

Characterization of Ni-Cd Nanostructured System Obtained by Chemical Reduction of Salts

V.M. Pugachev^{1*}, Yu.A. Zaharov^{1,2}, A.S. Valnyukova^{1,2}, V.G. Dodonov¹

¹Kemerovo State University; Russia, 650043, Krasnaya str. 6, Kemerovo, Russia

²Institute of Coal Chemistry and Chemical Material Science, 650000, av. Sovjetskii, 18, Kemerovo, Russia

Article info

Received:

25 May 2015

Received and revised form:

28 June 2015

Accepted:

26 July 2015

Nomenclature

XRD – X-ray diffraction;

SAXS – small angle X-ray scattering;

FCC – face-centered cubic compact.

Abstract

The process of obtaining of highly dispersed metal powders of Ni-Cd system by reduction of their salts by hydrazine in aqueous medium at high alkalinity was investigated. The possibility of production metal powders containing up to 50 mol% of cadmium is established and conditions for their synthesis are optimized. Phase composition, structural parameters, dispersity of solid products during the reduction process were studied by X-ray diffraction (XRD) and SAXS. The formation of metal solid solutions with FCC lattice contradicts to the known phase diagram for Ni-Cd and may be explained by increasing the energy of the particles in the nanostate. The formation of intermetallide NiCd₅ in the studied compositions area is caused by sequential character of reduction process; as a result the metal product on the initial stage of reduction is significantly enriched with cadmium.

1. Introduction

Highly dispersed polymetallic powders based on the iron group metals are quite interesting from both a technical and scientific point of view [1–3]. The main areas of their applications are based on magnetic and catalytic properties of these materials, which can vary significantly depending on the chemical and phase composition, dispersion and also on the fact whether the phases of a system are in equilibrium state or not. These questions – dependence of structural and phase state of these systems on sizes of the constituent particles (crystallites) and the synthesis conditions – are important for modern material science and physical chemistry of nanoscale and nanostructured systems. Among the main features of a general character detected during the synthesis and study of a number of systems based on iron metal group [4–11] are the following: 1) the formation and coexistence of non-equilibrium phases; 2) the formation of phases belonging to a significantly higher temperature than during synthesis; 3) the formation of solid solutions with considerably greater content of a second component than it follows from the phase diagrams.

Besides, there was not revealed the formation of intermetallic compounds which are known, in particular, for Fe-Co and Fe-Ni systems. Perhaps this is caused by the proximity of the properties of iron group metals, because of what the energy gain by the formation of ordered states, like intermetallic compounds, compared with solid solutions (disordered state) is small. In this regard, the hope for intermetallic compounds formation in the system Ni-Cd is certainly more.

2. Experimental

The synthesis of powders of investigated system was carried out using the method close to procedure of synthesis of individual metals in the row Fe-Cu including their mutual systems [6–7] and also taking into account [12]. In this case coprecipitated hydroxides subjected to reduction by hydrazine (in the form of hydrazine hydrate) under the high alkalinity conditions. In some cases, these hydroxides are monophasic solid solutions in the other – it may be two different solid solutions. The formation of such a highly mixed nanoscale states (both on physical and on chemical level) ultimately promotes the formation of mixed metallic phases.

* Corresponding author. E-mail: vm1707@mail.ru

Usually the temperature required when reduction previously studied systems is 360–370 K. However, at high values of standard redox potential the process can be undertaken at a lower temperature (for example, in the case of copper). By the value of the redox potential, the system Ni-Cd is close to the system Fe-Ni. So for the hydroxides of iron, nickel and cadmium the values -0.877 ; -0.72 ; -0.81 V respectively are known. Nevertheless, obtaining the metal product in the Ni-Cd system proved possible only at significantly more severe conditions – at the boil the reaction mixture at about 500 K.

Base composition of initial reaction mixture is following: metal salts – 0.34 M (Me), sodium hydroxide – 4 M; hydrazine – 4 M. With the purpose of optimization and depending on metals ratio, the composition has considerably been varied.

The obtained high-dispersed powders were investigated by usual X-ray diffraction (XRD) and SAXS techniques. Phase composition and structure parameters determination were carried on DIFREY-401 (Russia) and D8 ADVANCE (Germany) X-ray diffractometers. SAXS measurements were carried out using small-angle X-ray diffractometer KRM-1 (Russia). In all cases Fe $K\alpha$ radiation was used. The mathematical treatment of X-ray diffraction data was performed with the help of computer programs created by the authors [13] and also by means of Microsoft Office.

3. Results and Discussion

Unlike the previously studied metals in the row Fe-Cu and their mutual systems the reduction process of mixed or partially mixed Ni-Cd hydroxides is characterized by an induction (latent) period. Its duration is 5–45 min and depends on initial concentrations of reagents in the reaction medium and ratio of metals. Generally the smaller is content of cadmium in the system and greater the overall concentration of the reagents, the shorter is duration of the induction period. However the reproducibility of induction period duration is not quite reliable: at the same initial conditions, the duration of the induction period may differ even twice.

Since the process is carried out in boiling mode its duration is limited by time of liquid phase evaporation. Under certain conditions due to large induction period the reduction reaction may not start at all. As a result yet we failed carry out the reduction process for the compositions containing more than 50 mol% of cadmium.

Carrying out the reduction process for a limited time allows to fix the different stages of conver-

sion of intermediate solid product from precursors into a final products. So at the cadmium content of 10 mol% after 10 and 20 min of reduction process, X-ray diffraction pattern reveals almost only the diffraction lines of hexagonal brucite structure of mixed Ni Cd hydroxide. During these 20 min a significant change of the profile of the diffraction reflections takes place – they become narrower that indicates on hydroxide crystals growth (aging effect). It is well seen also from SAXS data (Fig. 2).

The strongest reflex 111 of metal FCC phase (about 56 degrees) in 20 min is still very small, but then the process goes faster and already in 30 min the amounts of hydroxide and metal become comparable. This is seen both on XRD patterns (Fig. 1), and on size distribution curves (Fig. 2). The transformation of initial substance into a final product looks clearer depending on the time since the apparent beginning of reduction reaction (a color change of the reaction medium) (Fig. 3).

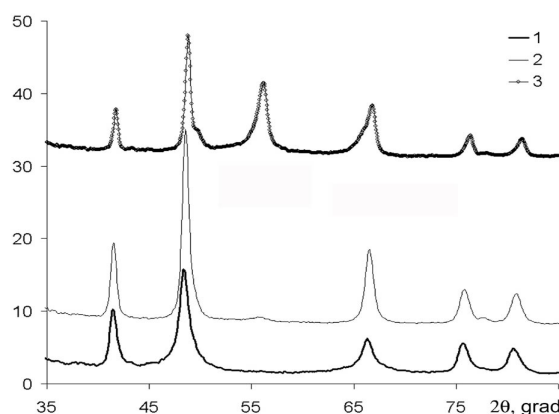


Fig. 1. XRD patterns for the reduction during 10 (1), 20 (2) and 30 (3) min; 10 mol% of cadmium.

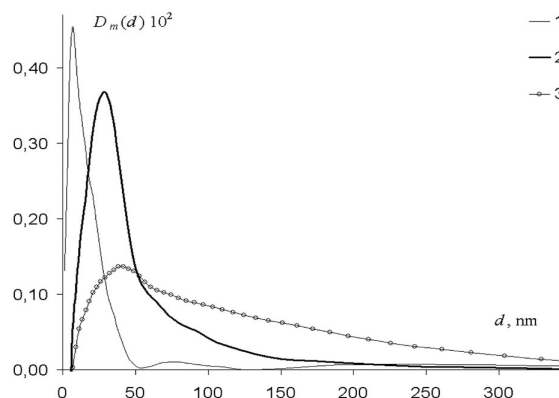


Fig. 2. The particle size distribution in the products of incomplete reduction of nickel-cadmium hydroxides: 1 – 10 min of reduction; 2 – 20 min; 3 – 30 min; 10 mol% of cadmium.

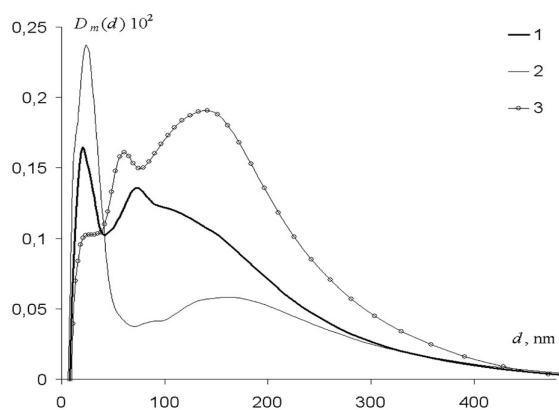


Fig. 3. The particle size distribution in the products of incomplete reduction of nickel-cadmium hydroxides: 2 min from the start of reaction (1), 4 min (2) and 8 min (3); 5 mol% of cadmium.

Another important feature of the reduction process is following: despite the fact that the rate of reduction process becomes in general slower with increasing of cadmium content, cadmium is reduced first. This can be seen (Fig. 1) from the shift of the reflexes of mixed hydroxide to larger angles. It is the result of reduction of cadmium content in it and therefore decreasing of lattice parameters.

The influence the amount of alkali on the reduction process is observed in the experiments using of 6–8 g of sodium hydroxide. Base composition (4 M) corresponds to 8 g of NaOH; at less quantity the initial concentration is proportionally smaller. It is clearly seen that a small change in alkalinity is generally significantly affect the rate of reduction. At equal time of reduction (30 min) the intensity of reflexes 111 (56.0 deg) and 200 (65.5 deg) of FCC metal phase increases while reflexes of the mixed hydroxide (all others) symbatically disappear almost to zero at 8 g of alkali (Fig. 4). Similarly, on size distribution function the fraction of 20–30 nm, belonging to a hydroxide phase, decreases in favor of basic mode 150–170 nm and mode 40–50 nm, obviously corresponding to phase of metal product (Fig. 5).

The considered area (up to 10 mol% of cadmium) is almost monophasic in regarding both to mixed hydroxides formation and the final metal product. The confirmation of solid metal solutions formation (besides the results of X-ray analysis) is the obtained by us dependence of the lattice parameters on the composition of system (Fig. 6). Hypothetical line shows how the lattice parameter should change at gradual replacement of nickel atoms by larger cadmium atoms and is built on the basis of elementary geometric representations.

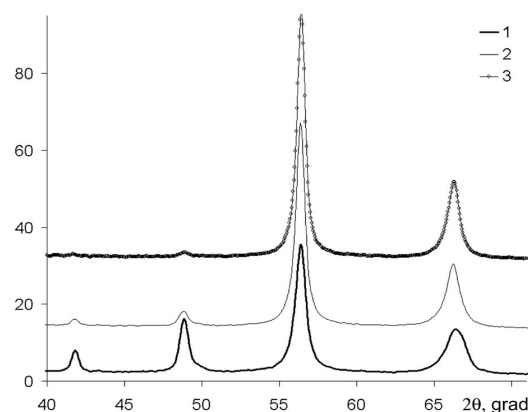


Fig. 4. XRD patterns at 30 minute recovery using 6 g (1), 7 g (2) and 8 g (3) of sodium hydroxide; 10 mol% of cadmium.

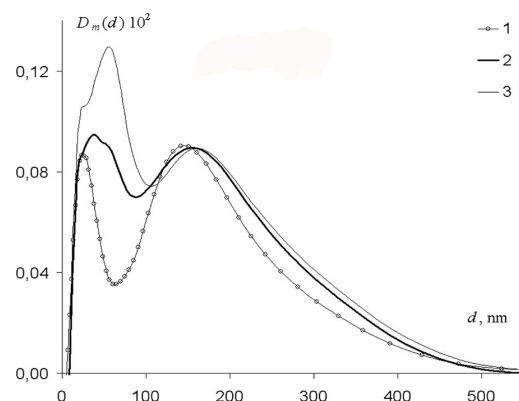


Fig. 5. The particle size distribution in the reduction products of nickel-cadmium hydroxides during 30 min effect of amount of alkali: 6 g (1), 7 g (2), and 8 g (3) of sodium hydroxide; 10 mol% of cadmium.

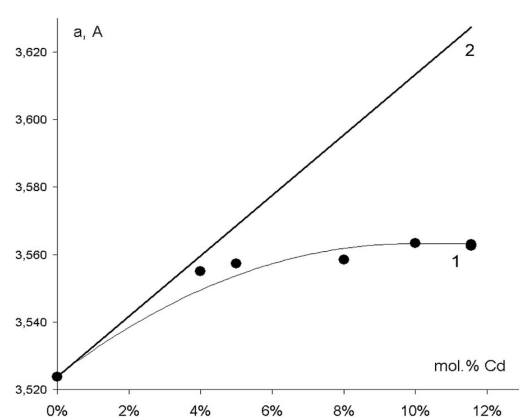


Fig. 6. The dependence of the lattice parameter of the metal phase (FCC type) from mole fraction of cadmium in the system: experimental (1) and hypothetical (2).

Formation of solid solutions of nickel and cadmium does not correspond to the known phase diagram for this system (Fig. 7) according to which the equilibrium phases in this area should be nickel

and intermetallide NiCd. That is, in this case, like in others nanostructured and nanosize systems we have studied, the formation of non-equilibrium (supersaturated) solid solutions takes place. The probable cause of their formation is mainly an increased energy of nanosized state.

According to the plot (Fig. 6), the observed solubility has a limit at about 8–10 mol%. A clear discrepancy between the experimental curve and the possible hypothetical line may indicate not only a more complex character of this dependence but also a possible presence (formation) of the second metal phase in small amounts insufficient for an explicit manifestation in the XRD.

Compositions with a higher proportion of cadmium at a base composition of the initial reaction mixture are reduced difficultly. To intensify the process it is necessary to increase the amount of hydrazine or reduce initial amounts of metal salts.

In the range of 10–50 mol% of cadmium the hydroxides are represented by two phases: mixed nickel-cadmium hydroxide and almost pure cadmium hydroxide. Both hydroxides have a structure of brucitetype. Reflexes of mixed hydroxide are located to the left of the lines of nickel hydroxide depending on the cadmium content in it. The position of cadmium hydroxide reflexes is very stable. This fact indicates that the cadmium hydroxide may enter into the lattice of nickel hydroxide during the precipitation with alkali, whereas the nickel hydroxide does not enter into the cadmium hydroxide lattice.

The final metal product is also two-phase. Besides the FCC solid solution, the intermetallide NiCd₅ is formed which characterized by only one intensive line of about 49.5 degrees. This intermetallide begins distinctly to appear on the XRD at 20 mol% of cadmium, especially in the early stages of reduction (Fig. 8). It is well seen that the ratio of the intensities of the main reflexes of the intermetallide (about 50 deg) and the FCC phase (about 56 deg) is rapidly changed in time in favor of the FCC phase. Besides, the intermetallide line shifts to larger angles due to enrichment of the intermetallic compound by nickel. All this suggests that cadmium is reduced faster than nickel (before nickel). If the content of cadmium is less than 10 mol%, the intermetallide is formed in a very small quantity; it can also change into other forms more enriched by nickel, mainly, the normal FCC solid solution. At the content of cadmium 20 mol% or more the intermetallide prevails in the metal product only in the early stages of reduction process. The amount of intermetallide in the final product correlates with a total cadmium content in the composition (Fig. 9).

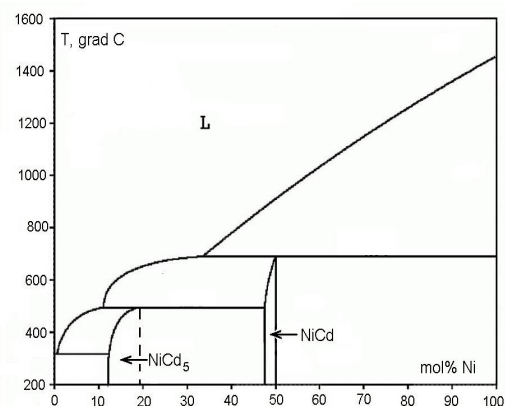


Fig. 7. The phase diagram of the Cd-Ni system [14].

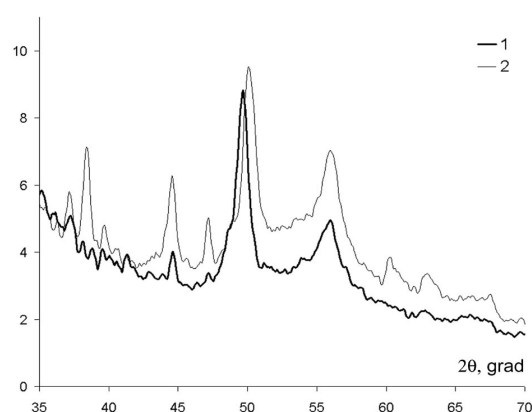


Fig. 8. XRD pattern in the recovery times of 12 min (1) and 15 min (2); 20 mol% of cadmium.

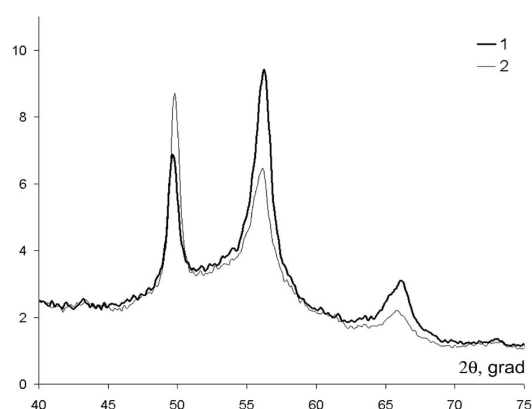


Fig. 9. XRD reduction products of compositions containing 25 mol% (1) and 30 mol% (2) of cadmium.

On the XRD the diffraction lines of intermetallide are commonly narrower than the lines of FCC phase, i.e. the intermetallide crystallites are larger. This is also seen on the particle size distribution functions (Fig. 10). The broadening of XRD line is about 0.5–1.2 degrees, that corresponds to the crystal size of 10–20 nm. But it is necessary to

take into account that the broadening is partly due to the inhomogeneity of the crystal composition, so the estimated crystallite size may to some extent be understated. The average particle size on the size distribution curves obtained from SAXS, of course, higher (100–200 nm), but this is natural, because it depends on the size of not only individual nanocrystals but also polycrystalline agglomerates. As a rule, quite definite correspondence is observed: the larger is crystallite size the larger is size of agglomerates. However, on the particle size distribution functions the modes corresponding to the individual crystallites, which form the polycrystalline agglomerates may appear. In this case, such modes are distinctly appearing in the area of about 20 nm, which coincides with the estimates of the crystallite size from the broadening of the diffraction lines.

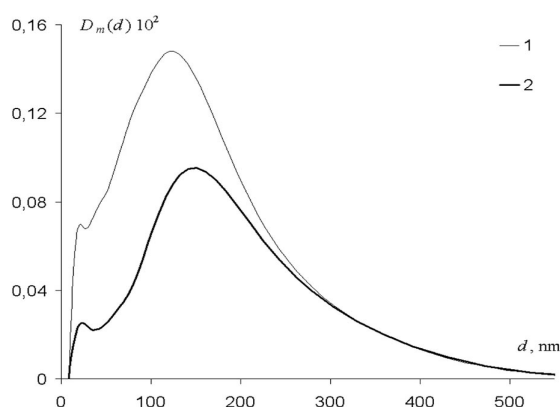


Fig. 10. The particle size distribution in the metal product: 25 mol% (1) and 30 mol% (2) of cadmium.

4. Conclusion

On the basis of results obtained in studied range of compositions it can be stated that the main peculiarities of Ni-Cd system connected with the synthesis conditions and nanosize factor are characteristic for systems of metals in the row Fe-Cu. The obtained high-dispersed powders at a sufficiently high content of the second component contain two non-equilibrium phases. It is caused by predominant reduction of one of the components on the initial stage of the reduction process. As a result, even at relatively small amount of the component which is reduced faster (sooner) obtained particles (crystals) may contain of this component much enough. That is why in such system is possible the formation of intermetallide NiCd₃, even if the content of cadmium in the system is only 15–20 mol%.

Acknowledgments

The present work was supported by the RFFI (grant № 16-33-00829 mol_a) and the Ministry of Education and Science of the Russian Federation (project 2014/64) and using equipment of the Collective Using Centre of Kemerovo Science Centre of Siberian Branch of the Russian Academy of Sciences.

References

- [1]. Yu.D. Tretjakov, E.A. Gudilin, *Vestnik RAN* 79 (1) (2009) p. 3–17.
- [2]. I.V. Melikhov, *Vestnik RAN*, 11 (2007) 988–996.
- [3]. A.F. Kravets, A.N. Timashevskii, B.Z. Yanchitsky, O.Yu. Salyuk, S.O. Yablonovsky, S. Andersson, V. Korenivski, J. Magn. Mater. 324 (2012) 2131–2135.
- [4]. Yu.A. Zaharov, A.N. Popova, V.M. Pugachev, V.G. Dodonov, *Polzunovskii vestnik [Polzunovsky bulletin]* 3 (2008) 79–83 (in Russian).
- [5]. Yu.A. Zaharov, A.N. Popova, R.P. Kolmykov, V.M. Pugachev, V.G. Dodonov, *Perspektivnye materialy [Advanced materials]* 6 (2008) 249–254 (in Russian).
- [6]. Yu.A. Zaharov, V.M. Pugachev, V.G. Dodonov, A.N. Popova, *Perspektivnye materialy [Advanced materials]* 3 (2010) 60–72 (in Russian).
- [7]. Yu.A. Zaharov, V.M. Pugachev, V.G. Dodonov, R.P. Kolmykov, O.V. Vasiljeva, Yu.V. Shipkova, *Perspektivnye materialy [Advanced materials]* 11 (2011) 156–164 (in Russian).
- [8]. Yu.A. Zaharov, V.M. Pugachev, V.G. Dodonov, A.N. Popova, R.P. Kolmykov, G.A. Rostovtsev, O.V. Vasiljeva, E.N. Zyuzjukina, A.V. Ivanov, I.P. Prosvirin, *J. of Physics: IV Nanotechnology Intern. Forum (Rusnanotech 2011, Moscow); Conf. Series* 345 (2012) 012024–012031.
- [9]. A.N. Popova, Yu.A. Zaharov, V.M. Pugachev, *Mater. Lett.* 74 (2012) 173–175.
- [10]. Yu.A. Zaharov, V.M. Pugachev, A.N. Popova, V.G. Dodonov, Yu.V. Karpushkina, B.P. Tolochko, A.S. Bogomyakov, V.V. Kriventsov, *Bulletin of the Russian Academy of Sciences: Physics* 77 (2) (2013) 142–145.
- [11]. Yu.A. Zaharov, V.M. Pugachev, K.A. Dativ, V.G. Dodonov, Yu.V. Karpushkina, *Vestnik KemGU [Bulletin KemGU]* 3 (55) (2013) 77–88 (in Russian).
- [12]. A.D. Pomogailo, A.S. Rozenberg, I.E. Uflyand, *Nanochastitsy metallov v polimerah*, Moscow: Khimiya, 2000, 672 p.
- [13]. V.G. Dodonov, *Z. Kristallogr. Supplied issue*, 1991, № 4, p.102.
- [14]. *Diagrammy sostoyaniya dvoinykh metallicheskih system [The diagrams of binary metallic systems]: V.1, Ed.: N.P. Lyakisheva, Moskva: Mashinostroenie, 1996, 992 p. (in Russian).*