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Polymetallic copper-rhenium composite material

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A method to obtain new copper-rhenium composites on a steel substrate using a complex of dirhenium(III) cis-tetrachlorodi-μ-propionate with axial N,N-dimethylacetamide (cis-$[Re_2Cl_4(C_2H_5COO)_2(DMAA)_2]$) and copper metal as starting materials for low-temperature chemical vapor deposition, was investigated. The obtained copper-rhenium composite was studied by scanning electron microscopy and X-ray spectroscopy. According to the elemental analysis the composite contained 71.53% Fe, 25.45% Cu, 1.99% Re, and 1.04% Sn.

Composite / Rhenium / Copper / X-ray analysis / Scanning electron microscopy / Thermal decomposition

Introduction

The development of catalytic systems with active centers based on refractory transition metals is one of the challenges of modern inorganic chemistry.

We have been working on the development of catalytic systems based on rhenium [1] for more than five years.

A multitude of different methods of obtaining composite materials are known, *e.g.* to produce copper-diamond composites [2]; tungsten-copper composites protected with rhenium metal, by the CVD-method enhanced with plasma for details in rockets [3]; rhenium-tungsten carbide composites [4]; and many others [5-7]. A process has been developed applying a catalytic-active copper-rhenium composite material at low temperature with gas-phase thermal decomposition of organometallic compounds.

The method of gas-phase deposition of coatings, which was proposed by the English chemist Mond in 1889 and is now known as the CVD-method (chemical vapor deposition), is one of the most common methods for preparing coatings at present.

Despite the fact that the CVD-method was invented a long time ago, there are still problems to choose the starting materials for its application. Convenient compounds must satisfy the following requirements: high volatility at the relatively low temperatures of the CVD-process, stability below the operating temperature of the process, and sufficiently high vapor concentration to achieve an optimal growth rate of the metal deposit. These requirements are satisfied by the chlorocarboxylate of dirhenium(III) that we present below.

Experimental

In this research the starting complex was synthesized without using the autoclave method, by boiling equimolar quantities of tetrabutylammonium octahlorodirhenate(III) ($[(N(Bu)_4)_2Re_2Cl_8]$) in the corresponding acid under inert atmosphere. The purity of the complexes was checked by spectrophotometry [8].

Before depositing the composite, the steel substrate was polished with abrasive paper and degreased in dimethylketone.

The device for obtaining the composite consists of a tubular reactor, two heaters, an inlet for inert gas and a water seal (Fig. 1).

Following the CVD-method developed here, a polymetallic composite material based on rhenium was obtained by thermal decomposition of cis-$[Re_2Cl_4(C_2H_5COO)_2(DMAA)_2]$. It was established that the thermal decomposition of cis-$[Re_2Cl_4(C_2H_5COO)_2(DMAA)_2]$ consists of three consecutive reactions (Fig. 2). During the first stage of heating (290°C), two molecules of N,N-dimethylacetamide are removed from the complex; the second stage is a stage of cis-trans-isomerization and evaporation of the complex; on the third stage, in a zone of heater number 2, we observed thermal destruction of the trans-complex with deposition of metallic rhenium.

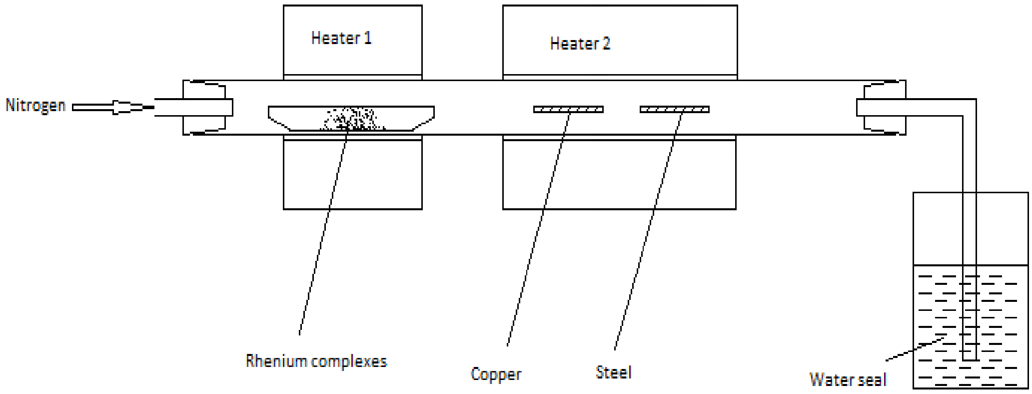

Fig. 1 Scheme of the reactor.

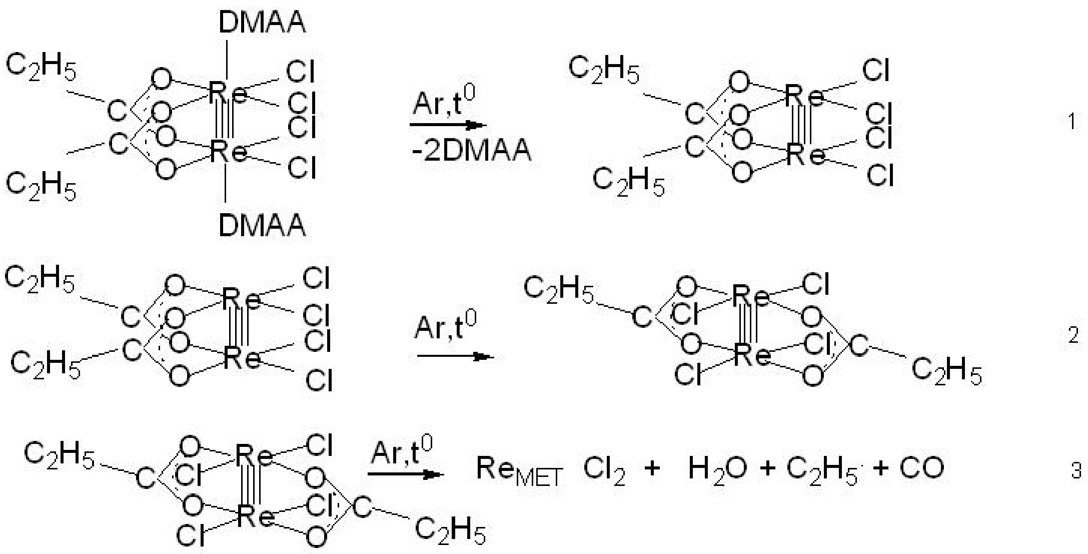

Fig. 2 Stages of the thermochemical decomposition of cis-[$Re_2Cl_4(C_2H_5COO)_2(DMAA)_2$].

The method involves heating the initial cluster in a stream of inert gas at a temperature of 290ºC on the heater 1 and 900ºC on the heater 2 for 1.5 h.

It is likely that the formed trans-complex decomposes on the first plate of copper with the formation of carbon(II) oxide and chlorine. Chlorine reacts with metallic copper, which results in the formation of copper(II) chloride ($CuCl_2$). Then, at higher temperatures, the copper(II) chloride decomposes with evaporation to copper(I) chloride and subsequent formation of Cu_2Cl_2 dimers. The obtained Cu_2Cl_2 is transported with volatile trans-[$Re_2Cl_4(C_2H_5COO)_2$] in the inert gas phase to a steel substrate, located next to the copper substrate. The decomposition of volatile trans-[$Re_2Cl_4(C_2H_5COO)_2$] occurs with deposition of metallic rhenium and reduction of the volatile Cu_2Cl_2 to metallic copper by iron and evaporation of iron(III) chloride $FeCl_3$ (boiling temperature 315ºC) on the steel substrate at 900ºC.

Analysis and discussion

Fig. 3 shows the copper-rhenium composite. The composite covers the steel substrate completely. On the surface of the composite we detect no defects such as cracks or exfoliations.

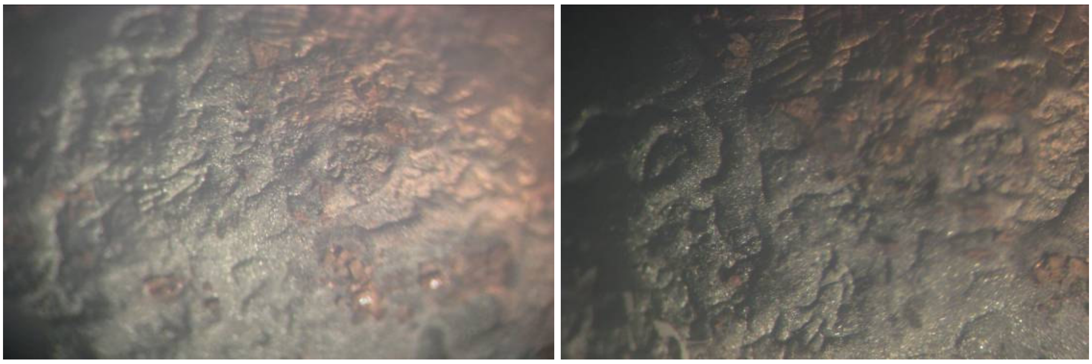

Fig. 3 Photos of the copper-rhenium composite.

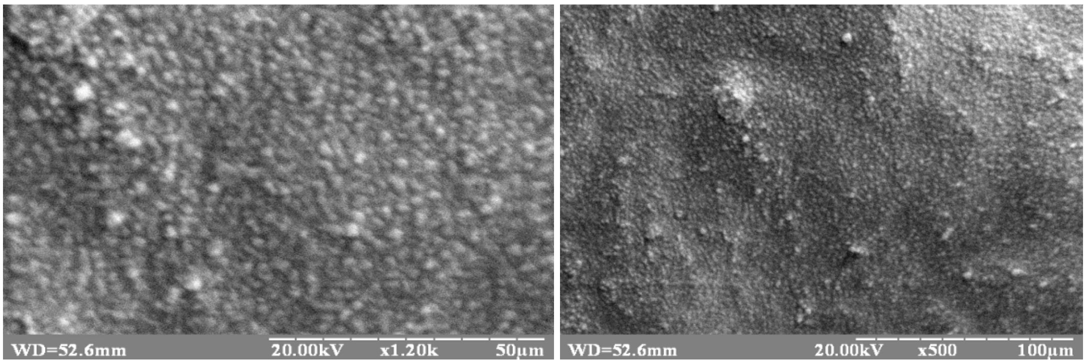

Fig. 4 SEM of the copper-rhenium composite material prepared by gas-phase reaction of trans-$[Re_2Cl_4(C_2H_5COO)_2]$ and dimeric Cu_2Cl_2 under inert atmosphere. The composite was obtained by thermal decomposition on a steel substrate at 900°C.

The obtained coating was investigated by scanning electron microscopy using an analyzer SEMMA-102-02 (Fig. 4). The size of the particles ranged from 10 to 25 µm. According to the micrographs, the coating was formed by homogeneous polycrystals and polycrystalline aggregates.

The formation of polymetallic material is the result of the process of formation and decomposition of volatile trans-$[Re_2Cl_4(C_2H_5COO)_2]$ and copper(I) chloride dimers. The decomposition of dimeric copper(I) chloride provides the transfer of ultra pure copper to the steel substrate from the copper plate, located in front of the steel substrate. The composition of the copper-rhenium composite (Fe – 71.53%; Cu – 25.45%; Re – 1.99%; Sn – 1.04%) was studied by micro X-ray spectral elemental analysis.

Metal chlorides were not detected on the surface of the composite. The coatings were tested in corrosive environments of acids and alkalies for 170 h. Appreciable changes in the structure were not seen. The thickness of the coating was 1.7-3.2 µm.

Conclusion

Simultaneous vapor coplating of several metals represents certain difficulties, especially in the choice of the starting substances. The main argument when choosing the precursors is their chemical inertness, *i.e.* they should not react with each other below the temperature of thermal decomposition. In this work we have implemented a new approach – instead of choosing two volatile precursors we used one precursor (a complex of dirhenium(III) with chlorocarboxylate) and copper metal, which reacted with each other, evaporated and coplated on a steel substrate.

The proposed method can be a prototype for obtaining new polymetallic catalytic systems for petrochemical industry, catalysts for neutralization of industrial and traffic emissions, in organic synthesis, *etc*. The obtained material can also be used for the production of refractory protective coatings based on rhenium and other refractory metals for rockets.

Using the method of chemical vapor deposition we can obtain new materials with new properties and deposit ultra-pure metals, because crystallization from the gas-phase has a powerful purifying effect.

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