

INVESTIGATIONS INTO CATALYTIC ACTIVITY OF LaNi_5 IN SYNTHESIS OF CARBON NANOTUBES

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Introduction

Numerous methods of synthesis allows preparation of carbon nanotubes (CNT) of different purity and, consequently, with different properties. In particular, this is also related to their sorption properties. Data of different authors on CNT hydrogen capacity may differ by an order due to different conditions for synthesis. Conditions for sorption and hydrogen capacity especially depend on the state of hydrogen (at equal other conditions).

CNT saturation with activated hydrogen occurs under milder conditions.

Any of the hydride-forming metals or alloys may be used for hydrogen activation when its sorption-desorption thermodynamics satisfies the certain conditions.

However, reversible sorption capacity and chemical activity of all the hydride-forming materials greatly depend on the state of their surface. Electronegative impurities (O,N etc.) present on the surface result in deterioration in kinetics of hydrogen sorption. Penetration of impurities into the particle bulk decreases its capacity and leads to its decrepitation.

When particles of hydride-forming metal were covered with protective layers, sorption kinetics and other operating characteristics were deteriorated.

This work is aimed to verify the hypothesis on creation of the hydrogen penetrable, hydrogen-sorbing protective layer of nanostructural carbon on the surface of the hydride-forming particle.

Nanostructural carbon is supposed to be a barrier against electronegative impurities. Dynamic equilibrium of hydrogen sorption-desorption processes will allow the metal particle to be donor of activated hydrogen for nanostructural carbon.

Experimental

LaNi_5 (MmNi_5) intermetallide of AB_5 type was used as a metal hydride-forming component.

We have attempted to grow nanotubes on the intermetallide surface by two methods:

1. Catalytic pyrolysis of acetylene.
2. Electro-erosion sputtering of the alloy of AB_5 type in liquid hydrocarbon.

In the first case intermetallide was mixed with catalyst for CNT synthesis - Ni/Cu (98 wt.%/2 wt.%). The mixtures were prepared beginning from the proportion $\text{NiCu}:\text{LaNi}_5 = 1:1$. The concentration of LaNi_5 fraction was gradually increased by mixing in the ball mill in hydrogen at $P=0.5$ MPa.

Catalytic activity of the mixtures prepared has been investigated in regard to the CNT growth. The mixtures passed through the furnace for catalytic pyrolysis (the apparatus was designed in laboratory 67 in Institute for Problems of Material Science of National Academy of Sciences of Ukraine).

The electric spark erosion apparatus was used in the second case. (The apparatus was also designed in laboratory 67 in Institute for Problems of Material Science of National Academy of Sciences of Ukraine). Hydrocarbons and their mixtures were used as sources of carbon.

Results and discussion

In the first case, in hydrocarbon pyrolysis, CNTs grow on all the mixtures up to the proportion $\text{NiCu}:\text{LaNi}_5=2:98$. At this proportion CNTs do not form on pure LaNi_5 . Therefore, in spite of the fact that intermetallide contains a high amount of nickel, which is catalyst for CNTs growth, CNTs do not form in these experimental conditions.

In the second case, during electric arc LaNi_5 sputtering in the hydrocarbon medium, different carbon-hydrocarbon layers form on the surface of particles. CNTs (Fig.1), similar to those produced by this method on pure nickel [1], have been found only on the particles prepared in solvent-2355.

Conclusions

In catalytic pyrolysis of hydrocarbons in the range from 800 to 1200 °C, LaNi_5 is not catalyst of the CNTs growth at the given experimental conditions.

However, during electric erosion sputtering of this alloy in hydrocarbons (of certain composition), CNTs may grow on the surface of LaNi_5 particles formed.

We can agree with this conclusion if we do not take into consideration the fact that intermetallide might be separated into components in the electric arc, and CNTs might grow on the particles enriched in nickel like in [1-23].

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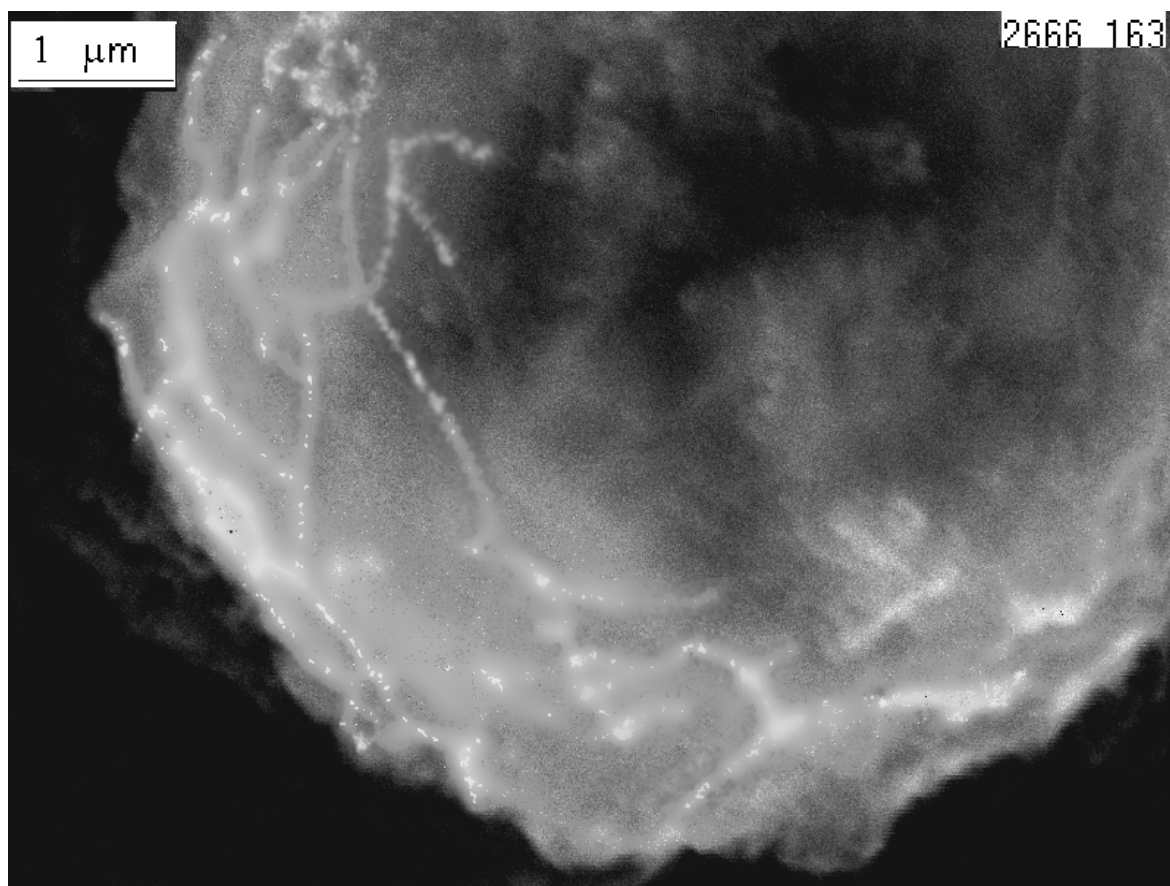


Fig. 1.

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ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОЙ АКТИВНОСТИ LaNi_5 ПРИ СИНТЕЗЕ УНТ

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Введение

Многочисленные методы синтеза позволяют получать углеродные нанотрубки (УНТ) различной чистоты и следовательно с различными свойствами. Это, в частности, отражается и на их сорбционных свойствах. Литературные данные по их водородоемкости, полученные разными авторами, могут отличаться на порядок из-за различных условий синтеза. Условия сорбции и водородоемкость особенно зависят от состояния водорода (при равных других условиях).

Насыщение УНТ активированным водородом проходит в более мягких условиях.

Для активации водорода можно использовать любой гидридообразующий металл или сплав, термодинамика процессов сорбции-десорбции которого отвечает заданным условиям.

Однако реверсивная сорбционная емкость и химическая активность всех гидридообразующих материалов в значительной степени зависят от состояния их поверхности. Наличие на поверхности электроотрицательных примесей (O, N и др.) приводит к ухудшению кинетики сорбции водорода, а при проникновении в объем частицы снижает ее емкость и приводит к декрепитации частицы.

Покрывание частиц гидридообразующего металла защитными пленками приводило к ухудшению кинетики сорбции и других эксплуатационных характеристик.

В настоящей работе проверяется гипотеза создания на поверхности гидридообразующей частицы водородопроницаемой водород-сорбирующей защитной пленки из наноструктурного углерода.

Предполагается, что наноструктурный углерод будет барьером для электроотрицательных примесей. А динамическое равновесие процессов сорбции-десорбции водорода позволит металлической частице стать донором активированного водорода для наноструктурного углерода.

Условия эксперимента

В качестве металлической гидридообразующей составляющей использовался интерметаллид типа AB_5 - LaNi_5 , (MmNi_5).

Нанотрубки на поверхности интерметаллида пытались вырастить двумя методами:

1. Каталитическим пиролизом ацетиленом.
2. Электроэрозионным распылением сплава типа AB_5 в жидком углеводороде.

В первом случае интерметаллид использовали в смеси с катализатором синтеза УНТ Ni/Cu (98%мас./2%мас.). Смеси готовили начиная с отношения NiCu: LaNi_5 =1:1 с постепенным увеличением концентрации фракции LaNi_5 смешиванием в шаровой мельнице в среде водорода при $P=0,5$ МПа.

Полученные смеси исследовали на предмет их каталитической активности в отношении роста УНТ, пропуская их через печь каталитического пиролиза (установки, изготовленной в лаб. № 67, ИПМ НАН Украины).

Во втором случае использовали электроискровую эрозионную установку. В качестве источника углерода использовали углеводорода и их смеси.

Результаты и обсуждение

В первом случае при пиролизе углеводородов УНТ растут на всех смесях до соотношения концентраций NiCu: LaNi_5 =2:98. При этом соотношении компонентов и на чистом LaNi_5 УНТ не образуются. Таким образом, несмотря на высокое содержание в интерметаллиде никеля, являющегося катализатором роста УНТ, в данных экспериментальных условиях УНТ не образуются.

Во втором случае, при электродуговом распылении LaNi_5 в среде углеводородов, на поверхности частиц образуются различные углерод-углеводородные пленки. Только на частицах, полученных в растворителе – 2355 были обнаружены УНТ (рис. 1), подобные полученным этим методом на чистом никеле [1].

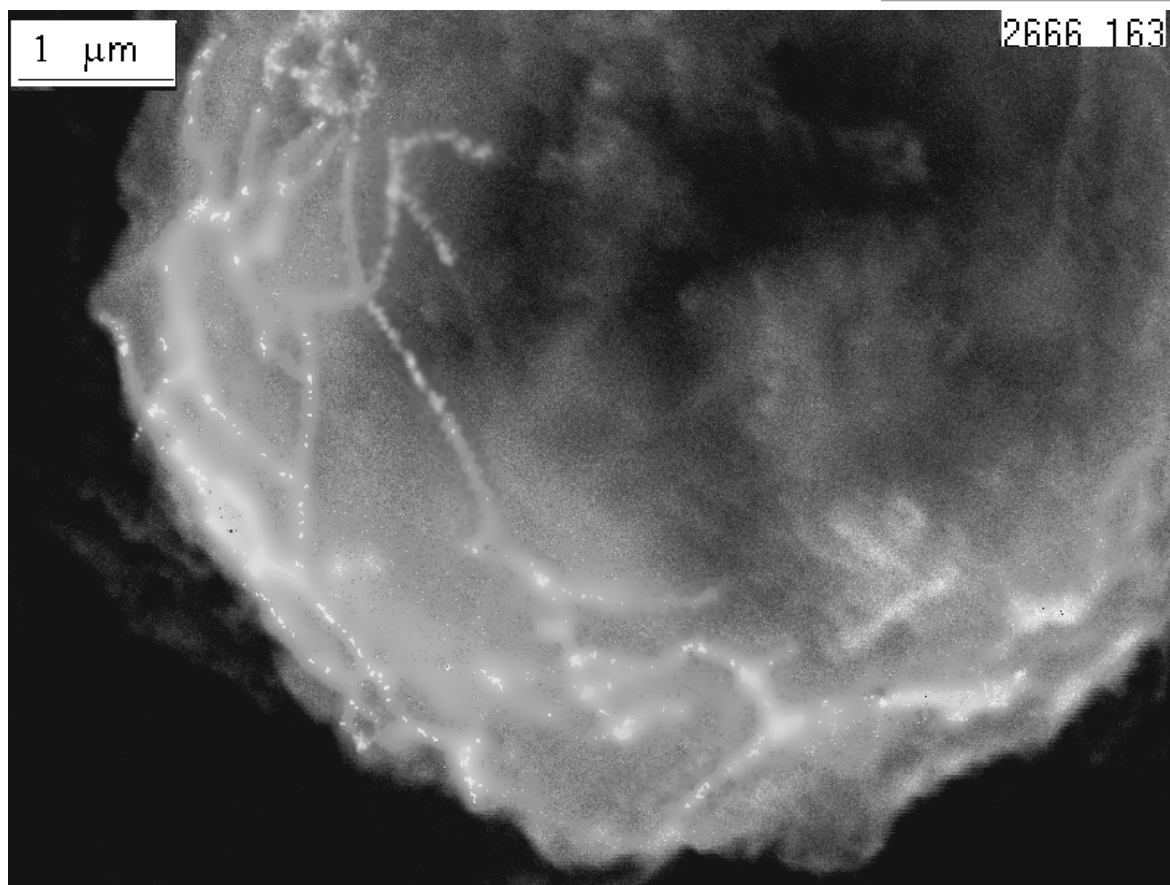


Рис. 1.

Выводы

Интерметаллид LaNi_5 при каталитическом пиролизе углеводородов в температурном интервале $800 - 1200^\circ\text{C}$ не является катализатором роста УНТ при данных экспериментальных условиях.

Однако при электроэрозионном распылении этого сплава в углеводородах (определенного состава) на поверхности образующихся частиц LaNi_5 могут расти УНТ (рис.1).

С этим выводом можно согласиться, если не учитывать тот факт, что в электрической дуге интерметаллид мог разделиться на компоненты и УНТ могли вырасти на частицах, богатых никелем как в [1].

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