INDUSTRIAL TECHNOLOGIES FOR HYDRIDE MATERIALS PRODUCTION BASED ON $LaNi_5$

Mordovin V.P., Kassimtsev A.V[1]., Alekhin V.P[2]., Zhigunov V.V[3].

Baikov Institute of Metallurgy and Materials Science RAS , 49 Leninsky Av., Moscow, 117911 Russia
1 – ZAO "Polad", 1 Novotulsky str., Tula, 300016 Russia
2 – Moscow State Industrial University, 16 Avtozavodsky str., Moscow 109280 Russia
3 – Tula State University, 92 Lenin Av., Tula, 300600 Russia.

Introduction

Nowadays a number of trends in the hydrogen energy industry involved in researching hydride materials (HM) are on the brink of introducing such materials into industry. As a result there is obviously a vital need in technologies for industrial production of the said materials.

Results and Discussion

In the given report one could see the main characteristics of the industrial technologies concerning HM production based on $LaNi_5$ by means of metal components melting and by CaH_2 treatment of oxide and metal mixtures. Here one could also get an idea about the influence of these technologies on the structure and properties of the received materials.

The industrial technology of LaNi alloy production was developed by IMET RAS together with Moscow Experimental Plant of Quality Alloys. Melting operations were carried out in induction furnaces of OKB-869 kind (capacity 150kg, volume 100KW). Nickel of H-O grade was loaded right into a magnesite crucible. Lanthanum of LaM-1 grade was loaded into special bins inside the furnace to eliminate the danger of La burning out. Nickel was melted in vacuum (appr.$3x10^{-3}$ mm of mercury). Melting down of nickel completed, the furnace was injected with argon (0,4-0,6 atm) and then La was added several times. The melt was spilled into a pig iron casting form preliminary heated up to 200-300 C. Then the ingot was cooled down till 200-300 C directly in the furnace and later in the air media.

The alloy was graded LaNi-32. Samples for chemical analysis were taken from the upper, middle and bottom parts of the ingots. The analysis of 4 ingots showed that the La range in chemical composition was 30,34-33,79 (%,wt) which corresponds to the formula $LaNi_{5,43}$-$LaNi_{4,64}$. This results in the range of dissociation pressure of hydride phases formated while hydrogenating materials of such compositions appr. within 0,2-0,8 MPa {1}. The said range in the chemical composition within a single ingot could be referred to segregation processes when crystallising.

Micrographic and x-ray analyses showed the presence of only $LaNi_5$ in the composition. It could be explained by homogenuous areas of $LaNi_5$ under temperatures higher than 1000 C and also by rapid crystallising (tempering) while cooling down in the metal casting form with an intensive heat-removing path which allowed to fix a single-phase state.

During real sorbtion tests the material with the mixed composition had a sloping plateau on the respective isotherm of its interaction with hydrogen of medium dissociation pressure (appr. 0,4 MPa) and sorbtion capacity of 150-160 cm^3/g.

All in all there were produced more that 3 tn of this material using the said technology and it was delivered to various institutions (Gas institute NASU, Institute of Machine Manufacturing Problems NASU, MSU, etc.)

Large-sized lots of HM based on $LaNi_5$ were produced using another industrial technology – CaH_2 treatment of oxide and metal mixtures (hydride-calcium method) {2}. The essence of this method for $LaNi_5$ alloy could be expressed as:

$$0{,}1La_2O_3 + Ni + 0{,}3CaH_2 \rightarrow 0{,}2LaNi_5 + 0{,}3CaO + 0{,}3H_2$$

(reaction conducted under T= 1000 - 1200 C). The basic stages of the method are the following:

1. mixing of charge components;
2. charge treatment under high temperatures resulting in La reduction from oxide and alloy formation;
3. hydrometallurgical treatment of the received products aiming at CaO removal, which appears during reaction interaction of the charge components;
4. drying and sieving of alloy powder.

Peculiarities of the said method include producing of powder alloys, which is one of the conditions for HM application, and also relatively low temperatures of the process compared with the melting method. The mechanism of the alloy formating under temperatures much lower than the melting temperature of the received alloy $LaNi_5$

consists in the diffusive interaction of La formed out of oxide, with Ni and all this is activated by the fluid phase formation in the kind of low-melting eutectics acc. to the diagram of La-Ni state.

When developing this technology special attention was paid to the necessity of receiving homogenuous alloy powders with the phase compostion of $LaNi_5$ close to 100%. One of the peculiarities of $LaNi_5$ alloy acc.to diagram of La-Ni state is the absence of homogeneity under temperatures lower than 100^0C. That's why any deviations of chemical composition from stoichiometric one (La 32,13 %, wt) result under equilibrium conditions in the appearance of the second phases (La_2Ni_7) worsening the alloy properties. Long-term isothermic exposure and slow cooling process characteristic of CaH_2 reduction allow to define this process as thermodynamically equilibrium which serves as the base for the realisation of the foregoing case.

Taking into consideration many factors of the said process charge calculations are done with a slight excess of Ni compared with stoichiometric composition. This allows to produce alloys with the acceptable structure and satisfactory level of service properties.

Using this technology there were produced more than 16 tn of various alloys based on $LaNi_5$ within 1987-1993 to the order of different institutions.

The price of these materials turned out to be at that time 2-3 times lower than that of the materials received by melting method.

Conclusions

In this report one can find the main characteristics of two industrial technologies for producing of hydride materials based on $LaNi_5$.

It is also demonstrated in it that the melting technology results in the production of a single-phase alloy with chemical inhomogeneity within the homogenuous area.

There was developed a production method for getting cheaper materials by means of CaH_2 reduction, these materials having acceptable produceability and level of service properties.

References

1. B.A.Kolatchev, R.E.Shalin, A.A. Ilyin, Alloys – hydrogen accumulators. Referencebook, Moscow, Metallurgy, 1995.

2.A.V.Kassimtsev, L.I.Korneev, Technologies and properties of sorbents based on intermetallide Ni_5La. Non-ferrous metallurgy, 2002, #1, p.48-52.