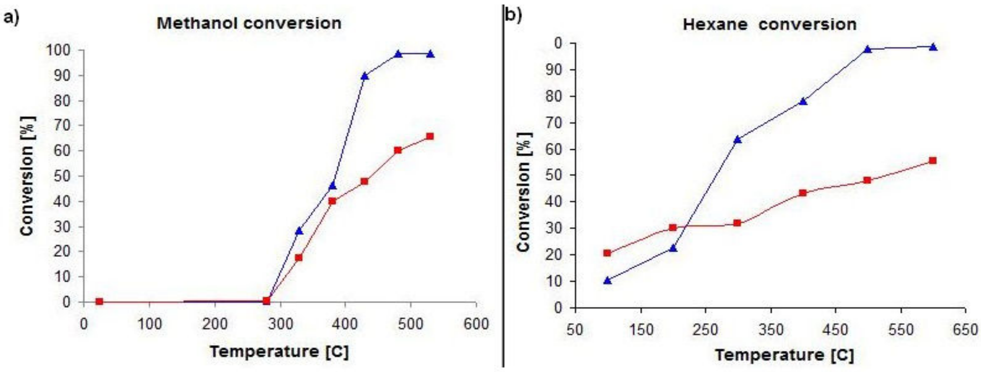

Fig. 1 Conversion of methanol (a) and hexane (b) on thin foils Ni_3Al (triangle).The conversion of methanol and hexane on quartz (squares) is provided as a reference

the hexane conversion on Ni_3Al foils is lower than on quartz, but with increasing temperature the trend reverses. Above the temperature of 230 °C the hexane conversion is much higher on Ni_3Al than in quartz. With the increase of temperature the degree of conversion increases and at 500 ^{o}C reaches approximately 100% (98%). Hexane conversion on quartz has maximum of 55% at 600 ^{o}C.

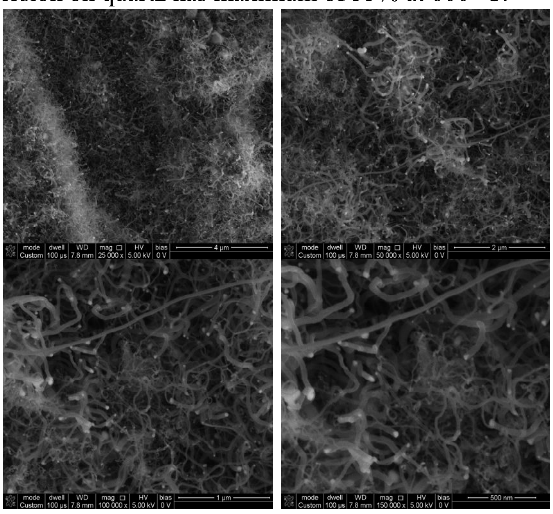

Fig. 2 Surface of Ni_3Al foils after methanol decomposition (SEM-SE) with carbon nanofibers and metal-like nanoparticles (very bright points in the picture)

On the surface of Ni_3Al thin foils after methanol and hexane decomposition the carbon deposit was observed. SEM analysis of the Ni_3Al foils surface showed a significant effect of the surface type on the morphology and an amount of deposited carbon (Fig 2 and 3). The carbon deposit consists of entangled nanofibres. At the ends of these nanofibres one can see the metal-like nanoparticles, probably Ni nanocrystalines (Fig. 2 and 3). After the hexane decomposition the nanostructures in the deposit are thinner and they are more twisted. This may be due to a higer number of carbon in the hexane molecule or to the absence of water in the products of hexane decomposition. It was discovered that the water in the reaction mixture favors the formation of nanostructures with fewer defects [11, 12].

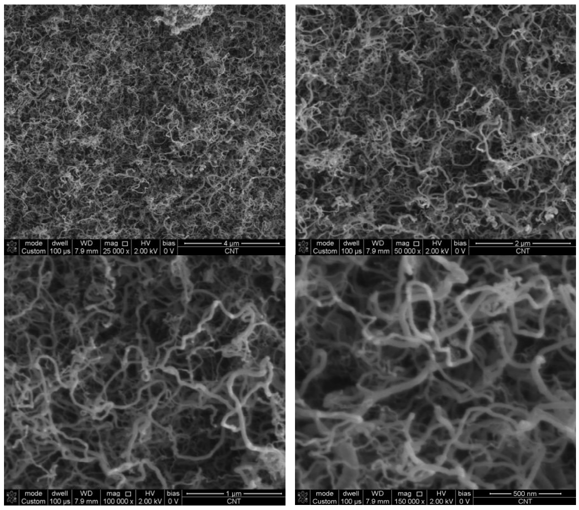

Fig. 3 Surface of Ni_3Al foil after hexane decomposition (SEM-SE) with carbon nanofibers

The findings is supported by the morphology of the resultedcarbon deposit after the methanol decomposition presented in this study. Futheremore, after the hexane decomposition the metal-like nanoparticles decorating the carbon nanofibres are poorly visible whereas in the case of the methanol decomposition products the metal-like nanoparticles are more pronounced (Fig. 4). This is probably due to a different mechanism of carbon nanofibres formation, which will be the subject of further research.

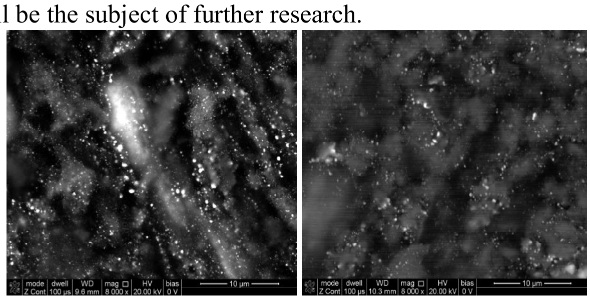

Fig. 4 SEM – SE and BSE view on surface of Ni_3Al microcrystalline foils after methanol (a) and hexane (b) decomposition.

BSE images (Fig. 4) show the presence of areas with different ratio of elements. Bright spots scattered on the whole

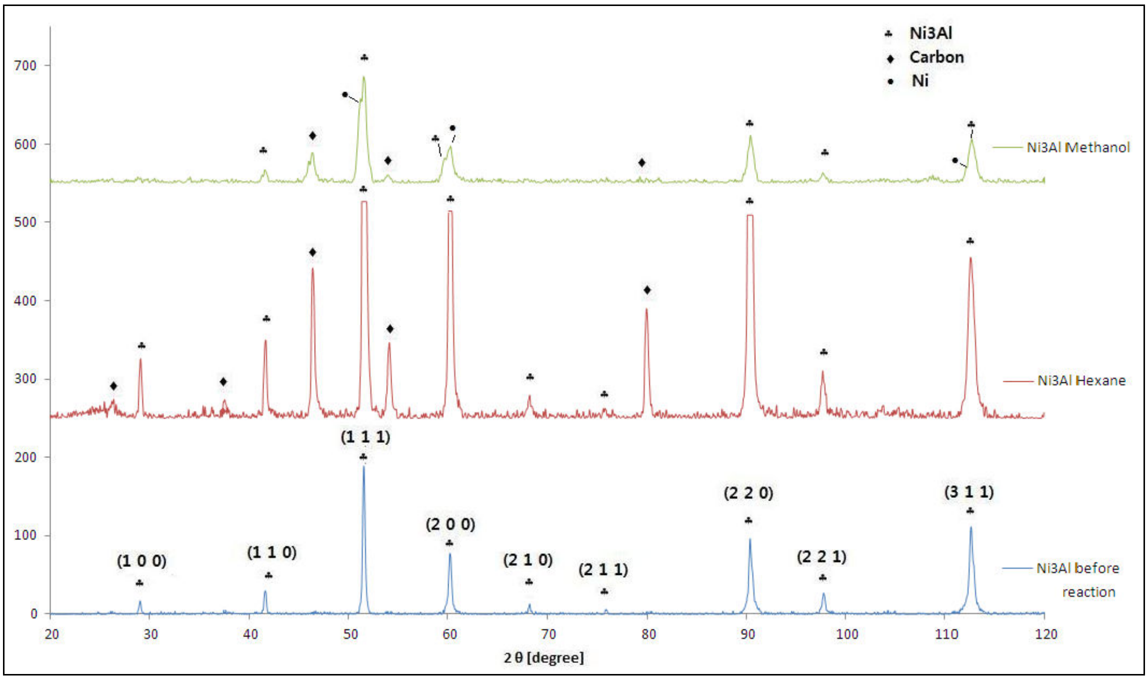

Fig. 5 X-ray diffraction patterns of surface products on Ni_3Al microcrystalline foils: before decomposition , after reaction in methanol, after reaction in hexane

samples after methanol and hexane decompositions are noticed. This observations was linked with metal-like nanostructures decorating the carbon nanofibers (Fig.3(a) and (b)).

For the comparison of x-ray diffraction patterns of the microcrystalline Ni_3Al foil before catalysis reaction and after methanol and hexane decomposition one can see that peaks from Ni and graphite appears in the spectrum. This proves the carbon deposit presence on the Ni_3Al surface after the decomposition reaction.

The XRD analysis of investigated microcrystalline Ni_3Al foils before and after experiments was carried out (Fig. 5). The existence of carbon and pure nickel on the surface of Ni_3Al foils after me thanol decompositions was confirmed. Probably the nickel X-ray diffractions patterns are an effect of mentioned existence of metal-like particles decorating the carbon nanofibers (Fig.3). The XRD investigations of the foils after hexane decompositions show only existence of carbon.

IV. Conclusion

Ni_3Al thin foils demonstrated good catalytic properties for hexane and methanol decomposition. Our main results are summarized as follows:

1) Conversion of methanol on thin Ni_3Al foils reaches approximately 100% above 530 ^oC which is much higher than methanol conversion on quartz (max. approx.65% at 530 ^oC).

2) The hexane conversion on Ni_3Al reaches approximately 100% at 500 ^oC whereas on quartz the hexane conversion is approx. 55% at 600 ^oC.

3) Carbon nanostructure formed during the methanol decomposition are ended with most probably Ni. After the hexane decomposition the metal-like nanoparticles decorating carbon nanostructures are poorly visible at all. This is probably due to a different mechanism of formation of carbon nanostructures, which will be the subject of further research.

4) Carbon nanostructures are thinner and more homogeneous after the methanol decomposition as compared to the nanostructures after the hexane decomposition. Probably it was caused by the absence of water in the products of hexane decomposition or due to a huger number of carbon in the hexane molecule.

5) Existence of carbon nanofibres and nickel nanoparticles on the Ni_3Al foils surfaces after methanol decompositions was confirmed by the X-ray diffraction analysis. The absence of Ni on surface Ni_3Al foils after hexane decomposition may be due to a smaller ratio of Ni in the deposit or different deposit structure. This issue will be the subject of further research.

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