

Bulk Metal Alloys as a Precursor of Dispersed Particles Catalyzing Growth of Carbon Nanofibers



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Abstract

Bulk metal alloys can be considered as a precursor of self-organized catalysts consisting of dispersed metal particles fixed within the structure of carbon nanofibers, which were grown as a result of catalytic chemical vapor deposition of halogen-substituted hydrocarbons. Being subjected to interaction with aggressive reaction mixture, the bulk alloy precursors undergo relatively fast process of metal dusting, which ends with complete wastage of initial metal item. The catalysts thus obtained are characterized with excellent long-term stability of operation along with high activity in decomposition of hydrocarbons of different nature. The approach described opens new horizons for a synthesis of nanostructured carbon materials including carbon-carbon composites of bimodal structure.

Keywords: Bulk metal alloys; Metal dusting; Self-disintegration; Carbon nanofibers; Catalytic chemical vapor deposition

Introduction

Industrially manufactured bulk metal alloys mostly being the resistive materials are widely applied in the heating systems (as a heating element), in the explosives and fireworks industry (as a bridge wire in igniters), in ceramic (as an internal support structure), etc. These materials are quite stable under both oxidative and reductive atmospheres, but undergo fast self-disintegration if exposed to carbon-containing (carburizing) medium at elevated temperature. The process of self-disintegration of metal items, also known as a metal dusting, is considered as an actual problem of modern chemical industry, which results in a wastage of chemical reactors [1-9]. Thus, steel reactors operated at 400-800 °C during hundreds hours become almost completely disintegrated into a dust consisting of dispersed metal particles and carbon. The situation becomes more complicated if the aggressive medium of halogen-substituted hydrocarbons is used [10,11].

There are a lot of papers devoted to the study on the mechanism of the metal dusting [1,3,6,7,9]. According to Grabke [1], the process goes through the following stages:

1. Decomposition of carbon-containing precursor with subsequent transfer of carbon into solid solution up to oversaturation.

2. Nucleation of metal carbide phase at surface and grain boundaries and its growth with protrusions into the bulk metal phase.
3. Nucleation of the graphite phase.
4. Decomposition of carbide to metal and graphite. Nano particle formed plays a role of catalytic sites for carbon nanofibers (or nanotubes) growth.

Formed catalytic sites (dispersed metallic or alloyed particles), being stabilized within the structure of carbon nanofibers, catalyze further formation of nanostructured carbon via catalytic chemical vapor deposition. Thereby, the process of self-disintegration (metal dusting) can be proposed as a novel approach to prepare dispersed metal particles from bulk metal precursors for the synthesis of nanostructured carbon [12-17].

Discussion

During the last two decades the process of metal dusting as a way to obtain nanostructured carbon materials attracts more and more attention [12-24]. Carbon nanotubes and nanofibers of various morphologies were produced over stainless steel, iron- and nickel-containing alloys. In all these cases, the surface

of bulk metals was intentionally subjected to controlled process of metal dusting yielding carbon deposits.

As it was already mentioned, the process of self-disintegration is characterized with prolong induction period (up to few hundred hours), when no visible changes take place. At the same time, if the halogenated hydrocarbon is used as a carbon source, the process accelerates significantly [10,11,25,26]. Thus, interaction of bulk nickel alloys (nichrome, chromel, alamel, etc.) with vapors of chlorinated hydrocarbons results in a fast metal dusting with induction period no longer than 3 hours at 550 °C. It should be noted that induction period shortens along with temperature increase. At the end of induction period, the weight of the sample sharply grows up, and the system became inverted into an ensemble of dispersed metal particles fixed within the structure of grown carbon nanofibers. These particles can be considered as self-organized catalyst, and can be applied for decomposition of any other carbon-containing substrates with formation of nanostructured carbon. Thereby it can be concluded that halogen contained in a molecule of substrate affects crucially the rate of metal dusting. HCl emerged in hydrogen-containing reaction mixture provides the occurrence of reversible chlorination-dechlorination process, which leads to quick chemical corrosion of bulk alloy surface. It should be also

emphasize that the addition of hydrogen excess into reaction mixture is required for dechlorination of the alloy surface [10].

The duration of induction period of the self-disintegration process can be shortened by using the pretreatment procedures [25,26]. Among such procedures, the most efficient are etching in a mixture of mineral acids (HCl/HNO₃=3/1, 2-3min) and redox activation (altering of oxidative and reductive treatment at 500 °C, 3 cycles, 90min). These methods make a rough reconstruction of the alloy surface that eases further formation of dispersed active particles.

While the considered alloys are resistive materials, they can be heated up to desired temperature by a direct supply of current. Decomposition of 1,2-dichloroethane in such regime is reported in Ref. [27]. In this case, besides the processes described above, hydrodechlorination and dechloro-coupling reactions take place leading to formation of ethane, ethylene and butenes within the gas phase products. At the resistive heating, the process of substituted hydrocarbon decomposition proceeds through the stages of C-H bond breakage, and hydrogenolysis and breakage of C-C and C-Cl bonds [28]. Unsaturated hydrocarbons and corresponding radical species formed as a result of hydrogenolysis undergo further pyrolysis over nickel crystallites.

Table 1: Maximal yield of carbon obtained over industrially manufactured alloys via catalytic chemical deposition of 1,2 dichloroethane after 2 hours of experiment. Concentration of hydrogen was 40vol.%.

S.No	Alloy	Temperature, °C	Carbon yield, g _C /g _{Al} *	Ref.
1	Nichrome (Ni-80%, Cr-20%)	600	67.5	[26]
2	Nichrome (Ni-80%, Cr-20%), resistive heating	700	24.1	[27]
3	Nichrome (Ni-60%, Cr-15%, Fe-25%)	600	7.3	[28]
4	Chromel (Ni-90%, Cr-10%)	700	6.3	[26]
5	Alumel (Ni-95%, Al-2%, Mn-2%, Si-1%)	700	1.6	[28]
6	Coptel (Ni-43%, Cu-56.5%, Mn-0.5%)	700	5.2	[28]
7	Kanthal (Fe-65%, Cr-30%, Al-5%)	700	3.0	[29]
8	Stainless Steel	700	0.5	[28]

*g_C -weight of carbon product; g_{Al} -weight of alloy sample

Table 1 summaries the data on carbon yield resulted from catalytic chemical deposition of 1,2- dichloroethane during 2 hours over different industrially manufactured alloys. As seen, among the studied alloys, nichrome (Ni-80%, Cr-20%) occupies the leading position. It allows one to obtain the carbon yield of 67.5 g_C/g_{Al}, which surpasses the values for other samples in one order of magnitude. If the resistive heating is applied (Table 1, row #2), the carbon yield over the same type of nichrome decreases in approximately three times, which is connected, as it was mentioned above, with occurrence of parallel processes [29]. The lowest carbon yield (0.5g_C/g_{Al}) was observed in the case of stainless steel, thus indicating that 2 hours is not long enough time for such kind of bulk precursor.

Besides the industrially manufactured alloys, similar solid solutions of predefined composition can be especially prepared via multi-stage route involving coprecipitation of salt followed by high-temperature reduction in hydrogen, or via single-stage route of mechanical alloying of metal powders in a planetary mill [30-32]. An advantage of the first approach is a guaranteed formation of solid solution with desired ratio of the metals and homogeneous distribution. The formation of solid solutions was confirmed by precise powder X-ray diffraction analysis [33-38]. Data on carbon yield over such alloys are shown in Table 2. As it follows, the nature and loading of an alloying metal affect noticeably the productivity of bulk precursor towards carbon. Thus, addition of iron worsens the catalytic behavior of the resulted alloy, while molybdenum, oppositely, significantly

enhances it. It should be mentioned that these especially prepared alloy samples being subjected to complete self-disintegration process under aggressive medium of 1,2-dichloroethane can also be considered as self-organized catalyst for further usage in decomposition of various organic substrates [39].

Table 2: Maximal yield of carbon obtained over nickel-based alloys prepared by coprecipitation via catalytic chemical deposition of 1,2-dichloroethane after 2 hours of experiment. Concentration of hydrogen was 40 vol.%; temperature in all experiments was 600 °C.

S.No	Alloy	Carbon yield, g _C /g _{Al} *	Ref.
1	Ni ₉₅ Cr ₀₅	24.0	[34,37]
2	Ni ₉₉ Cu ₀₁	27.0	[34,36]
3	Ni ₉₉ Co ₀₁	26.4	[34,36]
4	Ni ₉₀ Fe ₁₀	3.5	[34,38]
5	Ni ₉₂ Mo ₀₈	34.0	[28]
6	Ni ₉₅ Pd ₀₅	25.0	[33]
7	Ni ₉₅ Pt ₀₅	26.0	[28]

*g_C–weight of carbon product; g_{Al}–weight of alloy sample.

Self-organized catalysts obtained using both types of bulk precursors (industrially manufactured and especially prepared) were found to be quite active and extremely stable in catalytic decomposition of various hydrocarbons and their mixtures (C₂H₆, C₂-C₄ mix, C₆H₆) [40]. Additionally, it was shown that even chlorofluorocarbons can be efficiently decomposed, but in this case introduction of odd hydrogen into reaction feed is of great importance in order to bind the halogen atoms into HF and HCl. Surprisingly, the interaction of CF₂Cl₂ with submicron Ni crystals formed during the self-disintegration of bulk alloy precursor and fixed within the structure of carbon nanofibers causes their secondary disintegration which leads to formation of unique bimodal carbon nanomaterial.

All processes of catalytic chemical vapor deposition with formation of carbon nanofibers described above were considered within a concept of flow-through or ‘open’ systems, when the reagent(s) continuously inlets into the reaction volume and the gas phase products pass the volume away. On the other hand, application of so called ‘closed’ reaction volume system was recently shown to be perspective for synthesis of various nanostructured inorganic materials [41-46]. Regarding the decomposition of substituted hydrocarbons, the process has the same requirements as in the case of ‘open’ system: both halogen and hydrogen source substrates should present in a reaction volume. Thus, for example, the use of halogenated organics (hexafluorobenzene, hexachlorobenzene, 1-bromobutane 1-iodobutane, etc.) together with hexamethylbenzene (as an inner hydrogen source) was shown to initialize the metal dusting process of bulk NiCr alloy with formation of nanostructured product [46]. Depending on the nature of halogen-containing substrate, the starting temperature of active particles formation detected by means of a ferromagnetic resonance spectrometry was different. The approach additionally provides a possibility

to study the metastable reaction intermediates, which is inaccessible in the flow-through regime.

Conclusion

Preparation of the catalysts for various catalytic processes remains to be a challenge task. At the same time, creation of the appropriate, in most cases aggressive, conditions for the catalyst’s precursor might shift the system towards state of self-organization. One of the most illustrative examples of this phenomenon is a nickel-based catalytic system for chemical vapor deposition of halogen-substituted hydrocarbons resulting in formation of nanostructured carbon fibers. Conventionally used for this process Ni-containing catalysts supported on oxide or carbonaceous supports are known to be rapidly deactivated under the reaction conditions. Oppositely, bulk metal alloys subjected to interaction with aggressive halogen-containing medium were shown to undergo the metal dusting process, which ends with complete wastage of initial bulk item. The dispersed metal particles formed as a result of such self-disintegration were found to be quite stable and extremely active in decomposition of any other substituted and unsubstituted hydrocarbons that allows one to consider them as self-organized catalysts. The main regularities of the process are similar for the cases of external and direct (resistive) heating of the bulk alloy precursor, and if compare ‘open’ reaction volume systems with ‘closed’ one.

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